SOLAR ENERGY BASED HYBRID SYSTEM FOR THE TREATMENT OF DYE INDUSTRY WASTEWATER

THESIS

SUBMITTED TO

BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY

BABASAHEB
BHIMRAO
AMBEDKAR
UNIVERSITY
LUCKNOW
प्रज्ञा शील करुणा
ESTABLISHED 1996

FOR THE DEGREE OF

Doctor of Philosophy

IN

ENVIRONMENTAL SCIENCE

Submitted by

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2022

Dedicated to

My Parents

&

Lovely Teachers

CANDIDATE'S DECLARATION

I, **Pradeep Kumar Majhi**, solemnly declare that the research work embodied in this thesis titled **"Solar energy based hybrid system for the treatment of dye industry wastewater"** carried out by me under the guidance and supervision of **Prof. Naveen Kumar Arora, Head, Department of Environmental Science, Babasaheb Bhimrao Ambedkar University (A Central University), Lucknow (U.P.), India** and co-supervision of **Dr. Richa Kothari, Associate Professor, Department of Environmental Science, Central University of Jammu, Samba (J&K), India,** is an original work and is also approved by Departmental Research Committee (DRC).

I further declare that to the best of my knowledge, this thesis does not contain part of any work submitted for the award of any degree either in this University or any other University around the globe. I also declare that the thesis is essentially free from all kinds of plagiarism.

Date: 19/01/2022

p.k.m.

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CERTIFICATE

This is to certify that the thesis titled **"Solar energy based hybrid system for the treatment of dye industry wastewater"** submitted by **Mr. Pradeep Kumar Majhi** is an original research work and has not been previously submitted in part or full for the award of any other degree or diploma to this or any other university.

The thesis submitted to Babasaheb Bhimrao Ambedkar University, Lucknow satisfies all the requirements as stipulated in the *Doctor of Philosophy (Ph.D.) regulations -1999 as amended in 2008/2010/2013* and it is fit for submission and evaluation for the award of the degree of Doctor of Philosophy of the University.

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ACKNOWLEDGMENT

First and foremost, I bow to the Almighty, without whose grace this effort would not have blossomed and been completed. I am overjoyed to be able to offer my heartfelt gratitude to my supervisors ***Professor Naveen Kumar Arora****, (Professor and Head, Department of Environmental Science, School of Earth and Environmental Science, BBA University, Lucknow) and* ***Dr. Richa Kothari*** *(Associate Professor, Department of Environmental Science, Central University, Jammu) for their kind initiation, encouragement, sincere and attiring efforts and inspiration throughout the period of my lab work and preparation of this manuscript. Without their assistance and support, it would not have been feasible to present this study in its present form. I owe them a huge debt of gratitude for their diligent research analysis. I am extremely thankful to Prof. Sanjay Singh, Vice Chancellor, and the Registrar, B.B.A. University, Lucknow, for their unwavering support.*

Truly, the words at my fingertips are insufficient in spirit to communicate my heartfelt gratitude to late ***Prof. D. P. Singh****, for his excellent motivation, invaluable counsel, and genuine interest in achieving this goal,* ***Prof. Rana Pratap Singh****, Department of Environmental Science, and other faculty members including* ***Prof. S. K. Dwivedi, Mr. N.K. More, Prof. Shikha, Prof. Venkatesh Dutta, Dr. Narendra Kumar, and Dr. Jiban Singh****, Babasaheb Bhimrao Ambedkar University, Lucknow, for their unwavering support. I am also very thankful to* ***Prof. Praveen Kolar****, Scientist, North Carolina State University, the United States of America for guiding me to handle lab-scale experiments with very low experimental errors during the training program conducted by the Central University of Haryana, India. There are no words to adequately express my gratitude for my parents, sisters, and other family members.*

Their aspirations and dreams inspired me to continue my education. It would not have been possible without their unwavering support, patience, inspiration, affection, and encouragement. Finally, I will be eternally grateful to **Dr. Vineet Veer Tyagi** *(Associate Professor, Department of Energy Management, Shri Mata Vaishno Devi University, Katra, Jammu and Kasmir) who has stood beside me in mind, body, and spirit while I faced the challenges and obstacles of this research. Their encouragement, assistance, and support have aided me in not only overcoming but also persevering and excelling. I wish to express my heartfelt appreciation to my seniors, friends, and juniors,* **Dr. Mahesh, Dr. Dhananjay, Dr. Dipesh, Mr. Bhanu, Mr. Saroj, Mr. Ajay, Mr. Bilal, Mr. Shasank, Mr. Pankaj, Mr. Akhandal, Misses Prangya, Mr. Vivek, and Mr. Pradeep** *for their technical assistance in document preparation, cordial assistance, innovative ideas, and prefectural encouragement throughout the course of study. I would also like to thank my lab members* **Dr. Virendra, Dr. Vinayak, Dr. Shamshad, Dr. Arya, Miss Anita, Miss Rifat, Mr. Atin, Mr. Harmohan, Miss Gagan, Miss Kajol, Mr. Shubham, and Miss Anu,** *for their courteous assistance, innovative ideas, and prefectural encouragement throughout my research. I am thankful to* **Mr. Aviral, Mr. Jain, Mr. Ranjeet, Mr. Nagesh, Mr. Rahul, and Shri Ramsagar Bhaiya** *for their support. Aside from that, I'd like to express my gratitude to Ananya and Aradhya, for their patience and cooperation while I worked on my thesis. Their self-sacrifice for my superiors enabled me to complete this research.*

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Date: 19/01/2022

Place: LUCKNOW

Pradeep Kumar Majhi

PREFACE

According to the current systematic statistical scenario of pollution, the earth is in grave danger from itself and environmental pollution is generally cited as one of the most serious threats facing humanity. These serious environmental problems are the results of *Homo sapiens'* unconscious anthropogenic actions, such as industrialization, urbanization, deforestation, and population growth, which result in serious environmental problems such as greenhouse gas emissions, energy shortages, and water contamination. Water contamination is the most serious of all the pollutions because of its uncontrolled, insensitive use, particularly in the industrial and urban growth sectors. Water, on the other hand, is widely used by societies and humans, yet it is frequently mistreated in terms of environmental pollution. Only 1% of the world's freshwater is available for human consumption willingly. Around 20% of all water used on the earth comes from groundwater sources, and this number is growing, particularly in arid regions. Irrigation consumes 67% of global aggregated groundwater, followed by industry (11%).

Colors are prevalent in human sentiments because they are a part of human culture and lifestyle. These are common dyes that have been used to create a variety of textile items in a variety of industries. When toxic dyes come into contact with surface water, aquatic species face a serious threat to their survival. These dyes are chemical substances that attach to surfaces or fabrics and color them. Due to its tenacity, dye ejection into the hydrosphere is a major source of pollution as it dries out water, inhibits sunlight penetration, and prevents aquatic flora and fauna from photochemical and biological activities. According to estimates, there are over 100,000 commercial dyes, with an annual production of over 7×10^5 tonnes. Total dye consumption in the textile industry exceeds 10,000 tonnes per year, with approximately 100 tonnes of dyes discharged into waterways each year. The vast majority of dye-contaminated textile manufacturing industries are concentrated in Asia. Dye-contaminated textile industries consume more quantity of dyestuffs (about 80% of the total dye production). India has become a major exporter of dyestuffs and dye intermediates, particularly reactive, acid, vat, and direct dyes. Textile and dye processing, both of which use a wide range of dyes and chemical additives, are two of the most important industries that generate dye wastewater. The dyeing and finishing operations, which involve the input of a diverse range of chemicals and dyestuffs, the majority of which are organic compounds with complex structures, are the main units in these dye-using industries. The removal of color from textile and dyestuff manufacturing industry wastewaters is a serious environmental concern.

Textile production

Textile manufacturing is one of the world's largest and oldest industries. Textile production has shifted to countries with lower labor and material costs in Asia, particularly China, India, and Bangladesh, supply more than half of the clothing and textiles consumed in the United States and the European Union. The textile industry has grown to be one of the most important business sectors in majority of these countries, and significant efforts are being made to boost production. The textile industry consumes a lot of water and has spread to nearly every part of India. It comes in composite and semi-composite forms. Uttar Pradesh, Andhra Pradesh, and West Bengal have 80, 54, and 40 textile industries respectively. Because of its toxicity and chemical nature, environmental scientists face significant challenges in the remediation of textile industry wastewater. In general, wastewater from the textile industry can be treated using both conventional and advanced treatment methods.

Traditional treatment methods include all common handling technologies such as physical, chemical, and biological treatment options, whereas advanced treatment methods include the highly developed function of contemporary techniques such as the use of nanomaterials, ion exchange treatment, reverse-osmosis, biomass-based treatment, and solar-energy-based treatment.

Hybrid treatment option

Because of specific limitations in individual treatment methods, a single treatment method for pollution reduction of textile dye effluent is not fully capable of reducing pollutants. As a result, the idea of combining more than one treatment system could be the best solution in this context, resulting in the advent of hybrid treatment technology. Merging more than one treatment system not only improves treatment efficiency but also reduces the formation of secondary pollutants. In this regard, for the current study, solar energy and algal biomass-based treatment have been hypothetically constructed and integrated for improved results in the treatment process quality.

The thesis has been divided into the following six chapters:

Chapter 1: Introduction and review of literature

Chapter 2: Materials and Methods

Chapter 3: Phycoremediation of textile industry wastewater by *C. pyrenoidosa*

Chapter4: Experimental evaluation of solar energy-based setup for the treatment of dye contaminated textile industry wastewater

Chapter 5: Experimental evaluation of novel Solar-Algal Hybrid Reactor for dye contaminated textile industry wastewater treatment: techno-economic assessment

Chapter 6: Conclusion and future recommendations

The chapter-wise description of the work is as under:

Chapter 1: Introduction

This chapter provides an overview of dye-contaminated textile industry wastewater availability, sources of generation, and environmental impact. The numerous treatment technologies for dye-contaminated textile industry wastewater have been described, together with their benefits and drawbacks in terms of the environment.

This study's literature review covers various treatment alternatives such as physical, chemical, biological, and highly sophisticated treatment technologies for the treatment of dye contaminated textile industry wastewater. After that, several objectives have been decided based on the literature survey to be fulfilled by the current study.

Chapter 2: Materials and Methods

This chapter elaborates the experimental methodologies those were used for this investigation. Each experiment's goal and analytical technique have been thoroughly addressed. It describes textile industry wastewater, its properties, the primary wastewater parameters involved, its reactive nature toward the adsorbent, *C. pyrenoidosa* algae as an adsorbent, its adsorptive behavior toward pollution, and dye removal from textile industry wastewater. This chapter also derivates scope on industrial thoughts on the immobilization process, its impacts on the industrial sector in terms of pollution reduction in various wastewater. This chapter describes the mechanism for the preparation of immobilized algae. In this study, solar energy is an important aspect. So, in this section, it has been discussed how to build up solar energy-based treatment system to reduce pollution. The algal-based setup, solar-energy-based setup, and hybrid-based setup all have been summarized here. All of the materials and methodologies utilized for the current study have been explained in the sections that follow:

Experimental design

As per the objectives, the present research work has been divided into three phases (Phase-I, II, and III) to make it more fruitful with significant findings such as:

- **Phase-I:** Algal based treatment
- **Phase-II:** Solar energy-based treatment
- **Phase-III:** Hybrid treatment (combination of both solar and algal-based treatment technology)

Chapter 3: Phycoremediation of dye contaminated textile industry wastewater by *C. pyrenoidosa*

The chapter discusses how *C. pyrenoidosa* could be used to minimize pollution and color in textile industry wastewater. While algae are ubiquitous and may be cultivated cheaply, further immobilization of free algae can boost the effectiveness of color removal. The current study compares dye removal under optimal and non-optimal conditions. It was discovered that the optimal temperature (50°C) of IAC removed most of the dye (98%) while only 92% was removed at ambient temperature. The conclusions of the current study were investigated using the thermodynamics function and pseudo-second-order kinetic model. According to the findings, *C. pyrenoidosa* species are particularly effective for removal efficiency in free algal cells, and when the free algal cells are immobilized, the removal efficiency improves significantly with temperature (up to 50°C). The reason for this is that when the temperature rises, the randomness of the dye molecules increases that enhances the pollution reduction efficiency. Thus, the current work provides novel insights on dye removal efficiency from industrial effluent, with a focus on the effects of pH and temperature.

Chapter 4: Experimental evaluation of solar energy-based setup for the treatment of dye contaminated textile industry wastewater

Dyes are always important for humans because they are a part of their lifestyle and culture. The dyes have been utilized in a variety of industrial sectors to manufacture a variety of textile items. These dyes are essentially chemical substances that attach to surfaces or fabrics to impart color. Dye-contaminated textile sector wastewater was treated using lab-scale-designed solar reactor with an optimal rate of flowrate, and the results were significant in terms of decolorization and COD reduction. Pollutional parameters (BOD, nitrate, and phosphate) were also examined before and after treatment with the designed solar energy-based reactor. However, improvements in COD reduction efficiency were seen more frequently than improvements in other pollution-related parameters. The highly induced ultraviolet radiation inhibited pathogenic growths and activities in wastewater effluents, which could explain why BOD, nitrate, and phosphate levels were not reduced significantly. This solar energy-based treatment concept is a renewable-based treatment approach that is more cost-effective and produces lesser secondary pollutants than other treatment methods. Even though various researchers have reported on a variety of treatment technologies for dye-contaminated textile industry wastewater, but in the current study, the color and COD reduction from dye contaminated textile industry wastewater have been focused to be reduced more significantly.

Chapter 5: Experimental evaluation of novel Solar-Algal Hybrid Reactor for cost-effective wastewater treatment: techno-economic assessment

Traditional technologies exacerbate pollution reductions by requiring high energy input and releasing large quantities of hazardous substances into the environment. These items are frequently expensive and difficult to obtain for researchers. However, while those approaches of pollution reduction capabilities are reasonable, the issues of sludge processing, supplemental energy use, and additional time requirement for the process pose very serious problems. However, due to the complex bonding of toxic chemicals in textile industry wastewater compounds, complete degradation is difficult. Textile industry wastewater is treated with advanced physical and chemical technologies such as coagulation, ozonolysis, advanced oxidation, membrane separation, and ultra-filtration. However, serious issues such as cost-effectiveness and secondary pollution generation make them unfeasible. The degradation of this highly polluted textile industry wastewater can once again be accomplished with a single treatment technology. Hence, combining two or more of these can technologies could enhance the reduction potential. Therefore, the current study is a suitable approach for degrading high-load pollutants while also filling in the gaps left by single-treatment technology. The hybrid systems are good at pollution reduction as well as delivering additional reductions in the number of resources required for the treatment process because they utilize extremely little energy during wastewater treatment. The treatment technologies vary depending on the methods used in the manufacturing process, whether manufacturing necessitates the use of raw materials, whether the system's capability is limited. The hybrid treatment system has been designed to be used for dye contaminated textile industry wastewater treatment with low energy inputs and less generation of experimental byproducts at the same time to work in a cost-effective approach for wastewater treatment.

Chapter 6: Conclusion and future recommendations

The majority of scientists welcome recent developments that are aimed at balancing the environment and reducing wastewater pollutants. But, it is quist difficult to handle these critical situations where anthropogenic and environmental negative activities are uncontrollable. Their impacts are massively degrading the water parameters which are required to be balanced for a sustainable environment. Recently, there are so many environmentally friendly wastewater treatment options have been emerged in the wastewater treatment sectors with very positive responses. But every single treatment has specific limitations for wastewater treatment. So, in this context, the current study has focused on using merged(coupling) treatment systems such as hybrid treatment systems. Using two or more methods is better for the environment because it uses fewer resources and manpower at the same time fulfills the limitations remained by a single treatment system. For the current study, two different treatment options like algal-based treatment and solar energy-based treatment option have been used individually and jointly for dye contaminated textile industry wastewater treatment. The dye contaminated textile industry wastewater was treated by solar energy-based treatment and also by *C. pyrenoidosa* individually at the same time by designed hybrid setup and it was concluded that the hybrid treatment technology was more efficient than both solar and algal treatment technology in terms of wastewater pollution reduction. The high-intensity ultraviolet radiations were capable of the degradation of toxic chemicals bonding of dye contaminated textile industry waster and *C. pyrenoidosa* was more efficient for nutrient reduction. So, when both the treatment technology combined the treatment efficiency increased as compared to individual treatment technology.

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ABBREVIATIONS

CO_2	Carbon Dioxide
TDS	Total Dissolve Solid
TSS	Total Suspended Solid
COD	Chemical Oxygen Demand
BOD	Biological Oxygen Demand
NCIM	National Collection of Industrial Microorganism
UV	Ultra Violate
OD	Optical Density
SEM	Scanning electron microscope
EDS	Energy-Dispersive X-ray
INR	Indian Rupee
SS	Suspended Solids
TN	Total Nitrogen
TP	Total Phosphate
H_2O_2	hydrogen peroxide
SPTR	Solar Parabolic Trough Reactor
SAHR	Solar Algal Hybrid Reactor
AOP	Advanced Oxidation Process
MBR	Membrane Bioreactor
PMR	Photocatalytic Membrane Reactor
SEBHTS	solar energy based hybrid treatment system
$CaCl_2$	Calcium Chloride
FAC	Free Algal Cell
IAC	Immobilized Algal Cell
CSP	Concentrating Solar Power
PV	Photovoltaic
SD	Standard Deviation

Chapter-1
Introduction and Review of Literature

1. Introduction

Currently, the comprehensive statistical scenario of contamination conveys the declaration that the earth is facing severe threats toward itself. Among the entire threats, the foremost issues are frequently associated with environmental sectors (Holkar et al., 2016). These major environmental issues are nothing, but due to the unconscious anthropogenic activities of *Homo sapiens* such as industrialization, urbanization, deforestation, and population growth which cause severe environmental tribulations such as greenhouse gas emissions, energy crisis, and water pollution (Verma et al., 2012; Hynes et al., 2020). Among all the environmental issues, water pollution is well-known as the critical one due to its random, insensible use mostly in industrial as well as urban development sectors (Holkar et al., 2016; Jegatheesan et al., 2016). On the other hand, water as a commodity is highly utilized by the communities/ human society, at the same time, it is highly mismanaged in terms of pollution generation into the environment. Less than 1% of the world's freshwater is willingly accessible for direct human use (Jakeman et al., 2016). Approximately, 20% of the total water used worldwide is from groundwater sources and this is rising quickly, particularly in dry areas. The statistics of global aggregated groundwater use are irrigation 67%, industry 11%, and domestic use 22%. A contemporary study estimates that withdrawal of global water will increase from $4.5x10^6$ million m^3/year to $6.9x10^6$ million m^3/year by 2025 (Rosa et al., 2019; Amore et al., 2012). Based on the prerequisite of water for diverse purposes in the present century, water-stressed situations create per capita water availability in the range from 1100 to 5100 m^3/year and is considered water scarcity when the availability reduces to 1000 m^3/year. The per capita water availability in 1951 was 5177 m^3/year when the total population was only 361 million. In 2001, as the population increased to 1027 million and the per capita water availability reduced drastically to 1816 m^3/year (Ahmad et al., 2020; Mishio et al., 2021) (illustrated in figure 1.1).

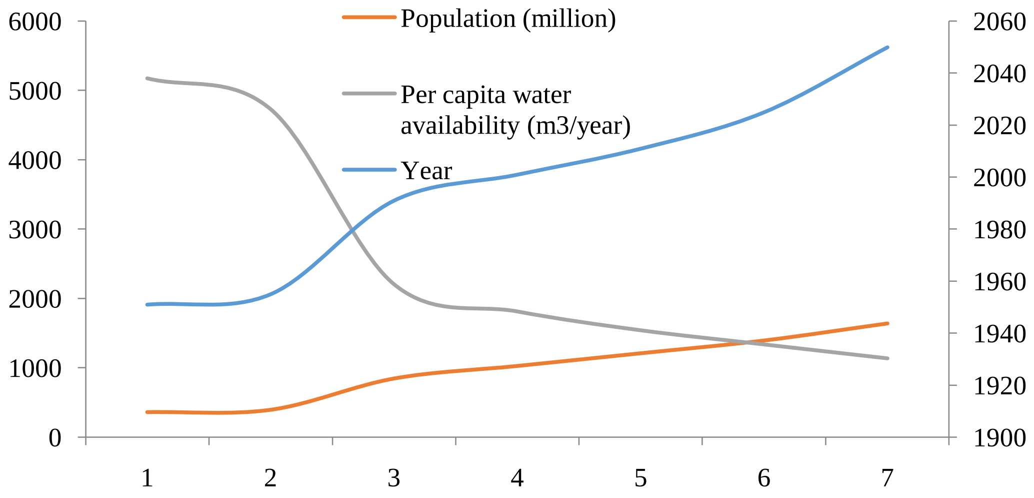


Figure 1.1: Per capita water requirement with population growth during 1951-2050 (Ministry of Water Resource, Government of India 2009; Ministry of Jal Shakti 2020; Ahmad et al., 2020)

The world's water crisis is not related to the substantial availability of water, but unbalanced, misjudgment of water importance**.** A modern-day study reports that collectively water extraction is going to increase with a range of 4.5 $\times 10^6$ million m3/year to 6.9 $\times$ 10^6 million m3/year by the year 2025 (McKinsey 2009; Ercin et al., 2014). Tannery, dairy, municipal, agricultural, hospital, and textile industries are the major industrial sectors for the large quantity of wastewater generation and among all of them, the textile sector is known as the foremost polluting industry for the environment. The details of textile industries and impacts have been discussed below:

1.1 Sources of wastewater

The wastewaters are generated from various sources as per uses in different sectors like industry, agriculture, and urbanization, etc. The sources are basically classified from industrial, agricultural, domestic as well as pharmaceutical sectors. Agricultural sector discharged wastewater is categorized into the point and non-point sources. The point sources involve: poultry waste, piggery waste, silage liquor, dairy farming waste, slaughtering waste, vegetable waste, firewater, etc. Similarly, the non-point resources involve sediment runoff, nutrient runoff wastewater. On the other hand, domestic discharge of wastewater involves washing, laundry, shower, kitchen, toilet, septic tank, school, hospital, hotel/ restaurant, office, small business activities, etc. Finally, the industrial sector possesses so many wastewater discharge sources such as canaries, milk dairies, sugar factories, breweries, beverages, abattoir, fertilizer, pulp, and paper industry, tanneries, yeast manufacturing, etc. Among all the sources of wastewater discharging, the domestic and industrial sectors are considered as the most important ones as highly toxic, compounds and biologically non-degradable chemicals are discharged by the industrial sector. Water pollutants may originate from point sources or dispersed sources. A point-source pollutant reaches water from a single pipeline or channel, such as a sewage discharge or outfall pipe. Dispersed sources are broad, unconfined areas from which pollutants enter the water body. Surface runoff from farms, is a dispersed source of pollution, carrying animal wastes, fertilizers, pesticides, and silt into nearby streams. Urban storm water drainage, which may carry sand and other gritty materials, petroleum residues from automobiles, and road deicing chemicals, is also considered a dispersed source because of the many locations at which it enters local streams or lakes. Point-source pollutants are easier to control than dispersed-source pollutants since they flow to a single location where treatment processes can remove them from the water. Such control is not usually possible over pollutants from dispersed sources, which causes a large part of the overall water pollution problem. Dispersed-source water pollution is best reduced by enforcing proper land-use plans and development standards. There are large numbers of industries that generate huge amounts of polluted wastewater to water bodies; these types of wastewater have been discussed in the following section:

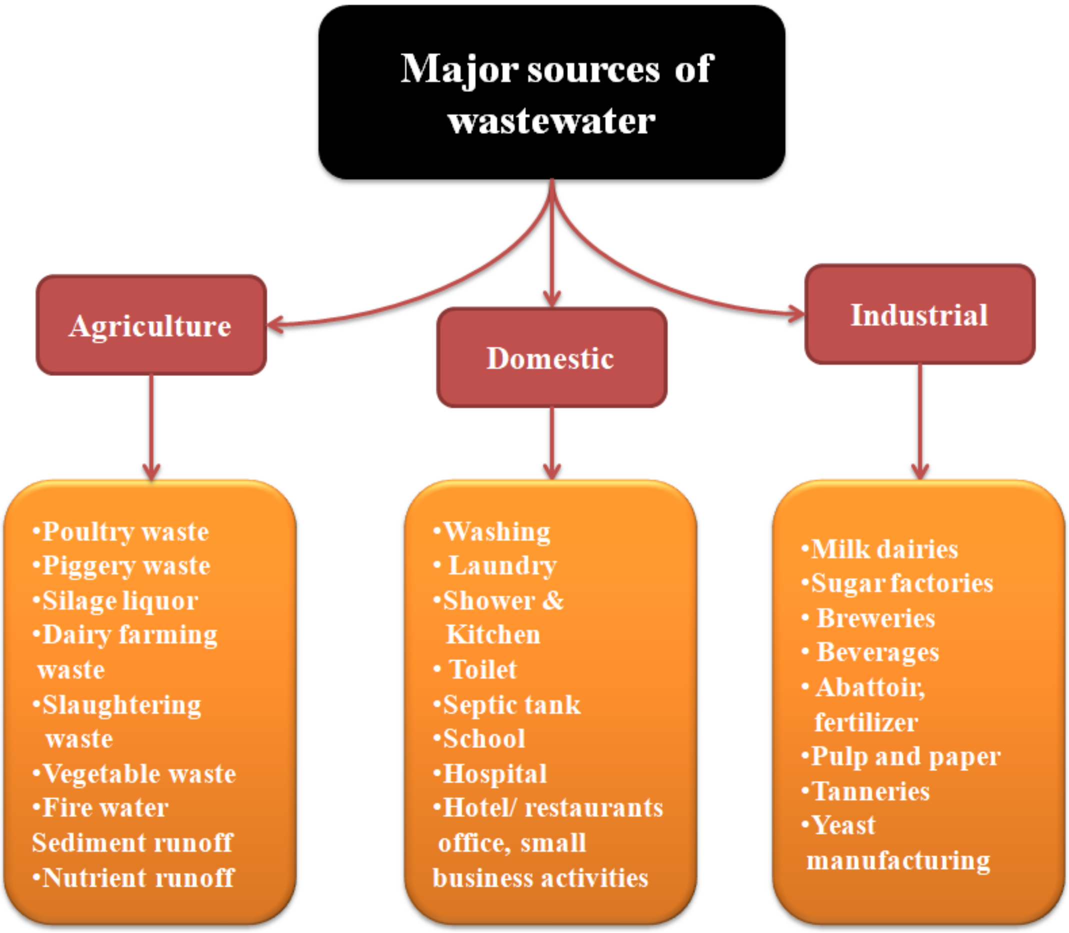


Figure 1.2: Sources of wastewater generation

1.2 Types of wastewater

Among all types of wastewater discharged into the water bodies, the domestic and industrial sector releases huge amounts of wastewater into the environment. These generated wastewaters are sometimes treated, and sometimes partially treated. Hence, they possess imbalance to the aquatic ecosystem whenever reached in freshwater bodies.

1.2.1. Types of industrial wastewater

Industrial wastewater is one of the significant sources of water pollution. Due to industrialization, the past few decades have witnessed high load of industrial discharge into oceans, lakes, and rivers. The discharge of industrial wastewater has caused deterioration of aquatic habitat and caused serious health effects among human beings. Industrial wastewater has been further classified on the basis of different types of pollutants and industries. As the contaminant load from a particular industry is distinct from others, therefore treatment methods should be designed in accordance with the type of discharge. The developing countries produce more wastewater in comparison to the technologically advanced nations; therefore establishment of improved technologies in those nations can significantly curtail the load of wastewater for treatment purposes and also for discharge into water bodies.

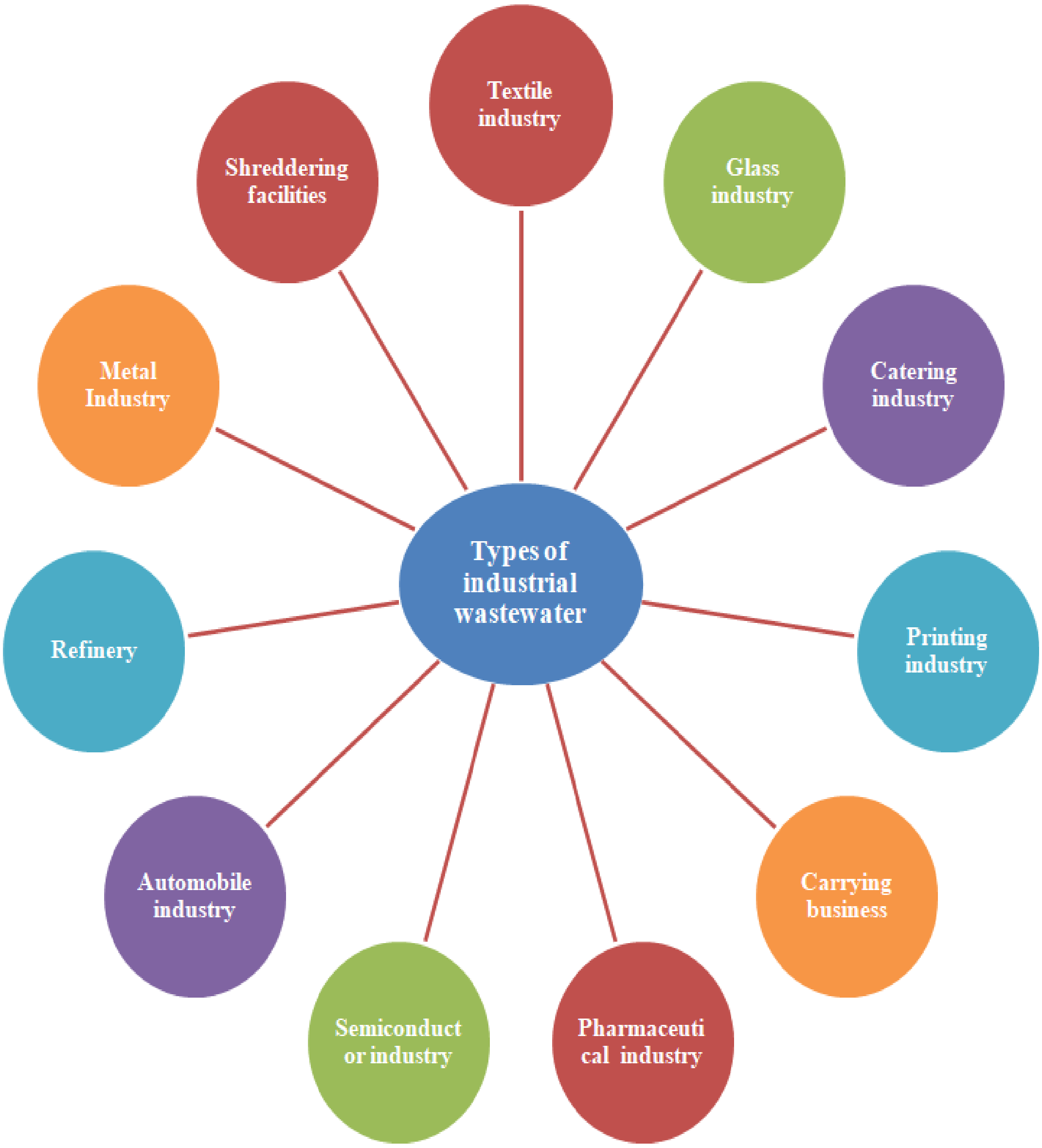


Figure 1.3: Types of industrial wastewater

This reality envisages the truth that the pollution from the industrial sector is going to move from developed countries with a factor rate to a range of developing countries towards the 21st century. The revolution in the industrial sector, the generation of higher advanced machinery engines, and use of the petroleum fuel and products, the rapid development of chemical industries increased the environmental dis-balance. Due to the fiery growth of a variety of industrial sectors, a huge amount of water is consumed for that sector. During these industrial procedures, many kinds of raw materials and by-products, as well as wastes, mix with the water body. There are numerous categories of wastewater generated from different industrial sectors; at the same time every industry generates specific pollutants and combinations (illustrated in figure 1.4)

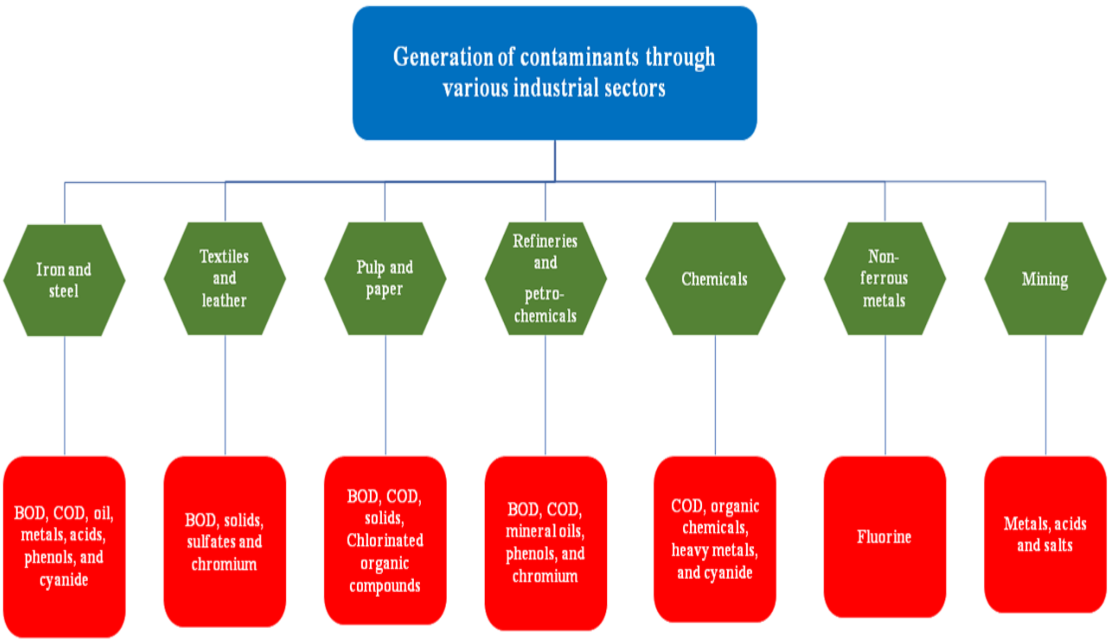


Figure 1.4: Different types of industrials sectors with pollutants generation

The pulp and paper industrial sectors use mostly the substances of chlorine-based, so, most of the by-products are generated from this industry are the organics of chlorine and dioxins at the same time it includes organic wastes and suspended solids. A range of phenols and mineral oils are discharged from the petrochemical industry. Similarly, the food processing industries are rich in high loads of organic material and suspended solids. Based on the industrial sectors, its sources of raw materials, and generation of pollutants the industrial wastewater could be divided into two types:

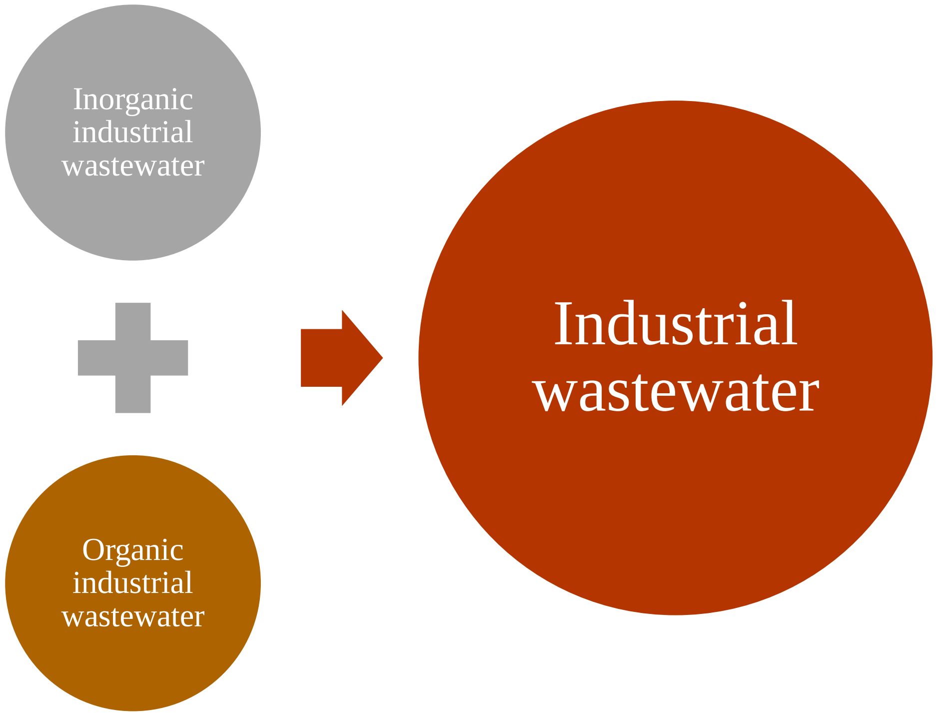


Figure 1.5: Industrial wastewater types

1.2.1.1 Inorganic industrial wastewater

The principal sources of inorganic industrial wastewater generation are from the steel and coal industrial sector, non-metallic minerals industrial sector, and industrial sectors for the surface processing of various metals. Several range of suspended matters are found in this wastewater which needs to be removed by using treatment methods like sedimentation, in some cases flocculation by using iron or aluminum salts, many times agents of flocculation and typical organic polymers. In several cases, wastewater is produced with a mixture of a variety of substances of solid and oils, and in many cases hold exceptionally harmful materials. That contamination may include gas-washing, blast-furnace wastewater holding cyanide, pollutants from the industries of processing of the metal holds solutions of acids or alkalines.

1.2.1.2 Organic industrial wastewater

Organic industrial wastewater contains the wastewater released from the chemical industries where organic materials are used as major raw resources. The wastewater holds several organic materials from a variety of sources and characteristics. These typical wastewaters could be treated with a range of preliminary treatments and after that the use of biological treatment. The sources of these industrial wastewaters are from the following industries:

- ❖ The industries developed hospital, superficial, dye-stuffs of organic basis, soaps industries, detergents of synthetic, herbicides and pesticides
- ❖ The industries of tanneries and leather
- ❖ Industries use textile dye for manufacturing
- ❖ The industries produce paper and cellulose
- ❖ The industries of oil refinement
- ❖ Industries of fermentation and brewery
- ❖ Industries of metal processing

1.3 Wastewater produced from various industries

All the composite types of wastewater generated from various industrial sectors are highly harmful to the environment and need to be treated before discharging in the water body. Among all the wastewater generated from various industrial sectors, textile industry wastewater is considered as highly toxic for the environment as it contains a huge among of non-biodegradable carcinogenic substances. The textile industry is one of the major culprits for producing huge of dye chemicals. Textile dye industries wastewater, sources of generation, quality issue, and environmental impacts and treatment options have been discussed in the following section.

1.4 Textile industry wastewater

Colors are always in the human sentiments as it is a part of human lifestyle and culture. These colors are nothing but, are representative dyes that have been used in an assortment of industrial sectors for the manufacturing of various textile products. Whenever these toxic dyes come in contact with surface water, it poses high challenge for the survival of aquatic organisms. These dyes are basically chemical compounds that attach themselves to surfaces or fabrics to impart color. The dye expulsion into the hydrosphere possesses a significant source of pollution due to its recalcitrance nature. It provides objectionable color to the water bodies, reduces sunlight penetration, and resists photochemical and biological activities on aquatic flora and fauna (Paździor et al., 2019)**.** As per global estimation, more than 100,000 commercial dyes are known with an annual production of over 7×10^5 tonnes/year**.** The total dye consumption in the textile industry worldwide is more than 10,000 tonnes/year and approximately 100 tones/year of dyes is discharged into water streams (Jegatheesan et al., 2016; Yaseen and Scholz, 2017). It is estimated that maximum textile processing industries are found in Asia and very few numbers are observed in African countries. The textile industry accounts for the largest consumption of dyestuffs (about 80% of the total dye production). India has emerged as a global supplier of dyestuffs and dye intermediates, particularly for reactive, acid, vat, and direct dyes (Mehta et al., 2021). The major industries that discharge dye wastewater include textile and dye manufacturing, employing a large variety of dyes and chemicals additives. The major units in these industries that utilize dyes are the dyeing and finishing operations, which require the input of a wide range of chemicals and dyestuffs that are majorly organic compounds of complex structure. The removal of color from the textile industry and dyestuff manufacturing industry wastewaters in consequence represent a major environmental concern due to their high persistence levels (Yagub et al., 2014; Lellis et al., 2019).

In India, the textile industry has been established in almost all parts of the country and has been formed in both composite and semi-composite plans. Utter Pradesh, Andhra Pradesh, and West Bengal contain 80, 54, and 40 textile industries respectively. From northern to southern, eastern to western corner, the textile sectors cover all the parts of the country with its spreading (illustrated in figure 1.6).

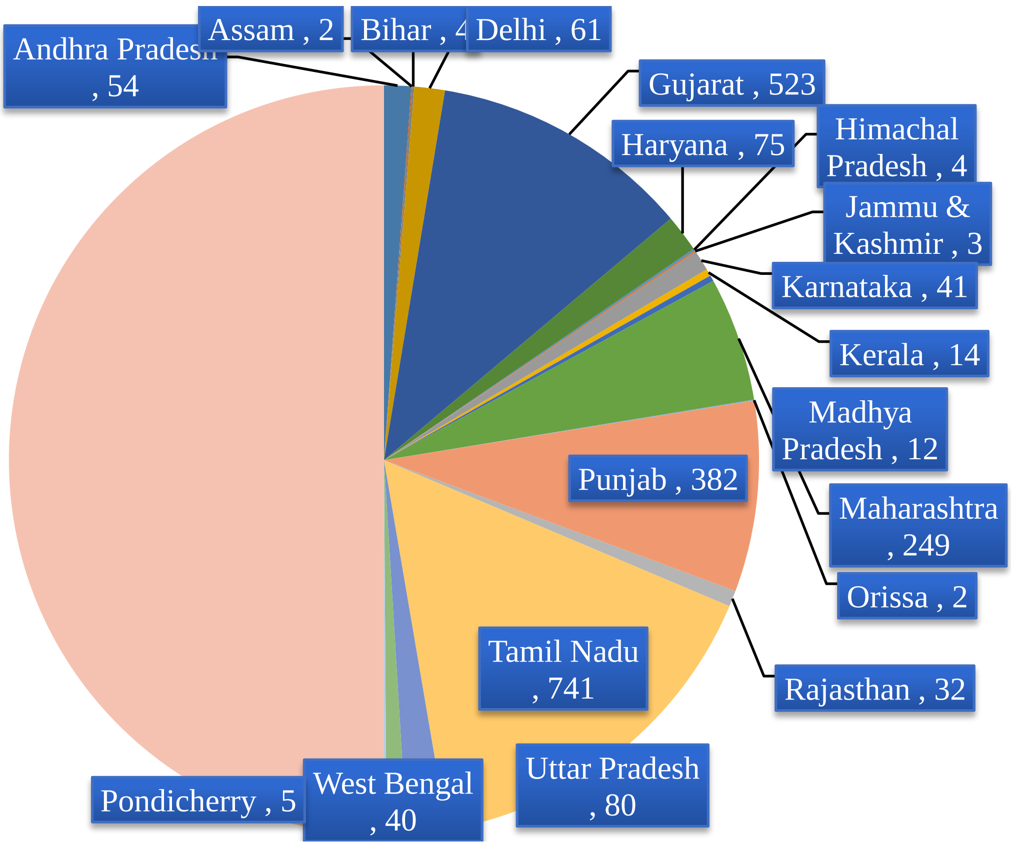


Figure 1.6: State-wise distribution of textile industries (Ministry of textile, Government of India; Goyal et al., 2019; Sidhu et al., 1999)

There are various mechanical processes through which the textile manufacturing industries undergo the production of the end product. Various processing steps have been discussed in the following section.

1.4.1 The textile process

The industrial production is involving the combination/ connection of various processing setups collaborating for the manufacture of the final product. These processes used in the industrial sector are called wet processes (Verma et al., 2012). The processing steps for the manufacturing of end products are categorized into eight sections (illustrated in figure 1.7) such as Sizing, Desizing, Scourcing, Bleaching, Mercerizing, Dying, Printing, and Finishing **(**Holkar et al., 2016). The primary step of dye processing is sizing where, the majority of loose, hairy, and projecting fibers are removed. Desizing is the second phase where mostly the gummy materials are screened.

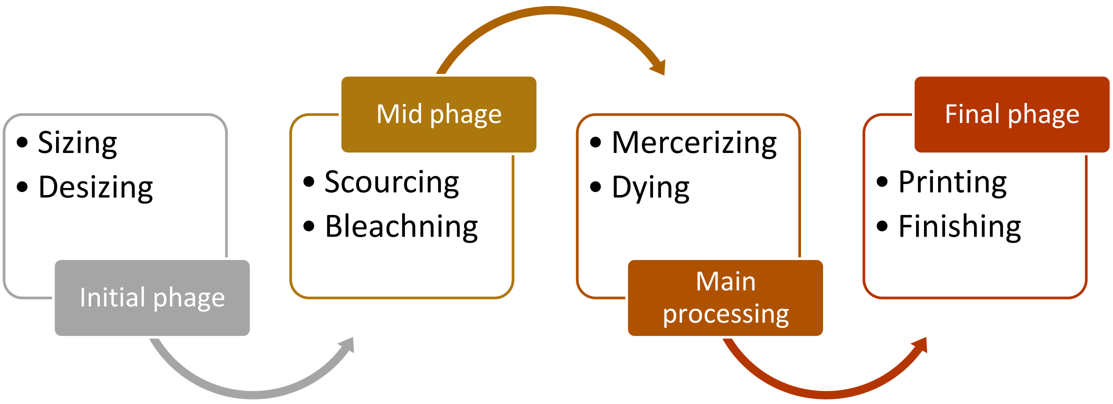


Figure 1.7: Flow diagram of dye manufacturing wet processes (Holkar et al., 2016)

Scourcing, bleaching, and mercerizing are middle adjacent phases where reduction of impurities, natural color, and increment of strength and luster of the materials occur respectively. These processing steps are very much crucial for each other. But, these processing steps possess so many disadvantages like consuming a huge amount of water during the process of manufacture. At the same instance, they also release enormous extent of pollutants combined with wastewater. The amount of water consumption in each processing step has been described in table 1.1.

Table 1.1: Various processing steps with water consumption (Holkar et al., 2016)

Steps	**Required water quantity (Litre/Kg)**
Sizing	The water required for sizing varies from 0.5 to 8.2 l/kg with an average of 4.35 l/kg
Desizing	The required water at this stage varies from 2.5 to 21 l/kg with an average of 11.75 l/kg
Scouring	The water required for the process varies from 20 – 45 l/ kg with an average of 32.5 l/kg
Bleaching	It varies between 24 to 32 l/kg But in cloth bleaching, the water requirement is much higher and it fluctuates between 40 - 48 l/kg
Mercerising	The water required for this process varies from 17 to 32 l/kg with an average of 24.5 l/kg
Dyeing	The water requirement for dyeing purposes (include all types and shades) varies from 36 – 176 l/kg with an average of 106. The effluent generation during the dyeing process fluctuates from 35 to 175 l/kg with an average of 105 l/kg
Printing	It is usually carried on the prepared fabric where it is applied to specific areas to achieve a planned design.
Finishing	The finishing process imparts the final aesthetic, chemical, and mechanical properties to the fabric as per the end-user requirements.

The processing of textile dye consumes water based on their requirements. The lowest amount of water is required for sizing steps (4.35 l/kg) whereas, desizing, scourcing, bleaching, and mercerizing steps require the moderate quantity of water (11.75, 32, 48, and 24 l/kg respectively), and on the other hand, processing requires a huge amount of water for manufacturing. It is estimated that an average of 105 l/kg of fabrics water is consumed in the dying-printing step individually, which is the highest among them. Each step consumes fresh water and at the same time discharges water with the large number of impurities and toxic non-biodegradable compounds (described in table 1.2).

Table 1.2: Specific pollutants generated from textile processing (Imtiazuddin et al., 2012; Toprak and Anis, 2017)

Process	**Compounds**
Desizing	Sizes, enzymes, starch, waxes, ammonia
Scouring	Disinfectants and insecticides residues, NaOH, surfactants, soaps, fats, waxes, pectin, oils, sizes, anti-static agents, spent solvents, enzymes.
Bleaching	H_2O_2, AOX, sodium silicate or organic stabilizer, alkaline pH.
Mercerizing	High pH, NaOH
Dyeing	Colour, metals, salts, surfactants, organic processing assistants, sulphide, acidity/alkalinity, formaldehyde.
Printing	Urea, solvents, color, metals.
Finishing	Resins, waxes, chlorinated compounds, acetate, stearate, spent solvents, softeners.

The characteristics of textile dye wastewater differ from industries as each industry has a specific guideline of the manufacturing process. Though several similar technologies are used in the various manufacturing industry several stern concerns like the way of resource utilization, the timing of machine running, and way of instrument handling create the parametric differences in the wastewater. The basic parameters of textile industry wastewater include pH (6-10), temperature (35-45°C), Biochemical Oxygen Demand (100 – 4,000 Mg/L), Chemical Oxygen Demand (150 – 10,000 Mg/L), Total Suspended Solids (100 – 5,000 Mg/L), Total Dissolved Solids (1,800 -6,000 Mg/L), chloride (1,000 – 6,000 Mg/L), total alkalinity (500 – 800 Mg/L), sodium (610 – 2,175 Mg/L), total Kjeldahl nitrogen (70 – 80 Mg/L) (Yaseen et al., 2019). Textile dye industry wastewater exhibits extremely high COD values as compared to other parameters. Temperature is normal (35-45°C) whereas, the pH is alkaline which ranges from 6.0-10.

Table 1.3: Specific pollutants generated from textile dye processing

Process	**Compounds**
Desizing	Sizes, enzymes, starch, waxes, ammonia
Scouring	Disinfectants and insecticides residues, NaOH, surfactants, soaps, fats, waxes, pectin, oils, sizes, anti-static agents, spent solvents, enzymes.
Bleaching	H_2O_2, AOX, sodium silicate or organic stabilizer, alkaline pH.
Mercerizing	High pH, NaOH
Dyeing	Colour, metals, salts, surfactants, organic processing assistants, sulfide, acidity/alkalinity, formaldehyde.
Printing	Urea, solvents, color, metals.
Finishing	Resins, waxes, chlorinated compounds, acetate, stearate, spent solvents, softeners.

The characteristics of textile dye wastewater differ with industries as each industry has a specific guideline of the manufacturing process. Though, several similar technologies are used in various manufacturing industries but, some serious concerns like the way of resource utilization, the timing of machine running, and way of instrument handling create the parametric differences in the wastewater. The basic composition of textile industry wastewater has been described in table 1.4.

Table 1.4: Basic composition/ parameters of textile industry wastewater (Paździor et al., 2018)

Parameters	**Ranges**
pH	6.0– 10.0
Temperature	35-45℃
Biochemical Oxygen Demand	100 – 4,000
Chemical Oxygen Demand	150 – 10,000
Total Suspended Solids	100 – 5,000
Total Dissolved Solids	1,800 -6,000
Chloride	1,000 – 6,000
Total Alkalinity	500 – 800
Sodium	610 – 2,175
Total Kjeldahl Nitrogen	70 – 80

**All the parameters are in Mg/L except pH and temperature*

Temperature is normal (35-45^0 C) whereas, the pH is alkaline which ranges from 6.0-10.0. Besides this, the other water parameters are found more than their permissible limit. The permissible limits of textile dye wastewater have been described in table 1.5.

Table 1.5: Permissible limit/standards (Holkar et al., 2016; Wang et al., 2020; Yaseen et al., 2019)

Parameters	**The limits of discharged concentration**	**The limits of discharged concentration for new factory**	**The special limits of discharged concentration**
COD	100	80	60
BOD	25	20	15
pH	6~9	6~9	6~9
SS	70	60	20
TN	20	15	12
NH_3-N	15	12	10
TP	1.0	0.5	0.5
S	1.0	Can not be detected	Can not be detected
ClO_2	0.5	0.5	0.5
Cr^{6+}	0.5	Can not be detected	Can not be detected
Aniline	1.0	Can not be detected	Can not be detected

**Except pH, all the parameters are in Mg/L*

The permissible limit is decided on the basis of raw materials and the type of dyes used for manufacturing and the standards are established by the governments in the state as well as the national and international levels (State Pollution Control Board and National Pollution Control Board). Dye has a broad range of applications in different textile industries. Various compound groups such as Acid, Azoic, Basic, Direct, Disperse dyes, Reactive, *etc* are multidimensionality used in many sectors (table 1.6).

Table 1.6: Application of dye groups

Group	Application
Acid	Wood, silk, paper, synthetic fibers, leather
Azoic	Printing inks and pigments
Basic	Silk, wood, cotton
Direct	Cotton, cellulosic and blended fibers
Disperse dyes	Synthetic fibers
Reactive	Cellulosic fibers and fabric
Organic pigments	Cotton, cellulosic, blended fabric, and paper
Sulfur	Cotton and cellulosic fibers
Vat dyes	Cotton, cellulosic and blended fibers

1.5. Potential treatment technologies

Based on the toxicity level and chemical nature, their remediations pose high challenge for environmental scientists. The treatment of textile industry wastewater can be generally carried out with conventional treatment and advanced treatment options (Hai et al., 2007). The conventional treatments take in every accustomed handling technology like physical, chemical & biological treatment options at the same time advanced treatments include the highly developed function of contemporary techniques like the use of nano-materials, treatment through ion exchange, reverse-osmosis, biomass-based treatment, and solar-energy-based treatment (Siddique et al., 2017; Bhatia et al., 2017; Crini and Lichtfouse, 2019). The foremost processes and application of several available treatment options for this purpose have been discussed in the following sections:

1.5.1 Adsorption

Adsorption is an exceedingly steady treatment opportunity for textile industry wastewater and has gained primitive consideration in recent times. It is a typical surface phenomenon where a layer or film of adsorbate is created over the surface of the adsorbent and its possibility could be physical as well as chemical as per the requirements. Researchers confirm that it is a cost-effective, persistent, economically feasible process and decolorization of textile industry wastewater is affected by the adsorption process but a series of factors are responsible for the processing rate such as contact time, pH of the test solution, nature of adsorbate, the surface area of adsorbate, and particle size of reactant solution (Arslan et. al., 2016; Bazrafshan et al., 2016). The adsorption mechanism is an exothermic process where heat is generated and Ven dar wall's force keeps on working causing the attachment of the adsorbent attaching to the surface of the adsorbate, making strong bond formation and 20-400 kJ/g.mole energy is liberated. It is directly proportional to the available surface area of the adsorbent while the chemical reaction goes on. The most efficient adsorbents in recent times could be activated carbon, silica gel, activated alumina, and synthetic zeolite for effective treatment benefits. The properties of these adsorbents vary from each other as listed in table 1.7.

Table 1.7: Adsorbents and their remarkable properties

Adsorbents	**Bulk density (*lbm/ft*^{3})**	**Heat capacity (BTU/°F/lb)**	**Pore volume (cm^{3}/gm)**	**Surface area (m^{2}/g)**	**Average pore diameter (A)**	**Regeneration temperature (°C)**	**Maximum allowed temperature (°C)**
Silica gel	44-56	0.22-0.26	0.37	750	22	120-250	400
Activated carbon	22-34	0.27-0.36	0.56.1.20	600-1600	15-25	100-140	150
Activated alumina	38-42	0.21-0.25	0.29-0.37	210-360	18-48	200-250	500
Molecular sieves, anhydrous sodium aluminosilicate	44	0.19	4			200-300	600
Molecular sieves, anhydrous calcium aluminosilicate	44	0.19	4			200-300	600
Molecular sieves, anhydrous aluminosilicate	3844		13			200-300	600

Factorial conditions are also responsible for the mechanism; the principle conditions like adsorbent types, nature of adsorbate, pH of reactant media, temperature (exothermic process, increasing temperature decreases adsorption), and the presence of other solutes in the reactant media can critically disobey the process.

1.5.2 Membrane filtration

The physical separation of substance while using the semi-permeable membrane which is guided by the propelling process across the membrane includes Micro Filtration (MF), Ultra Filtration (UF), Nano Filtration (NF), and Reverse Osmosis (RO).

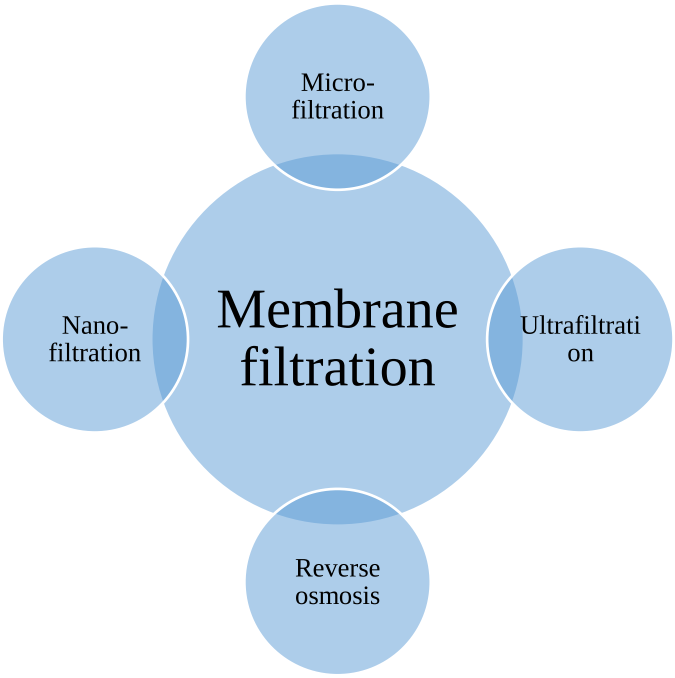


Figure 1.8: Membrane filtration

Microfiltration includes the separation of suspended particles having diameter range between 0.9-90 microns. Ultra-filtration is the process between microfiltration and nano-filtration and the pore ranges are between 10-1000A. Pore size between 0.5 -1.5 nm is used for the nano-filtration. Reverse osmosis is a highly advanced membrane filtration process where 96-99 % of NaCl and 99% of inorganic salts are rejected. The modules of membrane filtration, include many modules like the tubular module, hollow fiber module, spiral sound module, and plate, and frame module. The membrane filtration method, a widespread treatment technology, is capable to concentrate and detach dye incessantly from wastewater. Rather than other treatment methods, it has special features like resistance to temperature and unfavorable chemical surroundings. However, the major demerits associated with the technology include the disposal problem after treatment, elevated capital price tag, and the option of blockage, and membrane substitution. This method of the filtration process is quite appropriate for water recycling in a textile plant in a case where the effluent contains very low dye concentration other than it is unproductive to diminish the solid content dissolved in it that makes the water recycle a complicated assignment (Lau et al., 2009; Hube et al., 2020).

1.5.3 Ion-exchange

The ion exchange process can separate both cation and anion dyes from the dye contaminated textile industry wastewater by passing the dye contaminated textile industry wastewater over the resin of ion exchange till the accessible exchange sites are saturated. The ion exchange materials could be both natural and synthetic based on their requirement for the treatment process. The cationic resins have the functional group: anionic group similarly, the anionic resin has the catatonic functional group. This either could be a batch (resin is stirred with water process completion and spent resin is removed, regenerated, and reused) or a continuous process (water is passed through a packed resin, column and when exhausted, the resin is regenerated and reused). The major applications of the ion exchange process could be the removal of hardness, de-alkalization, de-catalyzation, demineralization, and nitrate removal. The benefits of this technique comprise not much loss of adsorbent on revival, solvent recovery after the process. The foremost disadvantage is its less cost-effectiveness. Another disadvantage is mostly the organic solvents are costly so, the ion exchange technique is not useful for various types of dyes. Again the ion exchange technique is not the most accepted treatment technique at the same time it is of no use for various types of dye removal from textile industry wastewater (Holkar et al., 2016; Hassan et al., 2018).

1.5.4 Irradiation, oxidative processes, and ozonation

By radiation**,** the need of adequate amount of dissolved oxygen is mandatory for organic substances for the reduction of pollutants efficiently. Generally, very rapidly the dissolved oxygen is consumed, in this case, a steady and sufficient provider is required, which adversely affects the cost of this process. This method suggests that only a few types of dyes can be removed by this treatment mechanism (Asghar et al., 2015). The oxidative process is one of the frequently used techniques for dye removal based on chemical applications. For best utilization of the treatment process, hydrogen peroxide (H_2O_2) is considered the most important oxidizing agent. The process efficiency is directly dependent on the activation process of H_2O_2 by which the rate and reduction of dye removal have been based. On the other hand, Ozonation is the process that discharges the effluents with very low dye concentration and COD which is suitable for aquatic pollutant degradation. This technique is widely preferable for double-bonded textile dye molecules. Another advantage of this technology is its easy applicability in a gaseous state, so the secondary wastewater generation and sludge production are very less. In the alkaline state, the decomposition rate of ozone is high. Generally, this technique is not widely accepted due to its low cost-effectiveness which limits the efficiency and utilization in current research aspects (Hassan et al., 2017; Holkar et al., 2016).

1.5.5 Photochemical/ electrochemical

The photochemical treatment process breaks down the dye molecules into carbon dioxide (CO_2) and (H_2O) by utilizing ultraviolet radiation with the existence of H_2O_2. The mechanism behind the treatment is the production of high concentration hydroxyl radicals (OH). The UV radiance could be applied for the activation of chemicals like H_2O_2 at the same time the rate of dye removal from textile industry wastewater is dependent on the intensity of UV radiation, pH of text solution, nature, and structure of the dye. The prime benefits of photochemical-based treatment include minimal generation of secondary pollutants and the odors of dye changes with the effect of UV light (Soares et al., 2017; Al-Mamun et al., 2019). During electrochemical-based treatments, oxidation is observed at electrodes where the difference of potential is applied. Based on this theory, numerous techniques are designed as cathodic and anodic methods. The photochemical and electrochemical-based treatment technologies are suitable for efficient dye reduction at the same time it is also essential for COD reduction from dye industry wastewater. These methods show supplementary advantages like no need for harmful chemicals and no generation of high-load toxic secondary pollutants after the treatment process. But, keeping the cost-effective assessment with other conventional treatment technology, much-elevated differentiation is observed as the use of external electric power input is equivalent to the chemicals for any chemical treatment process.

1.5.6 Sodium hypochloride (NaOCl) and cucurbituril

This technique is based on the use of Cl^- which attacks the textile dye molecules and enhances the treatment process. This process initiates and catalyzes the azo bond cleavage, much suitable for most the dye types for color removal. The proportion of chlorine indicates the pollution remediation as its concentration is directly proportional to the dye reduction rate. When it is discharged into water flows, possesses negative effects that make the process worldwide not acceptable (Siddique et al., 2017). On the other hand, the cyclic polymer of formaldehyde and glycoluril is Cucurbituril. Cucurbituril is well-known to outline host-guest composite with aromatic compounds and this is the exact process for dye reduction. Scientists reported about the credibility and feasibility of this process for dye removal and pollution reduction and should be incorporated with environmental aspects with many advantages. The high-cost requirement is the biggest demerit of this process which needs to be fixed for widespread acceptance (Siddique et al., 2017).

1.5.7 Degradation by bacteria, fungi, and algae

Bacterial cultures are capable and are efficiently used for pollution remediation from different wastewater categories. *Aeromonas hydrophila*, *Bacillus subtilis*, and *Bacillus cereus* were first reported to be efficient for wastewater remediation purposes (Hlordzi et al., 2020). The *Pseudomonas* are proficient in color/dye removal but, they need extended times of adaptation in the conditions for the desired mechanism. Researchers also reported that the bacterial consortium is proficient in removing the azo dye (sulfonated) (Pearce et al., 2003; Wang et al., 2020). Numerous fungi of the genera *Aspergillus*, *Fusarium*, *Trichoderma*, and *Penicillium* are efficient and responsible for high-quality pollution reduction and dye removal efficiency (Alexander and Thatheyus, 2021). *Neurospora crassa* is one type of fungi that could be used for diazo dyes by recent studies (Jamee and Siddique, 2019). *Schizophyllum commune* is also efficient for color/dye removal from textile industry wastewater (Asgher et al., 2013). *Trichoderma sp*., the strain is capable of degradation of toxic chemicals and able for decolorization (Syafiuddin and Fulazzaky, 2021). Microalga strains are capable of toxic dye degradation, color, and nutrient removal from the dye industry wastewater by phycoremediation. The algal species such as *Chlorella sp., Scenedesmus sp., Cladophora, Thalassiosira, pseudonana, Chlorealla vulgaris, Scenedesmus acutus, Scenedesmus obliquus, Scenedesmus subspicatus, quadrcauda, Sagrasuum nutan, Ascophyllum nodosum, S. vulgare, Fucus vesiculosus, Laminaria japonica, and Acrosorium unicinatum* are highly proficient for heavy metal, color and pollution remediation from different wastewater sources. Alga best utilizes the major sources of textile wastewater for its benefits, as it detoxifies these toxic substances and at the same time gains its nitrogen and carbon availabilities (Pathak et al., 2015; Holkar et al., 2016).

Table 1.8: Advantages and disadvantages of dye contaminated textile industry wastewater treatment technologies

Methods	**Description**	**Advantages**	**Disadvantages**	**References**
Adsorption	Solid supports are being used for color and pollutant remediation	Outstanding diminution of contaminant as well as an extensive range of dyes	Problems in restoration and adsorbent disposal create more difficulties	Jegatheesan et al., 2016; Bhatia et al., 2017; Siddique et al., 2017; Pattnaik et al., 2018; Crini and Lichtfouse, 2019; Pazdzdior et al., 2019; Pathak et al., 2020; Samsami et al., 2020
Membrane filtration	Physical separation from the source	Frequently remove every dye type	This process is costly for small and medium industries, high energy requirements creates problems of clogging	
Ion exchange	This is ion exchange resins based dealing	It is especially simple for restoration	This is a decent approach but not suitable for all the types of dyes	
Irradiation	Ionizing radiation-based treatment	extremely efficient in lab-scale	extremely cost needed and not efficient for every type of dyes	
Oxidative process	H_2O_2 is mostly used for this process	Mostly dependant on the activation of H_2O_2	Not significantly efficient for wastewater treatment, release of volatile compounds and aromatic amines	
Ozonation	Oxygen gas-based process	The process is altered in the gaseous state	Half-life is very short as well as very costly treatment method.	

Methods	Description	Advantages	Disadvantages	References
Photochemical/ electrochemical	H_2O_2-UV/ electric based treatment process	Sludge generation is very less in this process	Very costly, nonviable for small and medium scale industries	
Sodium hypochloride (NaOCl) and Cucurbituril	Cl^- based treatment process	Best suitable color removal for several dye types	Very costly	
Bacteria	Pathogenic degradation by using bacteria	Efficient for wastewater treatment	Requires more times for adaptation in the conditions for the desired mechanism, pH dependent	
Fungi	The degradation of wastewater By using fungi	Efficient for wastewater treatment	Requires more time for growth	
Algae	Nutrient removal process by using several micro-algal species	Best suitable for several dye types for color and nutrient elimination	The algal growth varies in different wastewater concentration creates issues, unstable system	

Apart from these treatments, there is another process called chemical treatment which requires chemicals for dye removal. There are certain limitations associated with this treatment in terms of high electrical energy consumption for reactors, need for specific equipment, a huge amount of chemical consumption, and creation of toxic secondary pollutants which adds to the waste disposal problems (Samsami et al., 2020). The merits and demerits of various dye contaminated textile wastewater treatment technologies are enlisted in table 1.8. The discussed treatment options for textile industry wastewater are proficient to disgrace the fabric dyes, but several serious problems like treatment eminence, production of derivative contaminant, elevated power effort makes them unsuitable. In this regard, innovation of essentially advanced, cost-effective, renewable-based treatment technologies is required to solve these issues. So, the combination of more than one treatment system could be more effective in this perspective, so that the gap/limitations of single treatment system can be fulfilled.

1.6. Solar Algal Hybrid Reactor (SAHR): innovative concept for dye contaminated textile wastewater treatment

As mentioned in the preceding sections of this article, a single treatment method for reducing pollutants from dye-contaminated textile industry wastewater is ineffective due to particular limitations in each treatment method. As a result, the concept of combining multiple treatment systems could be the best choice in this instance, leading to the development of hybrid treatment technologies. In order to achieve the best possible outcomes for dye-contaminated textile industry wastewater, solar energy and algal-based treatment have been hypothetically planned and combined in the following section.

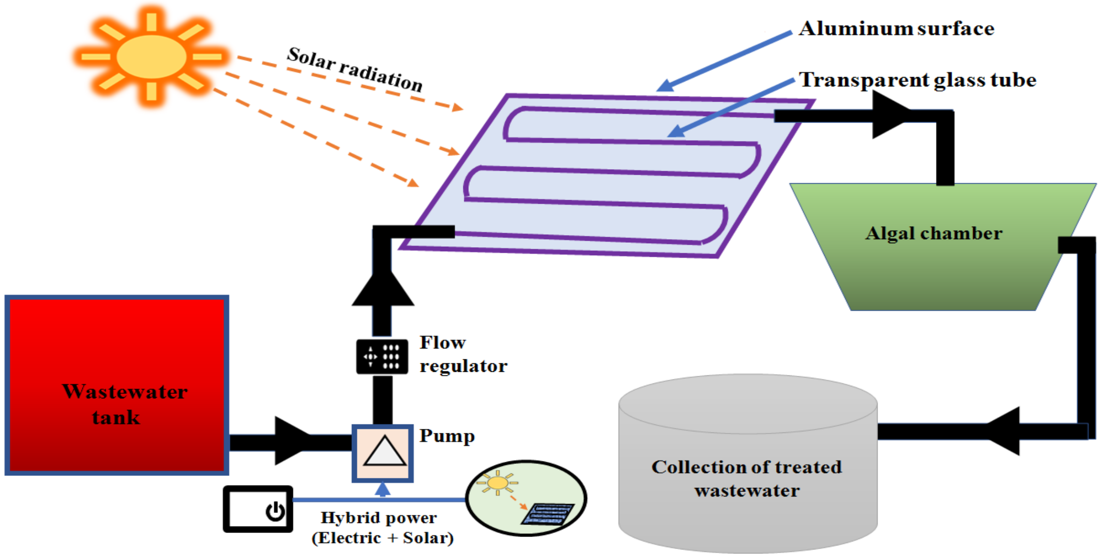
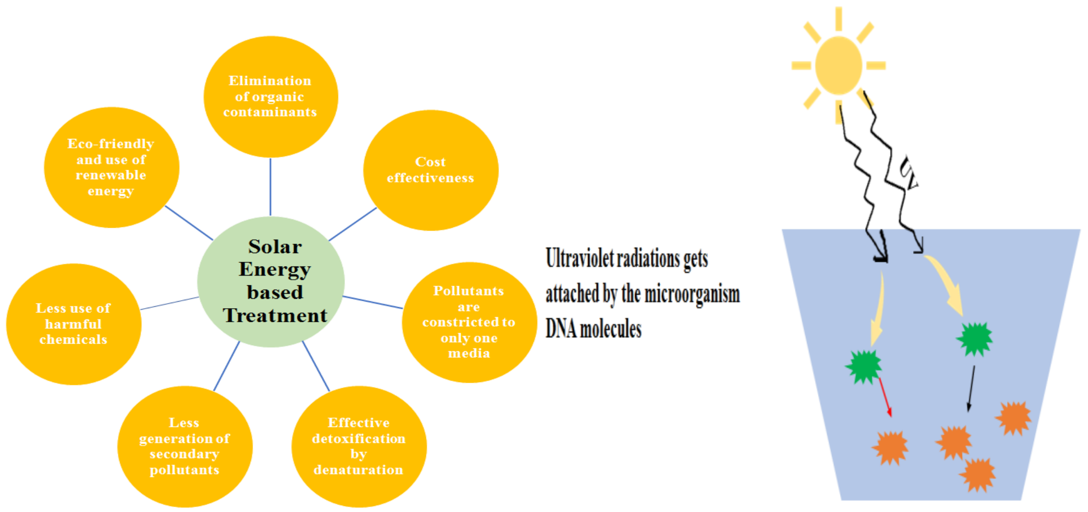


Figure 1.9: Sketch diagram of proposed SAHR

The parabolic trough collector hypothesis was derived from the applications of the production of solar thermal energy which is the best-suited idea for the present study. The SAHR could be made up of parabolic and reflective surfaces that are highly capable of concentrating the solar intensity on the glass tube (transparent tube) in such a way that it could focus on the focal line of the parabolic trough over which the reactant fluid is designed to flow. A manual movable system could be followed at two axes of the reflective surface holder to make the tracking technique smoother and movable in the direction of the sun such that maximum treatment efficiency could be achieved. The solar collector concentration factor is the ratio between the collector “aperture area” and “absorber area”. The cut-off area of the collector which interrupts solar radiation is known as the aperture area. Several impressions on profitable parabolic-trough collectors that have been designed to supply thermal energy are also available. The SAHR system of the reactor tube is a closed system that puts off volatile compounds vaporization. Even though photocatalysts are commonly used in the reactant fluid to influence chemical reactions and improve pollution reduction performance, they are not discussed due to their high cost. The solar algal hybrid system could be built in such a way that individual solar and algal treatment could be connected one after the other for wastewater treatment (as illustrated in figure 1.9). The wastewater would flow from wastewater tank to solar treatment method and from solar treatment method to algal treatment method. So, the wastewater is to be allowed to flow through a designed setup step by step like at the initial stage the water will flow from the wastewater tank to the connecting glass tube by the hybrid (solar/ electric) motor. The wastewater will be circulated through the transparent glass tubes that are connected and positioned over the reflective aluminum surface. Due to the increasing intensity of UV radiation falling on it, the most harmful chemical bonding between chemicals will be broken. At the end of the process, wastewater will move through a connected algal chamber, which could contain free or immobilized algal biomass. The alga is extremely efficient at removing high loads of nutrients. As a result, the wastewater that will be released into the associated algal chamber will have a low nutrient load. Finally, the wastewater could be collected after passing through two stages of the treatment process and similar patterns should be repeated during the treatment process to achieve the best possible outcome. Processing parameters such as flow rate, pH, and temperature all have a significant impact on pollution reduction, as will be discussed later in this article. High-intensity UV radiation is extremely proficient in the breakdown of exceedingly poisonous chemical compounds and is one of the most superior treatment technologies in modern point of times due to its elevated potentiality of toxic chemical compounds reduction and at the same time effortlessly accessibility without any price tag and besides this, it is a renewable energy-based treatment with several supplementary benefits (shown in figure 1. 10(a). Direct ultraviolet radiation neutralizes the toxic chemical and reduces pollution, as the

UV radiations get attached by DNA molecules of wastewater (as shown in figure 1.10(b). Diverse scientists critically reviewed the solar energy-based treatment and established it on a pilot and commercial scale.



(a) **(b)**

Figure 1.10: Necessity of solar energy-based treatment technology (b) pathogenic degradation by solar radiation

Several scientists have reported the impact of solar energy in particular to wastewater treatment like Rodrigues et al (2013) reported COD removal of 30.1 to 70% while experimenting on optimization and economic analysis of textile industry wastewater under-stimulated and artificial solar radiation and Patil et al (2019) confirmed only 30% of COD reduction while treating wastewater by parabolic trough collector. The parabolic collector is mechanically steady process essential for quality wastewater treatment and its necessity of solar parabolic collector has been illustrated in figure 1.11.

Figure 1.11: Requirements of solar parabolic collectors

The primary motive for using algae in the current hybrid setup is its ability to reduce nutrient levels in wastewater. Other treatment methods may be recommended based on their efficacy, but since algae are more effective in terms of nutrient reduction, it is more appropriate to use them in this research. The algae hold the benefits of safe, cost-effective, eco-friendly, non-pathogenic, photosynthetic, less production of toxic substances, and removal of CO_2 from wastewater. As algae play an important role in the tertiary treatment of textile industry wastewater, the regulated use of algae over-collected wastewater not only improves nutrient removal but also helps in the degradation of organic matter. Depending on the dye removal process, various algae are responsible for degrading different dye forms. Several dye removals by the wide range of algal strains have been illustrated in figure 1.12.

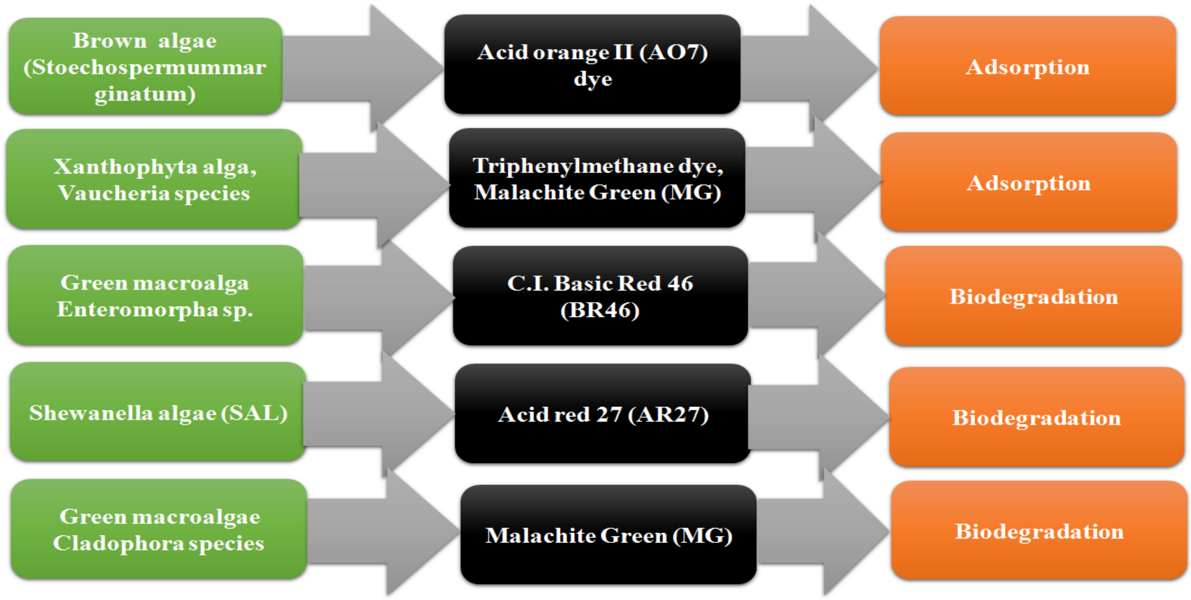


Figure 1.12: Types of algae used for different dye removal with different treatment techniques

Alga enhances the removal of nutrients, heavy metals, pollutants, pathogens and provides O_2 to heterotrophic aerobic bacteria to oxidize organic pollutants, and in turn, use the CO_2 released from bacterial respiration**.** Similar to this mechanism, photosynthetic aeration reduces operation costs and limits the risks for pollutant volatilization under mechanical aeration and studies have shown that algae could support the aerobic degradation of various hazardous contaminants.

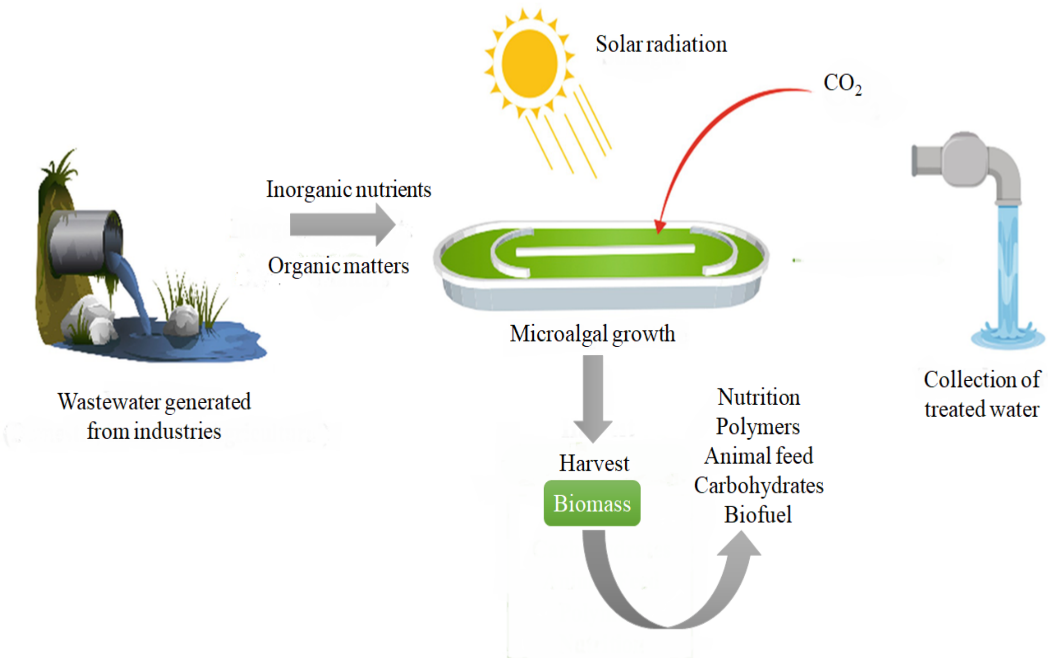


Figure 1.13: Phycoremediation approach of wastewater treatment

Nutrients are not concerned as hazardous materials and the removal of N-containing contaminants is quite interesting because its biodegradation leads to the formation of ammonium ions or nitrate. Alga itself utilizes nitrate and phosphate for its cell growth in the synthesis of cellular components. Thus, algae provide an effective way to remove nutrients than that any other treatment system**.** The group of heavy metals (Pb, Cr, Cd, Cu, *etc*) includes hazardous contaminants which are frequently present in textile industrial wastewater and algae can potentially remove these pollutants along with specific metal groups. It follows adsorptions as well as absorption methodology to uptake metal from industry wastewaters and can finally biodegrade hazardous organic pollutants. Oxidation through photosynthetic aeration is one of the most significant advantages of using algae as it reduces the cost of aeration, which causes high energy consumption in the conventional treatment plant. Many recalcitrant and toxic compounds are much easier to degrade aerobically hence the consortium of algae successfully degrade the organic matter (Udaiyappan et al., 2017)**.** A broad variety of algal strains such as *C. vulgaris*, *C. pyrenoidosa*, *Scenedesmus* sp., *Chara* sp., *Dunaliella* sp. *Scenedesmus acutus, Scenedesmus obliquus, Scenedesmus subspicatus, quadrcauda, Sagrasuum nutan, Ascophyllum nodosum, Sargassum vulgare, Fucus vesiculosus, Laminaria japonica, and Acrosorium unicinatum* and *Oscillatoria* sp. have been utilized for different wastewater treatment according to their specific removal efficiency could also be implemented for the current SAHR proposal.

The basic idea behind the use of solar parabolic through the reactor is its easy handling technique, efficient distribution of ultraviolet radiations, very low use of harmful chemicals, robust and resistance to environmental, very low operational cost conditions, resistance to temperatures lightly high (40-50 °C), no carbon emission and to end with extensively cheap and renewable-based treatment which provides scientific scopes for modern researches/ scientists. Several researchers are currently working to increase the efficiency at the same time minimize the costs of the process making it economically competitive with traditional remediation options. The basic idea behind the application of solar-energy-based-system is to substitute those treatment systems which run on fossil fuels-based technologies. Based on the extensive literature, combination of solar energy-based and phycoremediation, establishes energetic possibilities for elevated dye contaminated textile industry wastewater treatments. Along with these, several factorial conditions are responsible for the process validity which are essential to be discussed and are given below:

1.6.1 Factors responsible for SAHR

The implementation of SAHR necessitates the management of a number of variables, as well as a number of processing parameters that determine the wastewater treatment mechanism. The impact of these processing parameters changes with the change of chemical composition, available resource utilization, scientific mechanisms/ protocols followed by the treatment process. The high impact factorial conditions are very much crucial to maintain at the same time optimized with different experimental conditions (discussed below).

1.6.1.1 pH

SAHR is affected by pH, which is a key influencing factor in chemical reactions. A shift in pH may either catalyze or moderate the rate of reaction (wastewater treatment). As a result, pH assessment should be thoroughly investigated in order to ensure that the treatment process is as effective as possible. The optimum pH for dye contaminated textile wastewater treatment has been stated by researchers in various perfectives, which varies depending on the nature and experimental conditions. However, in the SAHR adsorption process, algae are used to treat wastewater, and alkaline conditions provide the best performance. The adsorption of metallic ions by microalgae is highly dependent on the pH of the solution, and many factors such as the surface functional groups of algae and the complexity of the metallic ions affect the adsorption behavior at different pH ranges. While, various uncertainties have been observed at different pH for wastewater treatment, such as Jalali-Rad et al (2004) who recorded maximum Cesium adsorption for Padina australis at only pH of 2. Textile-contaminated wastewater is typically alkaline, so optimizing it could help achieve the best possible outcome. So, in a hybrid treatment system, the pH value is the most essential part to consider. As the pH of the solution rises, the adsorbent acquires a net negative charge, which promotes the adsorption of behavior. Conversely, as the pH of the solution falls, the adsorbent acquires a net positive charge, which promotes the adsorption of anions.

1.6.1.2 Temperature

The temperature of dye-contaminated textile industry wastewater varies from 30 to 40 °C. The temperature rises to a certain point when running SAHR due to the effect of solar radiation. It plays a critical role in the solar algal-based hybrid treatment system, as rising the temperature of the reactant medium promotes higher solubility and the breakdown of toxic chemical bonds in wastewater, allowing the wastewater molecules to be attached by the micro-algal surface. At the same time, as the temperature of the wastewater rises, the randomness of the dye molecules rises, increasing the probability of dye molecules being attached to algal biomass. This means that the hybrid treatment system has a direct enchantment of adsorption. This weakness of treatment is that the temperature cannot exceed 50°C in order for the alga's structure to remain unaffected by high-intensity solar radiation and for the temperature to be monitored in such a way that the alga's vegetative structure would be protected and enforced for further emission reduction from wastewater. Fard and Fazaeli (2016) found that raising the temperature from 25°C to 60°C increased the degradation of azo dyes, with the optimal temperature range for azo dyes using CdS and Ag/CdS nanoparticles being 40-60°C. As a result, though SAHR is experimenting with dye-contaminated textile industry wastewater, temperature optimization is recommended for maximum efficiency.

1.6.1.3 Contact time and algal density

While SAHR is proportional to contact time, algal growth varies with different wastewater concentrations, and different algal strains are responsible for different growth times. More pathogenic degradation can occur if wastewater molecules are exposed to more sunlight. The rate of photochemical degradation of dyes present in textile wastewater increases as the duration of sunlight exposure to textile wastewater increases, but only up to a certain point. The adsorption is enhanced by increasing the contact time of the solution; however, increasing the contact time further would have little effect on the adsorption pattern. Due to an increase in adsorbing sites, an increase in algal density improves the adsorption of wastewater molecules. Furthermore, increasing algal biomass concentration reduces the absorption rate by shortening the distance between adsorption sites. The optical density of algae should be more precise in order to improve the performance of pollution reduction with a hybrid treatment system.

1.6.1.4 Solar intensity/ flow rate

SAHR is proportional to the intensity of solar radiation, but it is a highly variable factor that depends on the weather. At different times and under different weather conditions, the performance varies, and as the solar intensity increases, the rate of dye degradation increases. The degradation of dyes in wastewater is also affected by the wastewater flow rate. Fard and Fazaeli (2016) investigated the impact of flow rate on the degradation of azo dyes treated with CdS and Ag nanoparticles using solar energy. The flow rate is the amount of time that wastewater molecules are exposed to solar radiation and the algal chamber at SAHR. However, before attempting to use a hybrid treatment system, flow rate optimization must be investigated for the best results. It is to be considered that the concentrated collector requires clear sky so that more direct solar radiations can concentrate on the collector and cloudy climatic conditions are mostly unfavorable which marks the major demerit. In this context, it is a highly essential treatment system emphasizing the renewable energy-based treatment option.

1.7. Cost-effective approach of hybrid treatment

The traditional treatment technologies are costly to hand out and difficult for researchers to utilize. Though, the pollution diminution capability of those methods is reasonably fine but, serious factors like high sludge production, supplementary time consumption, high requirement of manpower and additional time requirement for final manufacturing product generation make them unviable. A single treatment system is capable to demean dye-contaminated textile industry wastewater but, in many aspects, it fails. Comparing conventional treatment technology with hybrid treatment options based on cost-effectiveness generates plenty of optimistic scopes for hybrid ideas. The hybrid technologies are exceedingly professional for contamination remediation from dye contaminated textile industry wastewater also derives ideas on the lesser need of operational resources. The maintenance cost, operating cost, capital cost, and energy requirement, manpower needs are lesser (comparing ratio of two treatment technology) in comparison with a single treatment system. The assumption of hybrid treatment options sometimes changes in specific cases with the manufacturing process being utilized, nature of raw materials, the complexity of used chemicals, the capacity of external power being imposed, and expertise of the operator as these process parameters change the major impact of cost-effective analysis. The foremost explanation behind the hybrid treatment option is more preferred as it shows immense opportunities for industrialists and researchers on the ground of treatment cost. The hybrid treatment options are more valid, reliable, and specific based on cost-effectiveness. Any treatment technology is considered novel and widely accepted when the used resources are a lesser amount cost consuming than its relative treatment technology. Based on the textile manufacturing process, wastewater generation, sludge production, and available treatment options for its treatment, solar-algal-based preferences are economically stable and create immense opportunities for pilot scale compatibility.

Environmental degradation and its restoration preferences should be looked forward by modern scientists. The coupling of more than one treatment system is favorable from environmental perspectives as it consumes less energy and labor at the same time it is more efficient for pollution remediation of dye contaminated textile industry wastewater. Recent science needs more certified treatment technologies favorable for ecosystem balance as well as pollution minimization. In this context, the hybrid treatment option is new innovative, cost-effective, less energy-consuming, and environmentally friendly treatment technology which is much needed for recent environmental pollution scenarios. This recent global scenario is fully dependent on new, novel treatment options where the expectation for high load pollutants could be easily minimized at the same time the hydrosphere imbalance could be avoided. The eco-friendly treatment system has been emerged by various scientists some years ago but, the success rate of these methods was very rare and in some specific cases, these methods were unable to gain attention for implementation and further enhancement. The present option of SAHR is an advanced option for dye contaminated textile industry wastewater treatment and is capable of fulfilling such expectations. Finally, to carry out the recent process on a long-term basis, proper importance/ preferences should be taken over this approach.

1.8. Other recent approaches for dye contaminated textile industry wastewater treatment

Researchers across the globe have developed many recent technologies for the removal of dye from textile industry wastewater. These recent techniques include biological methods, advanced oxidation process (AOP), nanotechnology, nanofiltration, *etc.* Besides these techniques, researchers have also opted for some hybrid techniques in order for better dye removal efficiency like membrane bioreactor (MBR), and photocatalytic membrane reactor (PMR) (Samsami et al., 2020). MBR technique is the integration of biological treatments and physical treatments. The removal efficiency of MBR for dye is 60-75% (Hoinkis et al., 2012). The advantage of MBR over conventional methods is its high efficiency in microorganism retention, low maintenance, less sludge production. However, the disadvantage associated with the technology is membrane fouling (Cosenza et al., 2020). PMR technique is the integration of chemical and physical treatments. The striking features of this technology include strong oxidizing properties and degradation of refractory organic contaminants (Samsami et al., 2020). Both the technologies are reliable, cost-efficient but the major drawback in their commercial implementation is membrane fouling.

1.9. Conclusion

Unhygienic wastewater is an incessant concern for the ecosystem and society. The contemporary accessible contamination diminution technologies for dye contaminated textile industry wastewater like bacteria, fungi, physical, chemical anaerobic, and aerobic techniques have potential for pollution reduction but, several stern disquiet composes them adversely. For that reason, a search for highly developed technologies with a cost-effective/low-cost option for their handling is necessary. So, in this context, integrating more than one progression increases the treatment efficiencies which not only eliminates the contaminated substances but also utterly degrades dyes. Solar radiation-induced degradation of contaminants is now explored by various advanced researchers and on the other hand, algae play a key role in nutrient removal. Hence, both the algal treatment system and solar energy-based treatment system are showing mutual advancement to each other as well as helping in dye contaminated textile wastewater treatment. Therefore, the combination of both the treatment systems (solar-energy-based-treatment with algal treatment system) can fulfill the remaining gaps with a single treatment system as a sustainable green approach.

Therefore, keeping all these challenges in mind with a low energy cost, following objectives have been formulated in order to prove the concepts by experimental validations:

1.10 Objectives

As per the above literature, the present study has been focused to fulfill the following objectives:

1. Selection of sites for industrial wastewater with the dye as contaminant, its collection and its physical and chemical characterization.
2. Designing of a solar energy based hybrid treatment system (SEBHTS) for detoxification and decolorization with possible end uses.
3. Parametric studies to optimize the process in designed reactor (pH, temperature, flow of wastewater and doses) with and without coupling of solar-algal technology.
4. Comparative techno-economic assessment of SEBHTS for green and clean environment with conventional methods of dye contaminated wastewater.

The extensive research design has been formulated to fulfill these major objectives and the requirements, materials, and methods, as well as results, have been discussed in the upcoming chapters.

Chapter-2

Materials and Methods

2.1 Introduction

This chapter describes the experimental methodology that has been used for this study with detailed elaboration. The purpose and analytical technique of each experiment has been discussed in detail. It outlines the textile industry wastewater, its characteristics; the major wastewater parameters involved with it, its reactive nature towards the adsorbent, the C. *pyrenoidosa* algae as adsorbent its adsorptive behavior toward pollutants as well as dye removal from textile industry wastewater. This chapter also derivate scopes on the industrial ideas on the immobilization process, its impacts in the industrial sector regarding pollution reduction in different wastewater. The process of mechanism for the preparation of immobilized algae has been discussed in this chapter. Solar energy is a key factor in this study. So, solar energy-based treatment setup for pollution reduction has been discussed in this section. The algal-based setup, solar energy-based setup, and combination of both i.e. hybrid setup have been summarized here. All the materials and methods used have been discussed in the following sections:

2.1.1 Glassware, chemicals and reagents

All the reagents for this study were prepared with the help of distilled/deionized water to avoid contamination. The plastic container and glassware were used for this study were washed followed by rinse with Milli-Q water. In general, all chemicals were of analytical reagent grade. All the aqueous solutions were also prepared in Milli-Q water.

2.1.2 Section of the site

To carry out the experiment for the study, the textile industry wastewater samples were collected from the local textile industry (Handloom Bhandar, Unnao, Uttar

Pradesh, India (26.55°N 80.49°E)). This area is called the industrial hub of Kanpur district as so many types of industries are found there. So, it was decided to collect the textile wastewater sample from this place. For this purpose, the plastic cans (20 L) were used to collect dye industry wastewater samples. Contamination is a major issue in laboratory experiments. So, the collected textile wastewater samples were stored in the laboratory at 4ºC to suppress/avoid any microbial activity for further experimental use.

2.1.3 Characteristic of sample

The initial physicochemical characterizations were accomplished by following the standard analytical procedures prescribed by American Public Health Association (2012). Afterward, to precede the batch experiment, the desired concentrations (test solution) of the textile industry wastewater were maintained by diluting with distilled water to investigate the adsorptive behavior of algal biomass. The UV visible spectrophotometer (HALO-DB 20, Thermo Scientific) was used to detect the optical density of dye industry wastewater (485 nm, λmax) after scanning the wastewater sample. To perform the study the textile industry effluents were converted into two concentrations (50% and 100%). The present study is focused on the treatment of real textile industry wastewater rather than concentrated forms. The real wastewater gives more ideas on the treatment efficiency and details the advantages as well as disadvantages of the applied mechanisms. Therefore, only two concentrations of textile industry wastewater were used for this present study.

2.2. Algal species: culture and growth

The fresh algal culture of *Chlorella* species was collected from the National Collection of Industrial Microorganism (NCIM, ID- 2738 Pune). Biochemical compounds of algal biomass are key factors and they play a crucial role in the production of large numbers of end products.

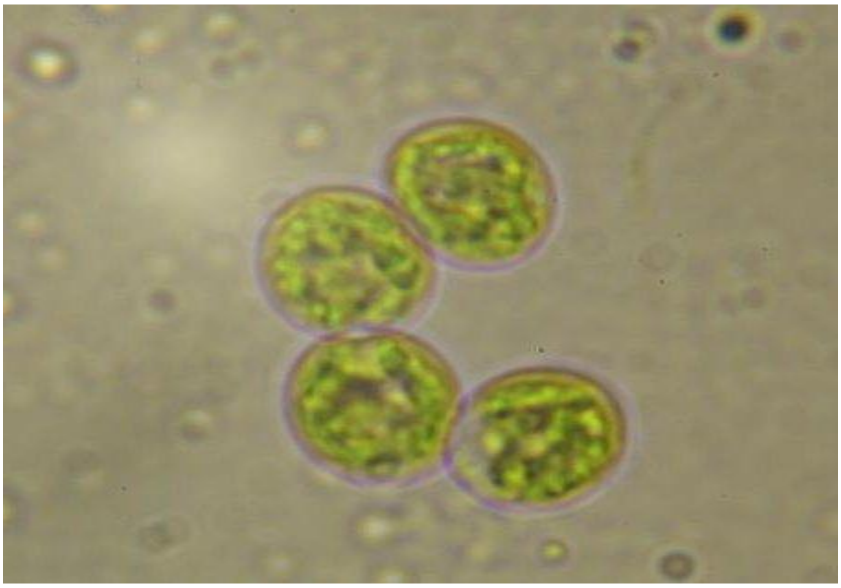


Figure 2.1: Microscopic image of *C. pyrenoidosa* (Jaiswal et al., 2016)

Table 2.1: Scientific classification of *C. pyrenoidosa*

Kingdom	Plantae
Division	Chlorophyta
Class	Trebouxiophyceae
Order	Chlorellales
Family	Chlorellaceae
Genus	*Chlorella*
Species	*Pyrenoidosa*

The collected *C. pyrenoidosa* species which was acquired from the National Collection of Industrial Microorganism (NCIM-2738), Pune, India was retained in BG-11 growth medium as summarized in Table 2.2 Algal cultures were manually agitated to provide homogenous nutrient distribution as well as to avoid algal threads stickiness. Nutrient medium and flasks in which algal cultivation took place were sterilized by autoclaving at 15 psi and 121°C temperature for 20 minutes.

Table 2.2: BG-11 composition

Stock solutions of nutrients	Quantity
*$NaNO_3$	15.0 g
**K_2HPO_4	2.0 g
**$MgSO_4.7H_2O$	3.75 g
**$CaCl_2.2H_2O$	1.80 g
**Citric acid	0.30 g
**Ammonium ferric citrate green	0.30 g
**$EDTANa_2$	0.05 g
**Na_2CO_3	1.00 g
Trace metal solution:	
*H_3BO_3	2.86 g
*$MnCl_2.4H_2O$	1.81 g
*$ZnSO_4.7H_2O$	0.22 g
*$Na_2MoO_4.2H_2O$	0.39 g
*$CuSO_4.5H_2O$ 0.08 g	0.08 g
*$Co(NO_3)_2.6H_2O$	0.05 g

**per litre; ** per 500 mL*

Afterward, the cultured algal species were harvested and used for the batch experiment in immobilized as well as free algal cells. The culture was exposed under florescent light for 12:12 h day and night cycle at optimum temperature 25±2ºC. Algal cultures were agitated homogenously for nutrient distribution as well as avoid sedimentation. Micro-algal growth was measured by taking optical density at 480 nm by using spectrophotometer (HALO-DB20 thermo-scientific).

2.3 Experimental design

As per the objectives, the present research work has been divided into three phases (Phase-I, II, and III) to make it more fruitful with significant findings such as:

- **Phase-I:** Algal based treatment
- **Phase-II:** Solar energy-based treatment
- **Phase-III:** Hybrid treatment (Combination of both solar and algal-based treatment technology)

Table 2.3: Experimental plan used for current research work

Phase-I (Chapter-3) **Phase-I Phycoremediation of textile industry wastewater by using both free and immobilized *C. Pyrenoidosa***	**Phase-II (Chapter-4)** **Use of Solar Parabolic Trough Reactor (SPTR) for treatment of textile industry wastewater**	**Phase-III (Chapter-5 and 6)** **Use of hybrid treatment setup for textile industry wastewater and comparative assessment among algal, solar and hybrid treatment system**
Selection of sampling site, collection of the sample, and its initial physicochemical characterization. Algal growth with BG-11 media. Phycoremediation of dye industry wastewater using microalgae *C. pyrenoidosa* by Free Algal Cell (FAC) and Immobilized Algal Cell (IAC) • Dose, pH, and temperature optimization with the best result obtained between FAC and IAC • Data assessments-study, statistical analysis, SEM, DES study of *C. pyrenoidosa*. The optimized results are to be used for hybrid treatment setup.	Solar energy based setup to be designed in lab-scale and textile wastewater was treated with it The process parameters (flow rate) to be optimized and the best result to be considered for the hybrid treatment system.	The hybrid setup was designed in lab scale Textile wastewater to be treated with designed hybrid setup with optimized experimental condition (dose, pH, and flow rate) • Impact of flocculants, dose, pH, flow rate on pollution and color reduction efficiency Cost-effectiveness and eco-friendly assessment

Phase-I consists of Phycoremediation of collected industry wastewater with several sub-phases. This phase also consists of several sub-phases where the phycoremediation process undergoes. *C. Pyrenoidosa* is used for this process. The efficiency of *C. pyrenoidosa* was checked for the treatment of textile industry wastewater. In the sub-phases, the immobilization of *C. pyrenoidosa* was also studied and its impact and an analytical between free algal biomass and immobilized algal biomass were discussed in this phase. Phase-II is focused on the solar energy-based treatment of textile industry wastewater. In this phase, the fabrication of solar parabolic setup was made in departmental location. The fabrication was made in such a way that it could be used further in phase III. Phase-III is the main study of this research. This phase is based on the fabrication of hybrid setup for the treatment of textile industry wastewater. In this setup a combined setup of both solar setup (phase-II) and algal setup (phase-I) was made. This combination is best suitable for the treatment of textile industry wastewater as discussed in the above literature discussion section. The total work design has been illustrated in figure 2.2.

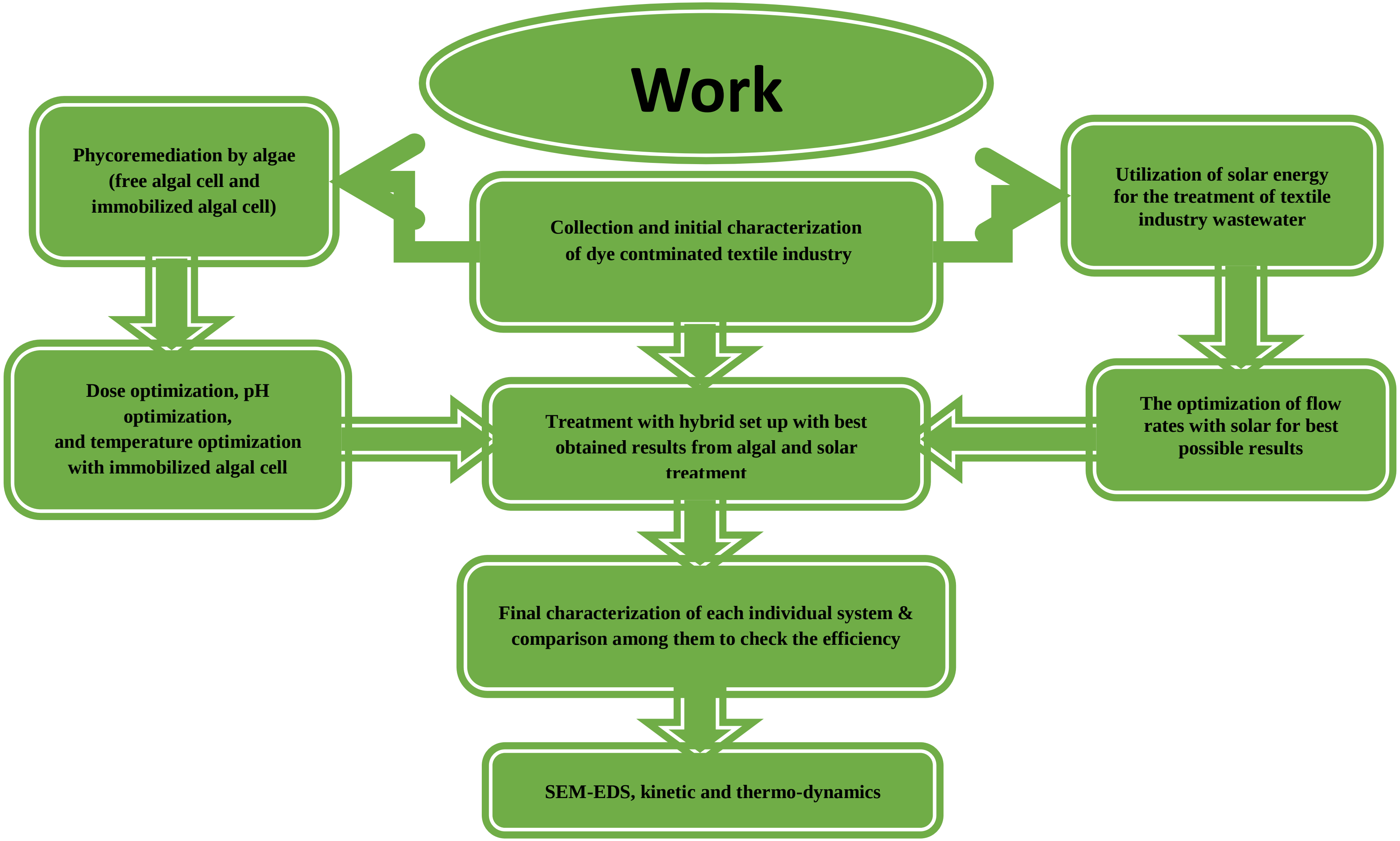


Figure 2.2: Work design of the proposed research work

After formulating the above work designing the individual experimental plans were conducted to fulfill the objectives have been discussed in the following sections:

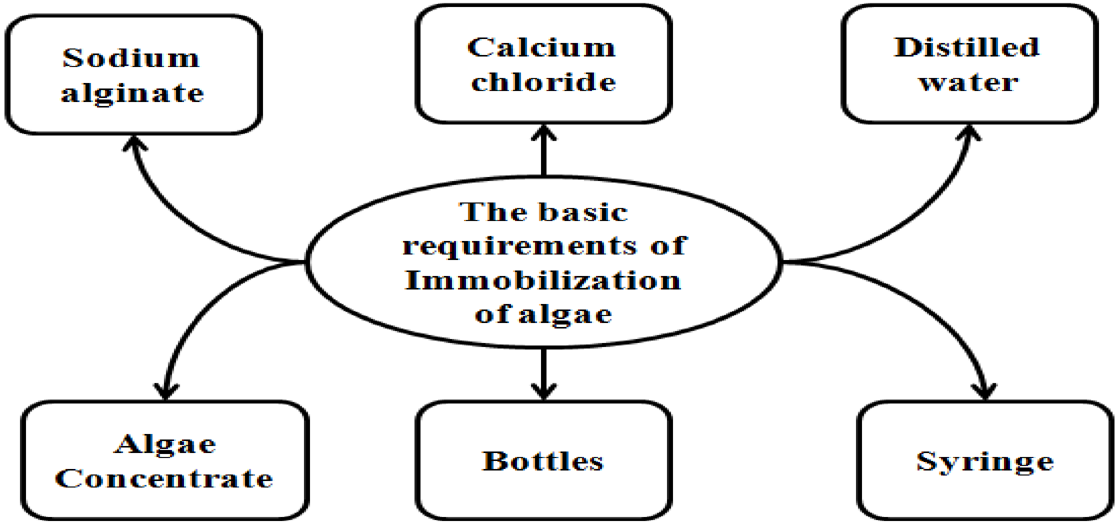
2.3.1 Phase-I: Phycoremediation of textile industry wastewater by using both free and immobilized *C. Pyrenoidosa*

The major objective of this experiment was to grow *C. pyrenoidosa* algal strain textile industry wastewater and investigate its potential for pollution reduction and color removal from textile industry wastewater**.** The algal strain grows in the textile industry wastewater by utilizing the nutrients like nitrate and phosphate available in the wastewater. When the nutrient availability is more the growth rate of algal strain is more. Again the growth depends on external factors like pH, light, and temperature of the surroundings. All these multiple variables are responsible for the growth as well as treatment of textile industry wastewater. Here, for the present study, the real textile industry wastewater was taken rather than synthetic wastewater, to make the process practically applicable. To study the potential of *C. pyrenoidosa* cell with real type textile industry wastewater for dye removal and pollution reduction experimentally, it was investigated with two concentrations of test solution (50% & 100%). The best pollution reduction efficiency between the two concentrations (50% and 100%) was calculated by analyzing the wastewater parameter of textile industry water before and after the growth period. The textile wastewater concentration (between 50% and 100%) where the best result for color removal and pollution reduction was only retained rather than the other one during this present experiment. Then another experiment was conducted for the pollution reduction and color removal of textile industry wastewater with immobilized algal biomass. The process of immobilization is a highly modern scientific procedure being applied in recent industrial as well as research areas. The mechanism of immobilization of *C. Pyrenoidosa* has been discussed in the following section:

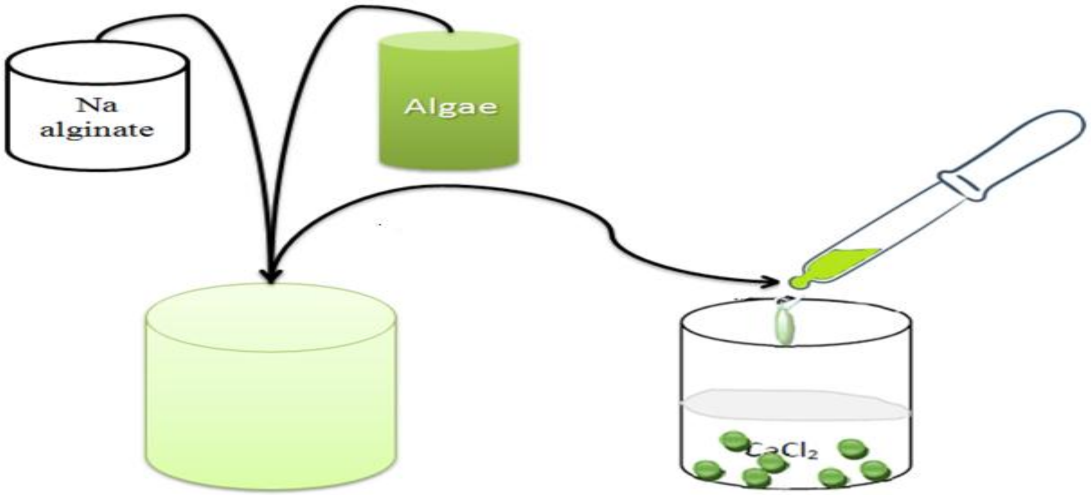
2.3.1.1 Immobilization of algal cells: process & mechanism

Algal immobilization is a sophisticated industrial process for reducing pollutants and here equal amounts of algal cell suspension and sodium alginate (viscous in nature) are assorted and added drop by drop to calcium chloride solution for the conversion of algae into immobilized form (illustrated in Figure 2.3). The inoculated algal strain is a highly dense culture with a 3.27 optical density. Calcium ions have the ability to connect alginate monomers, resulting in a gel form of calcium alginate. It doesn't assist in the adsorption process. However, the sodium salt of alginic acid ($C_6H_8O_6$) was chosen because of its intrinsic gelatinous structure, algal cell bio-adhesion, and low toxicity. The number of cross-link forms, the length of blocks with links, and the types of bivalent ions utilized all affect the strength of an alginate gel. The capacity to form gels is determined by intermolecular hydrogen bonding. When sodium alginate is dropped into a calcium chloride solution, gel beads form and cations permeate into the polymers via sodium alginate solution droplets. Calcium alginate serves as an enzyme, as well as an inert and insoluble substance that has the ability to bind algal cells towards pH and temperature.

Thus, living algae cells are captured and immobilized in small beads, which are then collected for future experimental purposes (Chakraborty et al., 2018; Al-rub et al., 2004; GTAC, 2016).



2.2 (a)



2.2. (b)

Figure 2.3: (a) Material required for the process; (b) lab-scale process for IAC

For the current investigation, the above-mentioned technique was used to immobilize the algae following the scientific protocol. Algal cells were immobilized with sodium alginate in a batch procedure using aqueous solution of alginate. In the laboratory, 1.5% sodium alginate solution and 2% $CaCl_2$ solution were prepared and the sodium alginate solution was then merged with the healthy algal cell suspension in a 1:1 ratio. A homogeneous mixture (natural polymer derivative of algal polysaccharide) was achieved by gently combining the algae and alginate. To achieve a homogeneous and circular surface, the algae-alginate mixture was added to a 2% $CaCl_2$ solution using a syringe pump (TRUTH glass surgical size: 20 ml, Luer-Lok tip with 30 mm needle size). When the mixture comes into contact with the $CaCl_2$ solution, the alginate entraps the algal beads and hardens them into homogeneous circular algal beads. Water may pass through alginate and into the bead because it is a hydrophilic polymer and before being utilized as a dye adsorbent, these algal beads were cleaned and maintained in distilled water (illustrated in figure 2.3).

The current study was split into two phases: the impact of (a) free algal cells (FAC) and (b) immobilized algal cells (IAC) on wastewater. On the basis of comparing results, the best cells were explored further at various temperatures, as described in later sections of this paper. The real wastewater was used for this study rather than artificial/ synthetic wastewater, as it has been researched in small numbers by researchers. Only two specific concentrations were chosen to identify the exact adsorption rate under real-world wastewater conditions. At every 20-minute interval of the experiment, the decolorization progress was measured using a UV spectrophotometer (HALO-DB 20) by reading absorbance at a maximum wavelength to identify the dye colors in wastewater.

According to the literature, the maximum wavelength of the HALO-DB 20 UV visible spectrophotometer at 485 nm supports the possibility of blue color dyes in wastewater.

2.3.1.2 Impact of algal cells on decolorization

The FAC and IAC were treated with a constant amount of algae ($2gL^{-1}$) that was exposed to two different concentrations of dye industry wastewater (test solutions of 50%, and 100 percent). After creating the required test solutions, the experiment was run for 180 minutes in a series of batch operations under the following conditions: dye concentration at room temperature (30°C-35°C) the samples were tested with a UV visible spectrophotometer (HALO-DB 20) at 485 nm to check if they had decolorized. The best result from IAC was then used to investigate the effect of temperature on the cell with a 50% concentration of wastewater.

2.3.1.3 Impact of temperature with IAC on decolorization

The test solutions were treated by four different temperatures (30°C, 40°C, 50°C, and 60°C) in order to make the study findings broadly applicable with ambient temperature ranges and the best possible dye removal efficiency in real wastewater. The batch experiment's temperatures were balanced for 180 minutes using a thermostat (Digital thermostat AC 220V, 1500W temperature controller switch, Amici Smart AC). After executing the experiment with the appropriate temperature ranges, the decolorization removal (%t) was measured with a UV visible spectrophotometer at (HALO-DB 20).

2.3.1.4 Mathematical calculations

After maintaining the batch experiment for the desired period, the percentage (%) of decolorization/dye removal and specific uptake was calculated by the following equations (1) and (2):

$$Specific\ uptake = \frac{c_0 - c_1}{x} \quad (1)$$

$$Decolourization\ (\%) removal = \frac{c_0 - c_1}{c_0} \times 100 \quad (2)$$

Where C_0 = initial dye concentration in MgL^{-1}; C_1 = dye concentration after adsorption in MgL^{-1} and x = adsorbent doses in gL^{-1}.

2.3.1.5 Adsorption isotherm study

Adsorption isotherms (Langmuir and Freundlich) and kinetic model (pseudo-second-order) were used to investigate the adsorption mechanism.

The sorption process of dye adsorption with the application of adsorbent was studied using the Langmuir isotherm.

. The uptake of dye was calculated by Equation (1) given by the

$$q = \frac{(C_i - C_f) * V}{1000 * m} \quad (3)$$

Where q is the amount of dye uptake (Mgg^{-1}), C_i and C_f represent the initial and final concentration of dye (MgL^{-1}) V is the volume of dye solution (ml) and amount of adsorbent is represented by the m (g).

To analyze the kinetics of the sorption process, the linear form of Langmuir isotherm is obtained by plotting 1/q vs 1/C_f can be obtained from Equation (4).

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\, b} + \frac{C_e}{q_{max}} \quad (4)$$

Where, qe represents the amount of dye adsorbed at equilibrium by adsorbent (Mgg^{-1}), C_e is the concentration of adsorbate at equilibrium in solution after adsorption

(MgL^{-1}); q_{max} is the Langmuir constant which represents the maximum adsorption capacity. Value of q_{max} and constant b calculated by using the intercept and slope. The maximum monolayer sorption capacity was obtained from Eq. 4 and the essential feature of the Langmuir isothermic model may be expressed in terms of equilibrium parameter or separation factor R_L dimensionless constant (Hameed et al., 2007). The value of R_L indicates the adsorption nature unfavorable if $R_L>1$, for favorable nature of adsorption R_L value ranges between 0 to 1 and irreversible nature of adsorption express By $R_L=0$. The value of R_L was calculated by using Equation (5):

$$R_L = \frac{1}{1 + bC_i} \tag{5}$$

The Freundlich isothermic model was also used to evaluate the efficiency of adsorbents. It's non-ideal and reversible, and it's not just for monolayers; it's also used in multilayer models. The isotherm is expressed by Equation (6).

$$q_e = K_f C_e^{1/n} \tag{6}$$

q_e and C_e define in above and K_f is expressed as Freundlich adsorption coefficient (Mgg^{-1}).

The linear form of Freundlich can be logarithmically expressed by Equation (7).

$$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log K_f \tag{7}$$

Thus, a plot established between q_e and C_e is a straight line, values K_f and n can be calculated from the slope and intercept of the plot. If the slope ranges in between 0 to 1, the surface is more heterogeneous and the process is favorable but if the value above 1 indicates the adsorption process is cooperative in nature and unfavorable (Tan et al., 2008; Guarín et al., 2018).

2.3.1.6 Adsorption kinetics

This research provides a pseudo-second-order kinetic model for dye adsorption with algae in addition to the Langmuir and Freundlich isothermic kinetic models (Simonin et al., 2016; Nuhoglu et al., 2009; Katheresan et al., 2018) and because of its accuracy, this kinetic is widely used for a variety of purposes in the research field. So, the surface binding with the dye removal concerning time can be calculated by pseudo-second-order kinetics, which has been expressed in the following Equation (8):

$$\frac{d_q}{d_t} = k_2(q_e - q)^2 \qquad (8)$$

Where k_2 represent the second order rate constant (g $mg^{-1}min^{-1}$) integrating the eq.(6) at initial condition (t=0 and q=0) and after some time (t=t means q=qt) which gives the expression of Equation (9):

$$t/q_t = 1/\, K_2 q_e^{2} + t/q_e \qquad (9)$$

Where K_2 is the equilibrium rate constant (g mg^{-1} min^{-1}); q_e is the amount of dye removed at (Mg g^{-1}) equilibrium; q_t is the amount of dye removed at time t in (Mg g^{-1}). Initial variables such as q_e and q_t are quantified by the following equation:

$$q = (C_0 - C_1\,) \times \frac{V}{M} \qquad (10)$$

Where, q = adsorbent capacity; C_0 = Initial dye concentration; C_1 = dye concentration after adsorption; V = total volume of the solution (L); M = Amount of algae used (MgL^{-1}). A straight plot is derived with the help of pseudo- second-order kinetic model between t/q versus t. With the help of this straight-line plot, different variables such as K_2 (rate constant), h (initial adsorption rate which was calculated by the formula: h = $k_2 \times q_e^2$), and q_e (Calculated adsorption capacity) were calculated.

2.3.1.7 Desorption study

The desorption experiment for FAC and IAC was also conducted with 200 ml of dye industrial wastewater in a 50% test solution and 0.25 gm of adsorbent, Because the change in pH assists to provide the result of desorption and propose the nature of dye and adsorbent behavior, acid hydrochloric acid (HCl) and base sodium hydroxide (NaOH) were utilized in the study of desorption (Yao et al., 2010).

2.3.1.8 Thermodynamic functions

The feasibility of adsorption over different temperatures can be calculated by developing Eyring and Arrhenius equations.

2.3.1.8.1 Eyring equation

The use of thermodynamic parameters has been used to investigate the adsorptive behavior of adsorbents. To determine the thermodynamic variables, the graph plotted between $\ln K_2/T$ vs $1/T$ was used to derive the thermodynamic parameters, i.e. Erying type plot. The Erying equation is used for a variety of purposes, including expressing the rate of reaction variance in chemical reactions as a function of temperature. The change in enthalpy (H), entropy (S), and Gibbs free energy (G) following adsorption at various temperatures was calculated using the Van't Hoff equation (Ayawei et al., 2017; Prasad et al., 2015). Further, other thermodynamic parameters such as, standard free energy changes (ΔG), the standard enthalpy changes (ΔH), and the standard entropy change (ΔS) was obtained from various temperatures with the following Equations (11) and (12):

$$Intercept = [\ln (kb/h) + \Delta S \quad (11)$$

$$Slope = [-\Delta H/R] \quad (12)$$

Where, kb = Boltzmann constant; h = Plank's constant; and R = Gas constant. The thermodynamic parameters are calculated using the slop and intercept of the straight line equation i.e. ΔH and ΔS. Gibb's free energy (ΔG) (Equation 11) has been calculated by the obtained value of ΔS and ΔH for different temperatures in Kelvin.

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

Where, ΔG = Gibbs free energy; ΔH = enthalpy; ΔS = entropy.

The above-mentioned equation was applied to investigate the mathematical relationship between dye adsorption by the algal adsorbent at different temperatures and times. Thermodynamic parameters were obtained from Van't Hoff graph.

2.3.1.8.2 Arrhenius equation

This is an integral multiple that calculates the connection between temperature, rate constant, and activation energy using temperature, rate constant, and activation energy as inputs. During a chemical reaction, it emphasizes the relationship between the rate constant and absolute temperature. In dye removal adsorption, the activation energy (Ea) is a key factor. The Ea is the minimum needed of energy required to begin any chemical reaction. It confirms that adsorption is a function of temperature, which can be expressed as:

$$Slope = E_a/R \quad (14)$$

Where, E_a = Arrhenius activation energy; R = Gas constant (8.314 J mol^{-1} k^{-1}).

2.3.1.9 Statistical analysis

Statistical analysis of the adsorption isotherm (Langmuir and Freundlich), as well as pseudo-second-order kinetics and thermodynamics studies, were investigated for experimental validation utilizing Microsoft Excel 2010 developed by Microsoft Corporation United States of America (USA). The sum of the error square (SSE %)

test was performed to validate the model, which was based on the mean of the triplicate data. It calculates the % error in the suggested model, and numerous publications use it to calculate the error as well (Katheresan et al., 2018; Vijayaraghavan et al., 2015; Satiroglu et al., 2002) which can be expressed by Equation (15).

$$\sum_{i=1}^{n}(q_e - q_i)^2 \tag{15}$$

2.3.1.10 SEM-EDS study

The scanning electron microscope is used with the specific scanner with focused beam of electron. So, to investigate the structural changes of the algal cell surface (both FAC and IAC) SEM (JEOL, JSEM-6490LV) was used to exemplify the structural surface with the morphology of the samples of dye loaded of alginate as like other researchers to support the findings (Hameed et al., 2007). For sample preparation of SEM, both the free algal cells and immobilized cells were collected from the wastewater sample and dried to remove moisture. Thereafter, the samples were crushed with mortar and pestle set in the laboratory and again dried to remove excess moisture and sent for analysis.

2.4 Phase-II: Use of Solar Parabolic Trough Reactor (SPTR) for treatment of textile industry wastewater

This phase has been focused on the treatment of textile industry wastewater with the designed Solar Parabolic Trough Reactor (SPTR). The SPTR is an advanced setup for the treatment of textile industry wastewater with the use of solar energy designed and fabricated on the lab scale. The concept is widely accepted in modern sciences where the parabolic surface is made up of a very reflecting surface. This reflecting surface is bent in such a way that it will concentrate the coming radiations from the sun over the focused area. The focused area is generally kept at the center of the parabolic trough. When the radiation falls over the parabolic trough it again reflects these radiations into the focused area. As per recent research, solar energy-based technologies can be classified into two types: concentrating solar power (CSP) technology and photovoltaic (PV) technology, and the CSP technology includes parabolic trough, linear fresnel reflector systems, and central tower receiver. For the present study, the most developed CSP technologies (parabolic trough) have been preferred to be used due to their easy handling technique as well as efficiency in concentrating elevated solar radiations. The mechanism of this SPTR is based on basic science assumptions where the intensity of radiations plays the key role in a chemical reaction. The radiation enhances the wastewater molecule to gain heat from sunlight so that the randomness of water molecules increases with a tricky speed. This high intensity of radiation is also capable to break the complex bandings of various toxic non-biodegradable chemicals. The design and fabrication details of SPTR have been discussed in the following section:

2.4.1 Designing of SPTR

The SPTR has been fabricated for the treatment of all types of wastewater. But, for the present study textile industry wastewater has been used to be treated. This setup has been based on the CPS principle. Here, this parabolic solar collector has been designed in movable way that it can manually track the sun from east to west during the treatment process. The parabolic reflecting surface concentrates the direct solar radiations on the receiver tube creates heat and enhances the wastewater treatments process (Fendrich et al., 2018; Compain. 2012; Kannan and Vakeesan. 2016). The SPTR has six important parts such as: reflecting aluminum surface, transparent glass tube, wastewater tank, (described in table 2.4). The parabolic reflective surface is made up of 1.5 mm of aluminum metal with the length of 2 meters and the glass tubes are 2 meters in length with 1.5 mm thickness. Over the aluminum surface, these 3 connecting glass tubes have been connected in a parallel form and connectors of hard plastic joint them so that wastewater can easily flow over the reflector. The wastewater tank is of 10 liter capacity with the working volume of 8 liters. To flow water through the designed SAHR an electric motor of 0.5 hrz power has been used. The whole designed setup stands over a woody stand which is designed in such a way that can track solar radiations manually in the daytime.

Table 2.4: Specifications of solar energy-based setup

Requirements	**Measurement**
The parabolic aluminum reflective surface	Thickness:1.5mm, length: 2 meter
Transparent glass tube	Thickness: 1.5mm, length: 1.5 meter
Wastewater tank	Capacity: 10 liters, working volume: 8 liter
Water holding capacity of the glass tube	4.5 liter
Electric motor	Power rating : 0.37 kw / 0.5 hp, voltage range : 180 to 240 volts
The plastic connector between glass pipes	Number: 2, length: 35 cm

The solar intensity was measured by solar intensity measurement device (KM-SPM-530) in W/m^2 for a total of 15 days with one-hour intervals on each day. Treated wastewater was collected and analyzed for physico-chemical parameters on each 5th day of the experimental duration. The initial characterization of wastewater and final characterization of wastewater were performed to conclude the potential of SPTR for the reduction of pollutants from textile industry wastewater.

2.5 Phase-III: Design and experimental evaluation of novel Solar-Algal Hybrid Reactor for cost-effective textile wastewater treatment

This phase is the important stage of this research work. Here, the major objective of the experiment has been focused on the treatment of textile industry wastewater with designed Solar Algal Hybrid Reactor (SAHR). The SAHR is an innovative and renewable-based low-cost approach where immobilized *C. pyrenoidosa* was used as an adsorbent in coupling with concentrating solar energy-based treatment. As we have discussed in the literature and review section that a single treatment is insufficient to treat the textile industry wastewater with very high efficiency. Some major gaps have remained in single treatment technology. To fulfill these gaps we have fabricated SAHR. This is a model where two treatment setups are connected adjacent to each other and the solar energy-based treatment and algal-based treatment are connected with a single reactor. So, in this study, the SPTR plays key role. As we mentioned in the previous section, SPTR has been designed in such a way that where more treatment options could be easily connected. So that, each hybrid method would enhance the treatment efficiency rather than a single treatment one. In this perspective, a separate algal chamber was attached with SPTR, sot that SAHR could be fabricated. The algal chamber was 8 L capacity with 32 gm (4 gm/L) of immobilized algal dosages, with working volume of 6 L. This immobilized algal chamber was attached in such a way that the textile wastewater will flow through the glass tubes (three) which are fixed over the parabolic trough and the same wastewater will flow through the immobilized algal chamber. The SAHR potential is dependent on the process parameters like pH, flow rate, and time of wastewater through the reactor and temperature. The process parameters and their impact on the potential efficiency of pollution reduction have been discussed below:

2.5.1 Process parameters

2.5.1.1 Flow rate

The flow rate is a key process parameter as the number of flows per unit time indicates the potential of pollution reduction efficiency. To examine the best suitable flow rate for SAHR the optimization of flow rate was conducted. For this experiment, the wastewater was flown through the SAHR with four different flow rates as 0.67L/minute, 1.3 L/minute, 1.95 L/minute, and 2.6 L/minute. The flow rate of the wastewater movement was maintained with the help of a plastic regulator. This optimization experiment was run for four hours for each circulations rate. Then, the best suitable flow rate for the treatment of textile industry wastewater was concluded on the basis of the efficiency of pollution reduction as after each flow rate the pollutional parameters like BOD, COD, nitrate, and phosphate were checked by following standard scientific protocol so that, we can decide the best flow rate, where the treatment efficiency will be more enhanced in comparison to other circulation rates.

2.5.1.2 pH

pH is another process parameter for the treatment of textile industry wastewater. When the pH of any kind of chemical reaction changes its impact on the end product of the chemical reaction also changes. It affects the rate of reaction and sometimes moderates the whole chemical process. So, to avoid such experimental errors we have performed with constant pH with SAHR. So, for the present study, the pH of the experiment was kept constant to avoid experimental errors After the experiment, the pollutional parameters like BOD, COD, nitrate, and phosphate, *etc* were analyzed to get optimized for color removal and pollution reduction.

2.5.1.3 Contact Time

For a chemical reaction, the contact time of reactants varies. The contact time is one of the major parameters where the results could differentiate the end product of any chemical reaction from another product. When reactants come more in contact with adsorbate, the rate of chemical reaction increases. Sometimes, this contact time varies with different chemical reactions and experiments. So, for the present study, the contact time was kept constant to avoid such differences. The SAHR running time was 14 days of period. The experiment was run in the daytime under the solar radiations from morning 9 am to evening 5 pm. Again, the wastewater was flown through the SAHR was measured with cycles and the number of cycles was measured. This number of circulations also was calculated as contact time. The solar radiation increases the randomness in the textile wastewater molecules. They get heat from solar radiation and influenced randomness so that, the complex chemical bondings break downs. Similarly, immobilized algal biomass will get more time with textile industry wastewater they will easily get attached to the surface of adsorbate due to the process of adsorption.

2.5.1.4 Temperature

Temperature is the major processing parameter for any type of chemical reaction. Both solar energy-based treatment and algal-based adsorption are highly dependent on the temperature of reactant media. More influence of temperature can increase the treatment efficiency of SAHR. But, for the present study too high temperature can cause damages to the algal cells. Based on literature study the *C. Pyrenoidosa* can best sustain in 30-40°C of range of temperature. So, for this present study, the experiment was designed to run in the moderate range of temperature so that, the

Chlorella Sp. will be safe and will be highly effective for pollution reduction. So, for the present research work, no addition of external temperature was performed to SAHR.

2.5.1.5 Efficiency of the process

The percentage of pollution reduction of wastewater effluents were calculated by the following equations:

Percentage of pollution reduction: $(C_0 - C_t)/C_0 \times 100$

Where C_0 is the initial concentrations of wastewater and C_t is the concentration of wastewater after a specific time (t) respectively.

Chapter-3
Phycoremediation of Dye Contaminated Textile Industry Wastewater by C. pyrenoidosa

3.1 Introduction

The chapter is focused on the pollution and color reduction of dye-contaminated textile industry wastewater with the use of *C. pyrenoidosa*. Many industrial sectors discharge huge amounts of wastewater/ partially treated wastewater to the fresh water bodies which affect the society and environment at the same time pollute the hydrosphere. The textile industry wastewater is known as one of the main industrial sectors for contributing huge number of chemical compounds to the water bodies. These toxic chemicals are highly toxic, and non-degradable. The toxic aromatic molecular structure of these compounds possesses challenges for its treatments. Due to its molecular structure, the dye contaminated textile wastewater compounds are biologically non-degradable (Yagub et al., 2014; Lellis et al., 2019). A large number of methods as being used for textile dye wastewater treatment with excellent economics and low energy consumption efficiency, the knowledge required for the large-scale design and application is conceivably lacking. So, the focus here is on the treatment system with an emphasis on the treatment quality, cost-effectiveness as well as low secondary pollutant generation. As discussed in the review of the literature section, despite significant pollution reduction capacity, nutrient removal from dye contaminated textile industry wastewater is still a challenge that causes many problems, and eutrophication of water bodies is one of them. So, controlled use of algae over dye contaminated textile industry wastewater will help nutrient removal also for the degradation of organic matters as algae play an important role in tertiary treatment of dye contaminated textile industry wastewater. So, in this context, various types of algae could be used. Algae enhance the removal of nutrients, heavy metals, pollutants, pathogens and provide O_2 to heterotrophic aerobic bacteria to oxidize organic pollutants, using, in turn, the CO_2 released from bacterial respiration**.** Under mechanical aeration, photosynthetic aeration is one of the treatment techniques that reduce the pollutant volatilization limit and is low cost, and studies have shown that microalgae may support the aerobic degradation of a variety of hazardous pollutants. The algae are naturally built without the vascular system of vegetative structure with a diverse group of photosynthetic organisms (Nguyen et al., 2020). When utilized in an adsorption process, algae are extremely stable and have a wide range of potentials for the adsorption of highly harmful substances (Wollmann et al., 2019; Wang et al., 2016; Wollmann et al., 2016). Algal species such as *Oscillatoria* sp., *Dunaliella* sp., *Chara* sp., *C. pyrenoidosa*, *Scenedesmus* sp., and *C. vulgaris* have been utilized as bio accumulators to remediate textile industry effluent (Pandey et al., 2019). Using immobilized *Scenedesmus quadricauda*, Chia et al (2014) showed promising increase with 100% indigo blue removal. El-Kassas and Mohamed (2014) investigated the efficiency of *C. vulgaris* for dye removal and found that it was capable of removing 100% of dye from textile industry wastewater. The dye removal efficiency of *Sphaerocystis schroeteri* was also investigated, with results of 63.8% (for blue dye) and 60.0 % (for yellow dye). In recent years, algal-based wastewater treatment has been regarded as the most promising technique and because of its great effectiveness in removing nutrients from industrial, municipal, and agricultural wastewaters, several studies have demonstrated the viability of utilizing algal-based treatment as an alternative to tertiary wastewater treatment (Cai et al., 2013; Gikonyo 2013; Lee et al., 2015; Whitton et al., 2015; Li et al., 2019). Pirkarami et al (2013) concluded the removal of dye by focusing on the degradation mechanism as well as economic efficiency (Pirkarami et al., 2013). Singh et al (2019) conducted the study with diesel exhaust emission soot as an adsorbent for the removal of dye. Rajabi et al (2016) observed the potential of magnetic nano-particles in the modified form with cetyltrimethyl ammonium bromide, which is a superior adsorbent for dye removal. Hassan et al (2016) studied various advanced oxidation processes for the degradation of direct blue 86. Bacteria, fungi, and algae as biochar are used as biological agents for the adsorption of pollutants as cited by various recent researches, either in living or dead cell forms. Foroutan et al (2019) studied the effect of cultivated algal carbon Fe_3O_4 and reported more than 98% of cationic dye removal from the aqueous solution under optimal conditions. Similarly, El-Kassas and Mohamed also reported the potential of *C. vulgaris* as a bioaccumulator of dye industry wastewater with 75% dye removal efficiency. Rymond and Kadiri (2017) reported 63.9% and 45.7% dye removal by using biological agents i.e. *C. Vulgaris* from blue and green dye respectively (Rymond and Kadiri 2017).

Chlorella species are freshwater microalgae, rich in chlorophyll content, and easily available, which helps in sunlight capturing for energy conversion and presently, these are part of active research due to excellent efferent characteristics. It has the potential to bind most of the toxic heavy metals from wastewater and in the remediation of organic pollutant load. It has a favorable surface area, which makes it suitable to remove dye molecules from textile wastewater. Very few studies are on real dye industry wastewater treatment using *C. pyrenoidosa* as an adsorbent and particular as an immobilized cell. Hence, the use of *C.* pyrenoidosa was selected for wastewater treatment with the novel approach as an adsorbent. Immobilization is an advanced industrial procedure used by researchers in recent days. The concept of immobilization is to maintain the Chlorella cell metabolically active in a gel matrix with limited mobility. Because the polymer's pores are smaller than the microorganisms', the cells are immobilized (trapped) alive within it, while the fluid flows through it and supports their metabolism and ultimate development, increasing the pollutants and nutrient removal efficiency. Kaparapu et al (2016) reported when the alga was immobilized with the help of alginate and carrageenan the potential of pollution reduction was improved and they also mentioned that nutrients like nitrate and phosphate were reduced with high efficiency. This statement was supported by De-Bashan et al (2010). They said the immobilized procedure is a highly advanced industrial procedure and could be implemented in various industrial sectors for pollution minimization. So, this mechanism was accepted and followed for the present experiment where the *C. pyrenoidosa* was used as an adsorbate for the treatment of dye contaminated textile industry wastewater in both free and immobilized algal form. Therefore, this chapter has been divided into two sub-phases. In sub-phase one, we have discussed the reduction of major pollutional parameters like nitrate, phosphate, chloride, BOD (Biochemical Oxygen Demand), and Chemical Oxygen Demand (COD) from textile industry wastewater, and in the second sub-phase the color removal efficiency of *C. pyrenoidosa* has been assessed from dye contaminated textile industry wastewaters. The detailed results of pollution reduction and color removal efficiency by *C. pyrenoidosa* have been discussed in following sections.

3.2 Study on the pollutional parameters of dye contaminated textile industry wastewater with use of *C. pyrenoidosa* at lab-scale

3.2.1 Material and methods

The material and methods section has been divided into three phases like the collection of wastewater samples and their parametric study, algal sample collection, preservation and growth, and running algal experimental setup with both free algal biomass and immobilized algal biomass.

3.2.1.1 Collection of wastewater samples and their parametric study

The details of wastewater sample collection have been described in the material and methodology section (chapter-2). The initial physicochemical characteristics have been described in table 3.1.

3.1.1.2 Algal samples collection, their preservation, and growth

Algal samples collection, their preservation, and growth have been described in the material and methodology section (chapter-2).

3.1.1.3 Experimental setup

The experimental plan has been divided into two phases: pollution reduction free algal biomass and pollution reduction with immobilized algal biomass. pH is considered as a key aspect in pollution reduction and when the pH of any chemical composition changes, every mechanism related to it also changes. Hence, it is an essential measure of any kind of chemical reaction. In this study, the initial pH of real textile industry wastewater was 8.2 ± 0.1. It was slightly more or less than the actual estimated number. It may be due to handling or technical errors in the laboratory. A slight variation in pH can affect the pollution reduction efficiency in both free and immobilized algal biomass. So, it was kept constant. To make the pH unchanged while running the experiment, it was balanced to 8 with the help of buffer solution. After the above process, the dye contaminated textile industry wastewater was treated with free algal biomass. The experiment was run for 14 days and after that, the wastewater parameters such as nitrate, phosphate, BOD, and COD were assessed. The dye contaminated textile industry wastewater was treated with immobilized algal biomass to check the difference in pollution reduction efficiency between free algal biomass and immobilized algal biomass.

3.1.4 Results and discussion

The results and discussion section contains the initial characterization of wastewater samples, pollution reduction with free algal biomass, and pollution reduction with immobilized algal biomass. The initial characterization details have been mentioned below:

Table 3.1: The initial characteristics of collected dye contaminated textile industry wastewater

Sl no	Physico-chemical parameters	Observation
1	Color	dark blackish
2	Order	Pungent smell
3	Temperature	27± 0.81^{o}C
4	pH	8.2 ± 0.1
5	Alkalinity	893 ±1.52
6	Conductivity	28±0.51,
7	Chloride	816±0.5 MgL^{-1}
8	Total solid	5004 ±2.08 MgL^{-1}
9	Total suspended solid (TSS)	100±0.57 MgL^{-1}
10	Total dissolved solid (TDS)	4904± 4.5MgL^{-1}
11	Nitrate	315±1.5 MgL^{-1}
12	Phosphate	3.73±0.57 MgL^{-1}
13	BOD	587±2.5 MgL^{-1}
14	COD	997.3 ± 1.52MgL^{1}

3.3.1 Pollution reduction with free algal biomass

Pollution reduction with free algal biomass shows its efficient nature towards reduction of high loaded nutrients as well as major wastewater parameters. It was observed that nutrients like nitrate and phosphate were reduced by 43.2% and 56.7% respectively and COD was reduced by 78.0% and similarly BOD was reduced by 71.4%, at the same time TSS and TDS were reduced by 15% and 36% respectively and 76% of chloride was also reduced in this process. The details have been given in table 3.2.

Table 3.2: Percentages of pollution reduction with free algal biomass

Sl No	Parameters	Percentages of reduction (%)
1	Color	-
2	Order	-
3	Temperature	-
4	pH	-
5	Alkalinity	49.2
6	Conductivity	21.4
7	TS	36.0
8	TSS	15
9	TDS	36.4
10	Nitrate	43.1
11	BOD	71.3
12	Chloride	76.4
13	Phosphate	56.7
14	COD	78.0

Again, the free algal biomass was converted into immobilized algal form by using standard scientific protocol as described in the material and methodology section (chapter- 2). Here, the same quantity of the algal biomass was used for the preparation of immobilized algae so that, the difference between free and immobilized algal biomass could be justified.

3.3.2 Pollution reduction with immobilized algal biomass

The results show significant enhancement in the reduction of major dye contaminated textile wastewater parameters (nitrate, phosphate, chloride, COD, and BOD). The immobilized algal biomass was used for pollution reduction as the application of immobilized algal biomass is drastically capable to remove undesired substances like organic pollutants, metals, and nutrients, *etc*. Kaparapu et al (2016) mentioned that when the free algal biomass was immobilized with the help of carrageenan and alginate it is more efficient to remove the nutrients like nitrogen and phosphorous as free suspended cells. De-Bashan et al (2010) mentioned that the algal immobilization technology is a highly improved biotechnological approach for the reduction of nutrients as well as pollutants.

Table 3.3: Pollution reduction with immobilized algal biomass

Sl no	Parameters	Percentages (%) of reduction
1	Color	-
2	Order	-
3	Temperature	-
4	pH	-
5	Alkalinity	50.3
6	Conductivity	28.5
7	TS	40.2
8	TSS	21
9	TDS	40.6
10	Nitrate	46.6
11	BOD	73.2
12	Chloride	75.3
13	Phosphate	59.4
14	COD	83.0

This process is an advanced cost-effective process, where it can be easily applied in industrial sector as well. During the present study, similar enhancement results were observed with balanced pH and immobilized algal biomass. It was observed 56.7% of phosphate was reduced with free algal biomass and 59.4% of phosphate was reduced with immobilized algal biomass. Similarly, 43.2% of nitrate, 71.4% of BOD, 78.0% COD and 46.7% nitrate, 73.3% BOD, and 83.0% of COD were reduced with free algal biomass and immobilized algal biomass respectively.

From the current results, it is confirmed that immobilized algae are more efficient in nutrients as well as pollutants reduction than free algal biomass. Wu et al (2020) used immobilized *Chlorella* sp. Wu-G23 (G23) and 70.8% of COD removal efficiency from textile industry wastewater. Ei Kassas and Mohamed (2014) studied the remediation of textile effluents with the algal species (*C. Vulgaris*) and reported 69% of COD removals. Lim et al (2010) studied the pollution reduction of textile industry wastewater with the help of *C. Vulgaris* and reported 44.4- 45.1% of nitrate, 33.1-33.3% of phosphate, and 38.3–62.3% of COD reduction respectively. The mechanism behind the high rate of pollution reduction of immobilized algal cells may be due to its surface area. When the free algal cells are reformed into immobilized form, it gets more surface area for reaction with reactant media. So, there is an ultimate enhancement in the area that came in contact with reaction media. So, pollution reduction ultimately will increase. Further, the pH of any reaction media is an essential factor. It is a rate-limiting factor in pollution remediation; it’s due to the transfer of dye molecules across the cell membranes (Saratale et al., 2011). The optimum pH for pollution reduction as well as dye removal ranges between 6 to 10 (Chen et al., 2003; Guo et al., 2007; Kilic et al., 2007). The rate of pollution reduction is superior in alkaline medium and gradually becomes slower in acidic medium but declines in high alkaline medium.

3.4. Conclusion

C. pyrenoidosa in the form of free and immobilized algal biomass were experimentally investigated towards contamination remediation. It was concluded that the reduction of major pollutional parameters were increased by a noticeable range with immobilized algal biomass than free algal biomass due to the availability of more surface area. When the surface area increases, the number of adsorbing sites on the adsorbing surface also increases. This mechanism of adsorption influenced the pollution reduction efficiency of immobilized algal biomass than free algal biomass. This is a new low-cost technology with green and sustainable approach, which requires low energy and less in sludge formation process about conventional treatment methods for dye contaminated textile industrial wastewater. This further enhances the scientific research ideas on pollution reduction in attachment with immobilization which could generate noble scopes for future research perspectives.

3.5 Application of free and immobilized *C. pyrenoidosa* for dye removal of dye contaminated textile industry wastewater in lab-scale

In this experiment, the potential adsorption study of *C. pyrenoidosa* for dye removal from dye contaminated textile industry wastewater has been studied in the form of free algal cells (FAC) and immobilized algal cells (IAC). Effect of concentrations of real dye industry wastewater (50% & 100%), temperatures (30°C, 40°C, 50°C & 60°C) at controlled pH and equal amount of algal cells (2gml^{-1}).

3.5.1 Materials & methods

Here, for the present experiment, to study the innovative behavior of immobilized *C. pyrenoidosa* cell with real type dye industry wastewater experimentally, it was investigated with two concentrations of test solution (50% & 100%). Details have been described in chapter- 2.

3.5.1.1 Wastewater: sample collection and characterization

The wastewater sample collection and its initial physico-chemical parameters have been discussed in chapter-2.

3.5.1.2 Algal species: culture and growth

The *C. pyrenoidosa* culture in growth medium has been briefly described in chapter - 2.

3.5.1.3 Immobilization of algal cells: process & mechanism

The immobilization of algal cells and their mechanism have been described in the material and methodology section (chapter- 2).

3.5.1.4 Experimental setup

The present experimental setup was alienated simultaneously into two co-joint phases, the impact of (a) Free Algal Cells (FAC), and (b) Immobilized Algal Cells (IAC) with wastewater. On comparative analysis, best cells were further investigated with different temperatures, discussed in detail in further sections of this study. As we have selected real wastewater rather than artificial/ synthetic wastewater for the present study, which has not been studied much.

3.5.1.5 Impact of algal cells on decolorization

The FAC and IAC were processed with a fixed amount ($2gL^{-1}$) of algae, which was exposed into two different concentrations of dye industry wastewater (test solutions of 50%, and 100%). After producing the appropriate test solutions and the experimental conditions such as dye concentration at room temperature (30°C-35°C), the experiment was run for 180 minutes in a series of batch processes. The isolates were evaluated with a UV visible spectrophotometer at 485 nm to see if they had decolorized (HALO-DB 20). The best IAC result was then used to investigate the effect of temperature on a cell with a 50% solution of wastewater.

3.5.1.6 Impact of temperature with IAC on decolorization

The test solution was treated by four different temperatures (30°C, 40°C, 50°C, and 60°C) to make the findings more relevant with ambient temperature ranges and the greatest possible dye removal efficiency in real wastewater. The batch experiment's temperatures were balanced using thermostat (Digital thermostat AC 220V, 1500W temperature controller switch, Amici Smart AC) for 180 minutes. After executing the experiment with the appropriate temperature ranges, the decolorization removal (%) was measured using a UV visible spectrophotometer at (HALO-DB 20) 485 nm at 20-minute intervals.

3.5.1.7 Adsorption isotherm study

The adsorption isotherm study has been described in the material and methodology section (chapter 2).

3.5.1.8 Adsorption kinetics

The Adsorption kinetics have been described in the material and methodology section (chapter 2).

3.5.1.9 Thermodynamic functions

The Eyring and Arrhenius equations could be used to calculate the feasibility of adsorption at various temperatures that have been described in the material and methodology section (chapter 2).

3.5.1.10 Eyring equation

The use of thermodynamic parameters has been used to investigate the adsorptive behavior of adsorbents that have been described in the material and methodology section (chapter- 2).

3.5.1.11 Arrhenius equation

The Arrhenius equation is an exponential function that derives a relationship among temperature, rate constant, and activation energy that has been described in the material and methodology section (chapter-2).

3.5.1.12 Statistical analysis

The use of statistical analysis for the current study with mathematical calculations has been described in the material and methodology section (chapter-2).

3.5.1.13 SEM-EDS study

SEM-EDS study with mechanisms has been described in the material and methodology section (chapter-2).

3.6 Results and discussion

The results of this study were extremely significant in terms of color removal from dye industry wastewater. For this process, it was discovered that IAC was more effective than FAC, and in the following subsections; the details of the findings have been discussed:

3.6.1 Effect of selected adsorbents (FAC and IAC) on decolorization in wastewater

The effect of C. *pyrenoidosa* (both IAC and FAC forms) on decolorization from dye industrial effluent has been the focus of this section. The significant effects of this study have been discussed in the following sub-section.

3.6.1.1 FAC

The experimental data revealed that using FAC as an adsorbent resulted in a considerable decolorization efficiency from dye industry effluent, with 74% removal efficiency from a 50% test solution and 67.6% removal efficiency from 100 % test solution. As shown in table 3.4, the specific uptakes of contaminants from dye industry wastewater were determined to be 1.04 and 1.94 using 50% and 100% test solutions, respectively.

Table 3.4: Percentages of dye removal and specific uptake for FAC

	% of Dye Removal		Specific uptake	
Time (minute)	**50% test solution**	**100% test solution**	**50% test solution**	**100% test solution**
60	57.2	52.2	0.81	1.50
120	73	66.7	1.03	1.92
180	74	67.6	1.04	1.94

3.6.1.2 IAC

The dye removal effectiveness rapidly decreases as the concentration of test solutions increases, according to the experiment using IAC as an adsorbent (i.e. between 50% and 100% test solutions, the 50% test solution has more possibilities to be highly removed by IAC dosages). As a result, 87% of the dye was removed from the 50% test solution, but only 77% of the dye was removed from the 100% test solution. Table 3.5 shows the specific uptakes of pollutants from dye industry wastewaters, which are 1.23 and 2.22 in 50% and 100% test solutions, respectively.

Table 3.5: Percentages of dye removal and specific uptake for IAC

	% of Dye Removal		**Specific uptake**	
Time (minute)	**50% test solution**	**100% test solution**	**50% test solution**	**100% test solution**
60	58.9	56.9	0.83	1.63
120	78.1	69.9	1.10	2.01
180	87.1	77.1	1.23	2.22

The highest decolorization removal was obtained with IAC (87%) in a 50% test solution, while the lowest removal was obtained with FAC (67%) in 100% test solution, according to the above comparative study between IAC and FAC as an adsorbate. The surface area between FAC and IAC is the major adsorption process and factor that causes the variation in removal efficiency. Immobilized algal cell surface biosorption ability is shown to be more comparable to the free algal cell surface. The greater surface area offers more contact space between dye molecules and algal cells, allowing dye molecules to bind to the immobilized algal cells more easily. Cell wall characteristics of algal biomass, according to Satiroglu et al (2002), play an essential role in biosorption, which is regulated by electrostatic attraction. The experiment revealed that the rate of decolorization was excessively high in the beginning compared to the later phase, with more than 50% of color removed in less than 60 minutes from both test solutions (50% and 100%) utilizing both FAC and IAC as an adsorbent. However, because it is dependent on the availability of dye molecules or the volume of the adsorbate, adsorbent, and the potential charge difference, it becomes slower with time. Hameed et al (2007) and Karagoz et al (2008) found similar results, and that is that the adsorption rate is higher at the beginning than in later phases. Furthermore, because alginate is an extracellular polymer with surface functional groups, it helps in the sorption of dye molecules onto the surface of the polymer during the dye removal process. This might be due to the release of metabolic intermediates with high coagulation capacity, as well as the dye remaining in the wastewater preferring to adsorb and settle on the surface of the polymers.

3.6.2 Effect of temperature with IAC on decolorization in wastewater

A specific experiment was performed using four different temperature ranges (30℃, 40℃, 50℃, and 60℃) and the adsorbent doses (IAC) were kept constant (2gml-1) for 180 minutes in the laboratory using 50% test solution to analyze the effect of temperature on decolorization efficiency. The dye removal rate was 92% at 30 ℃, and 94 % at 40 ℃, according to the current study. At 50℃, the dye removal efficiency was highest (98%); however, when the temperature rises (60℃), the dye removal efficiency drops from 98 to 97.5 % (table 3.6).

Table 3.6: Percentage of decolorization at various temperatures

Temperature (°C)	Decolorization (%)
30	92
40	94.5
50	98
60	97.2

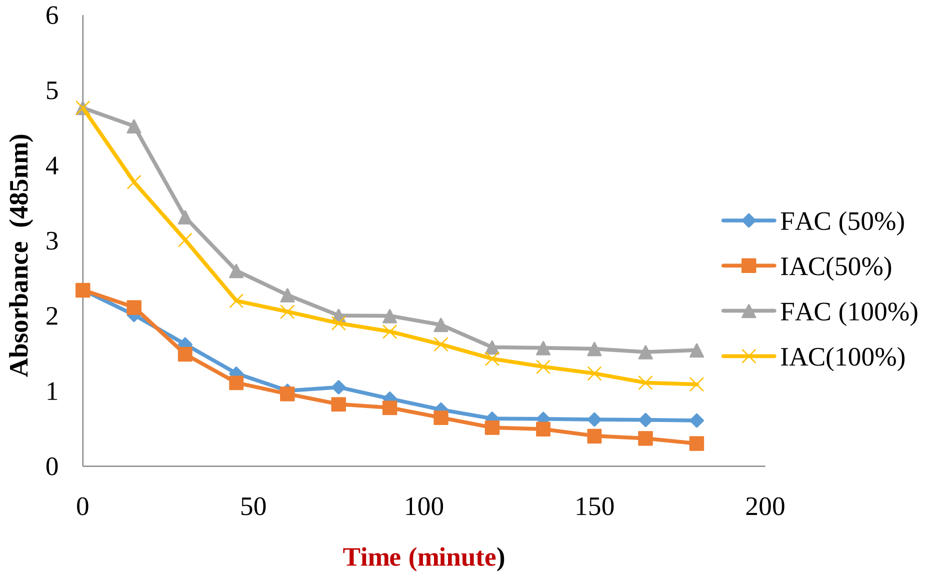


Figure 3.1: Adsorption with IAC (50%, 100%) and FAC (50%, 100%) at room temperature

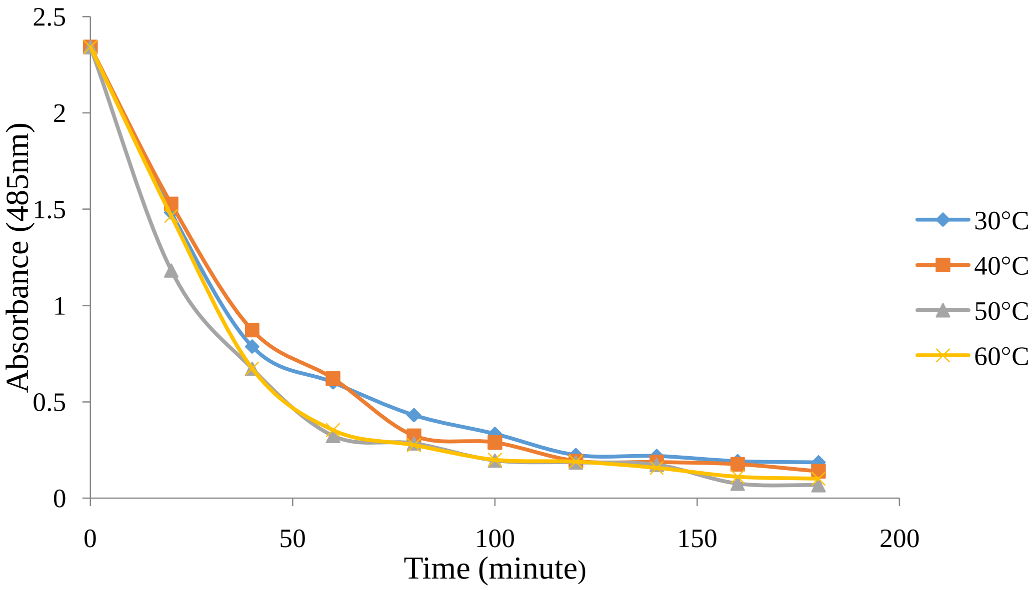


Figure 3.2: Adsorption with 50% IAC at different temperatures and time

The randomness or entropy of dye molecules with IAC is the mechanism behind this phenomenon. The adsorption process is directly proportional to the dye molecules' randomness. When the randomness of the dye molecules increases, the dye molecules' ability to attach to the adsorbent surface enhances. As a result, the dye removal efficiency increased as the temperature of the test solution (50%) increased from 30℃ to 40℃ and then to 50℃, but as the temperature increases to a saturation point, it decreases due to the availability of dye molecules and the surface area is reduced in comparison to the initial time.

To make the experimental results more trustworthy and valid, the adsorption isotherm with kinetic and thermodynamic functions was utilized (discussed in the kinetic and thermodynamic discussion section). Al-Degs et al (2008) concluded that the rate of adsorption is directly proportional to temperature. So when temperature increases the dye removal also increases from dye contaminated textile industry wastewater.

3.6.3 Effect of pH on adsorption

Any effluent's pH is a determining element, and variations in pH can have a direct influence on dye adsorption. Functional groups on algal cell wall components (i.e. functional groups transporting polysaccharides and proteins) also influence biosorption (Tagavifar et al., 2018). When the pH of the reaction media varies on a regular or irregular basis, the mechanism of the process changes. The pH discharge requirements for dye-contaminated textile industry wastewater are reported to range between 6 and 9 (Nandi et al., 2017). Mohan et al (2008) utilized Spirogyra sp. to study azo dye sorption at various pH levels and revealed that very low and very high pH levels directly affect biosorption phenomena such as protonation or un protonation of functional groups on the algal cell surface, as well as an increase in hydroxyl ion, resulting in the formation of aqua-complexes, delaying azo dye sorption (Mohan et al., 2008).

3.6.4 Adsorption isotherm study

In this work, the Langmuir and Freundlich isotherms are utilized to characterize the biosorption process, which is a frequently used adsorption mechanism.This investigation obtained a maximum biosorption capacity (qmax) of 15.66 Mgg-1, energy of binding (K_b) of 0.71 LMg-1, and a correlation coefficient (R^2) of 0.99. The Langmuir isotherm can be articulated by computing the RL factor (Separation factor) as indicated in table 3.7 and finding a value between 0 and 1, favoring biosorbent sorption.

Table 3.7: Equilibrium model parameter for Langmuir and Freundlich isotherm

	Langmuir isotherm constant				Frendulich isotherm constant		
Temperature	**Maximum adsorption capacity q_{max} (Mgg^{-1})**	**Energy of adsorption b (L/Mg)**	**Correlation coefficient (R^2)**	**Separation factor (R_L)**	**Adsorption intensity (n)**	**Adsorption coefficient K_f (Mgg^{-1})**	**Correlation coefficient (R^2)**
30°C	10.34	0.58	0.98	0.033	1.11	0.23	0.96
40°C	12.54	0.68	0.99	0.028	1.32	0.34	0.96
50°C	15.66	0.71	0.99	0.027	1.38	0.39	0.97
60°C	15.94	0.74	0.99	0.026	1.41	0.43	0.97

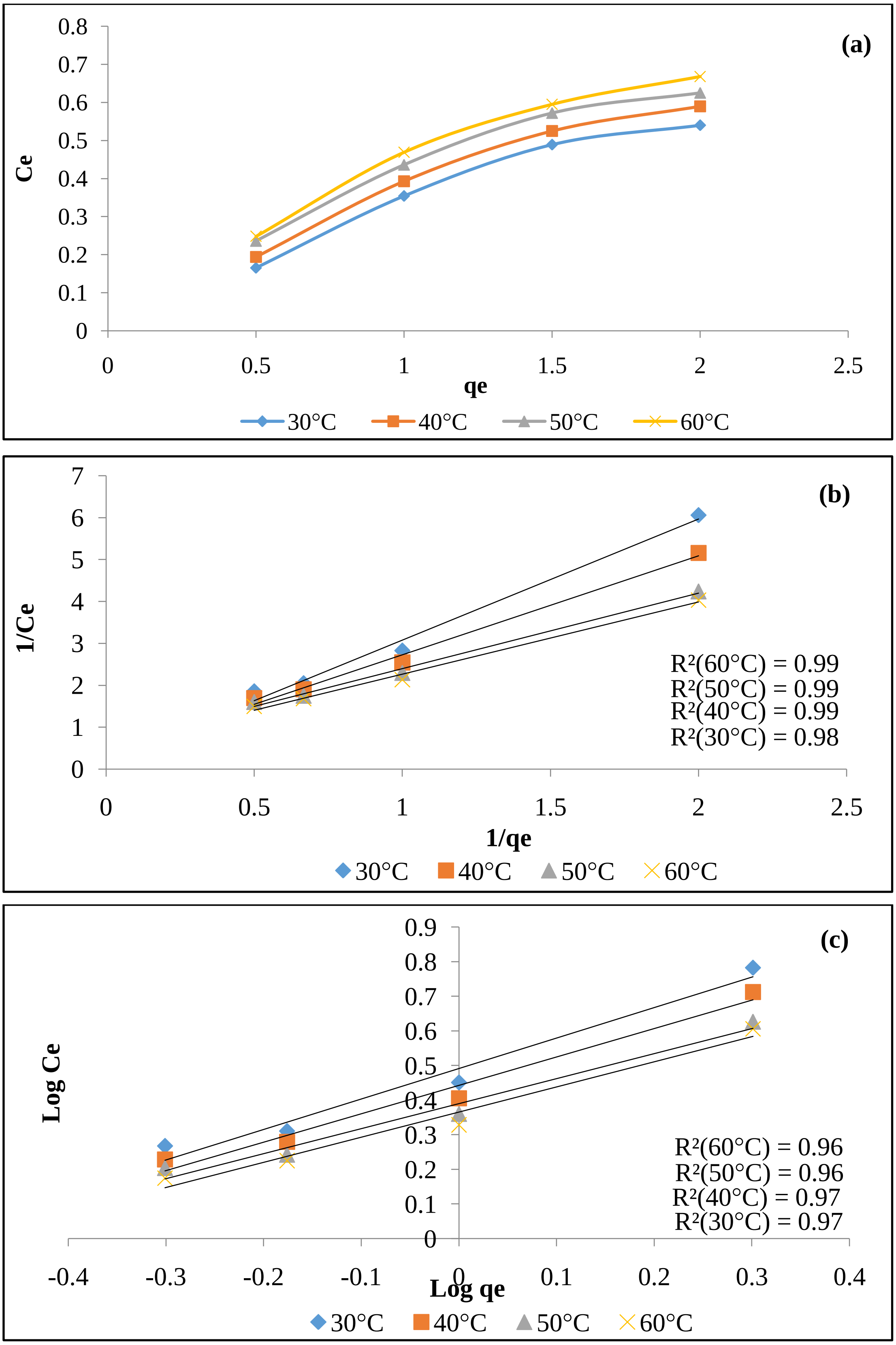


Figure 3.3: Relation between q_e and C_e (b)linear of form of langmuir isotherm and (c)linear form of frendulich isotherm

In this work, the Freundlich isotherm explains the adsorption coefficient (Kf) 0.39 (Mgg^{-1}) with dye uptake adsorption intensity (n) 1.384 and correlation coefficient (R^2) 0.97. The value of n found between 0 and 1 in the Freundlich isotherm gives a fair indicator of dye absorption by biosorbent. With all specified temperatures, the Langmuir isotherm (R^2 =0.99) explained the dye uptake better than the Freundlich isotherm (R^2 =0.97).

3.6.5 Kinetic model and thermodynamic function

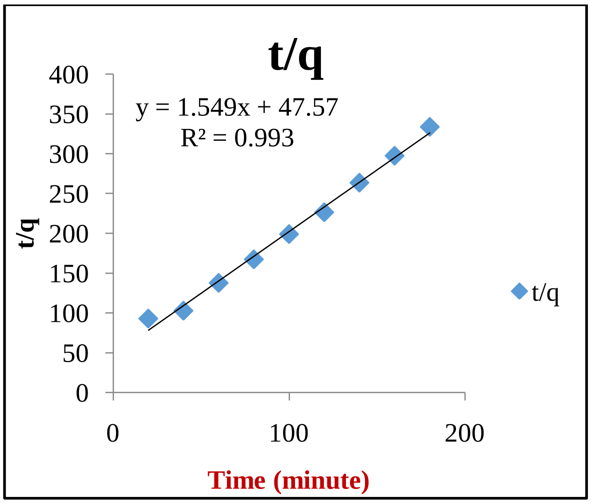
Over the experimental data, the thermodynamic pseudo-second-order kinetic model was used. The plot derived between t and t/q is shown in Figure 3.4, indicating a significant relationship between the temperatures (R^2 >0.9). This graph likewise shows that the rate constant increases as the temperature rises, with values ranging from 0.012 to 0.047 (table 3.8). It is evident that as the temperature rises, the rate of dye removal increases. The initial adsorption rate, 'h' was determined in the same method and the initial adsorption rate increased as the temperature increased. The maximum adsorption rate (0.047 $Mgg^{-1}m^{-1}$) was achieved at 50°C, whereas the lowest adsorption rate (0.012 $Mgg^{-1}min^{-1}$) was obtained at room temperature (30°C).

Table 3.8: Pseudo-second order kinetic variables

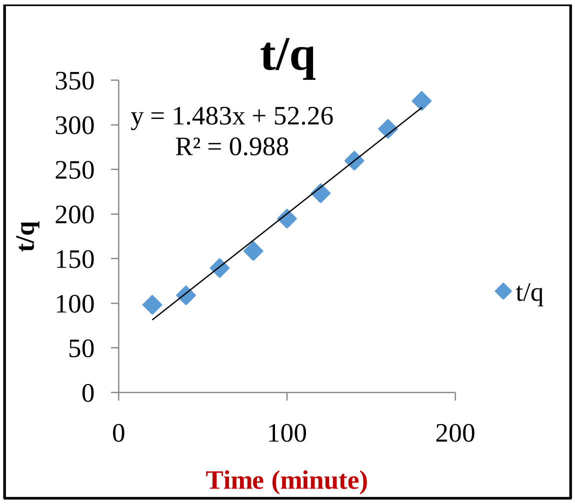
Temperature (°C)	**K_2**	**q_e**	**H**	**R^2**
30	0.047	0.666	0.012	0.99
40	0.048	0.714	0.024	0.98
50	0.121	0.625	0.047	0.99
60	0.056	0.666	0.025	0.98

Table 3.9: Thermodynamic functions of dye removal

Thermodynamic parameters	Values KJ mol^{-1}	
Enthalpy, ΔH	37.34	
Entropy, ΔS	1.15	
Activation Energy, Ea	37.61	
Gibb's free energy, ΔG	Temperature (Kelvin)	ΔG
	303	-311.89
	313	-323.42
	323	-334.95
	333	-346.48



a



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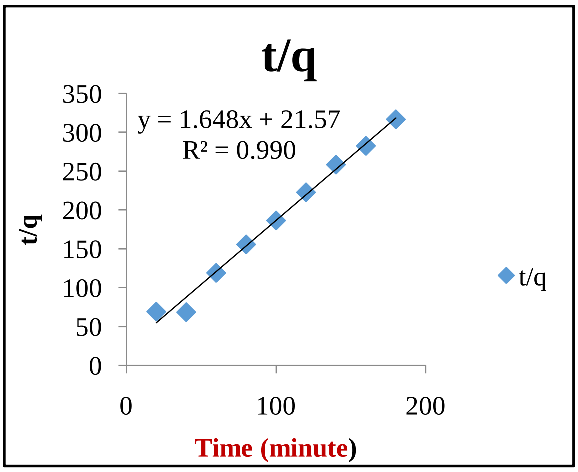
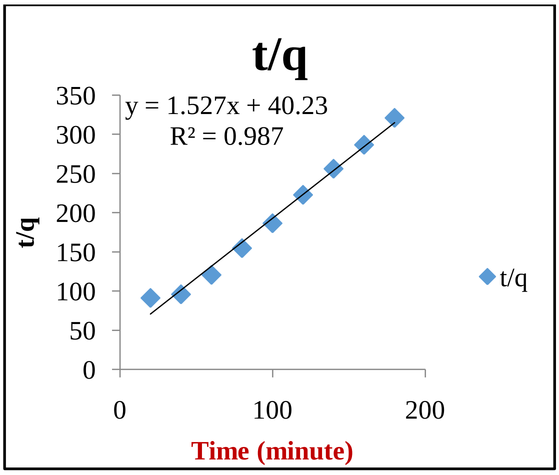
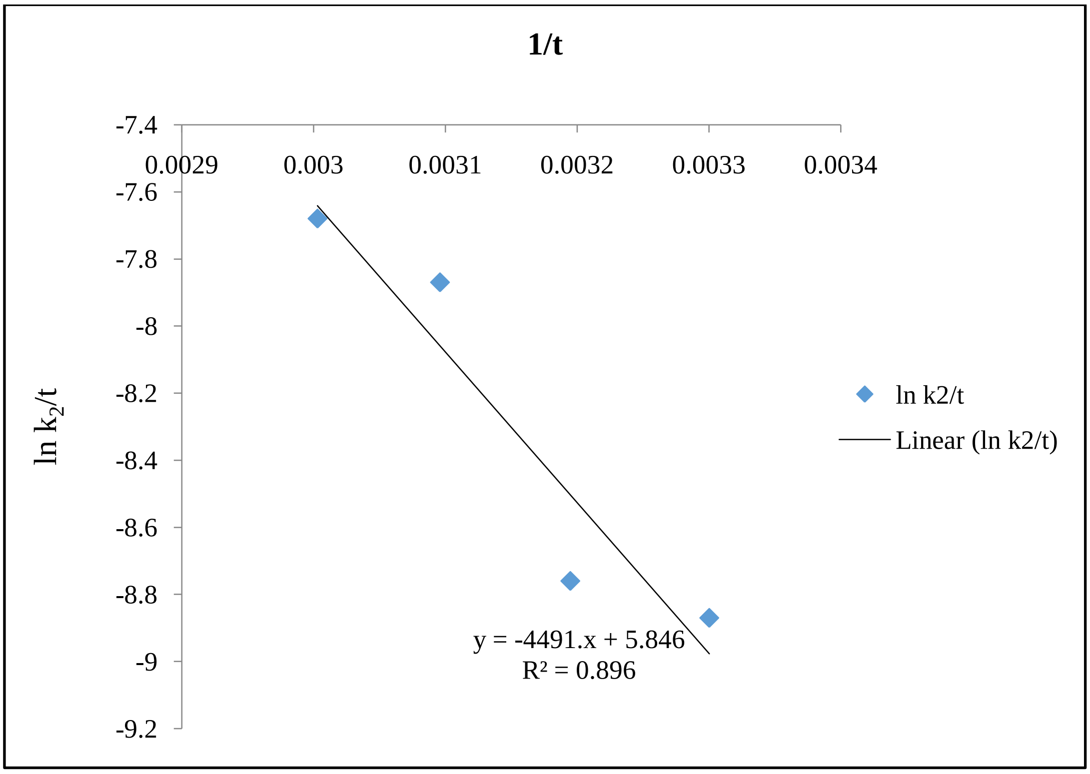


c



d

Figure3.4: Pseudo-second order rate constant at different temperature (°C) i.e. (a) 30°C, (b) 40°C, (c) 50°C and (d) 60°C



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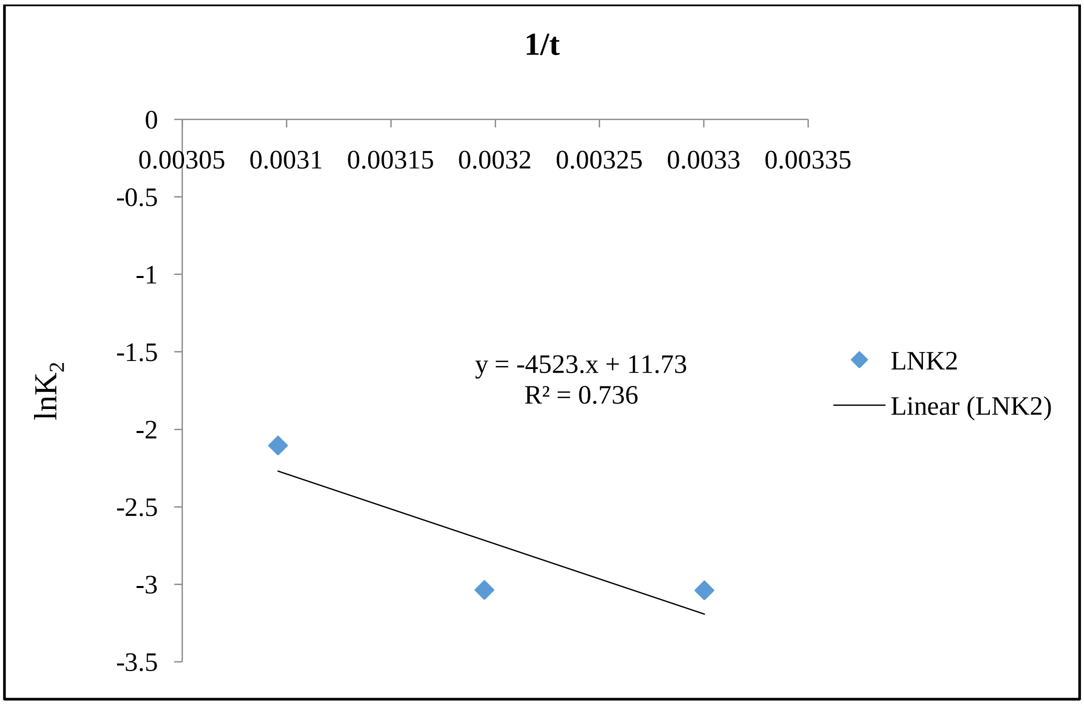


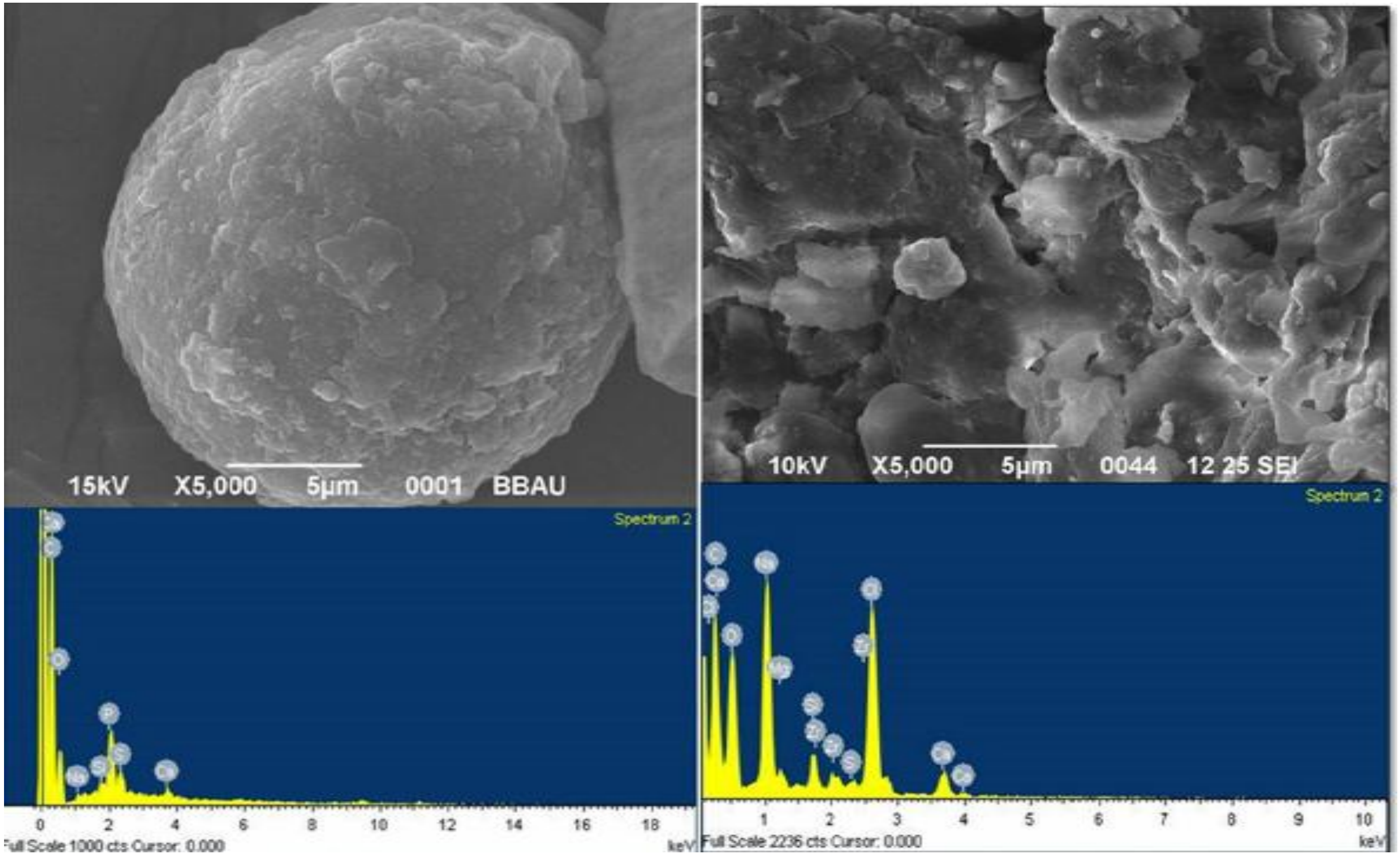
b

Figure: 3.5: Thermodynamic variable functional plot at various temperatures (°C) with Eyring (Ey) and Arrhenius plot (Ea) equations

The enthalpy (ΔH) and entropy (ΔS) have been calculated with the intercept and slope of Eyring plots and the ΔH value was found positive which signifies that the adsorption to be endothermic in nature. So, there are possibilities of physical adsorption. Mittal et al (2013) reported that with the increase of temperature, the rate of physical adsorption increases (Mittal et al., 2013). The same positive observation was found in entropy (ΔS) that clears that entropy is directly proportional with temperature and ΔG value vale found negative, but it does not affect the rate of adsorption. Nuhoglu and Malkoc (2009) said the positive value of ΔH indicates the reaction is endothermic whereas, ΔS signifies the increase of randomness with the increase in temperature (Nuhoglu and Malkoc 2009). The calculated activation energy is 37.61 $kJmol^{-1}$, which was derived with the help of the Arrhenius plot (lnk versus 1/t) as described in table 3.9. The activation energy possesses essential role in the chemical reaction, as it is the minimum amount of energy required to start a chemical reaction. The study pointed to 50ºC as the ideal temperature for dye removal, because maximum efficiency was observed at this temperature.

3.6.6 SEM and EDS analysis

Figure 3.6 elucidates the SEM image taken IAC (before and after treatment) during this study of treatment of dye industry wastewater. Specific differences in the morphological and structural differences of the surfaces have been observed. The figure clearly shows that there are a number of cavities and pores are found on the surface before treatment on the *C. pyrenoidosa* cell that has the capability for trapping the dye molecules present in the aqueous test solution. So, the number of pores available on the surface is directly related to dye adsorption. Nautiyal et al (2016) also confirmed the similar morphological pores and cavities on the algal surface. The molecules attached to the surface of the algal adsorbent were analyzed by EDS (Figure 3.6). The EDS mapping analysis shows Ca, Mg, Na, Zn, S, Cl, C, S, and O are present on the surface. The structural and morphological analysis reveals that IAC has the capability to remove elemental waste from dye industry wastewater in greater proportion than FAC. The EDS analysis of IAC shows higher elements than FAC. Therefore, it is clear from the SEM and EDS images that IAC has significant potential to remove wastes from dye industry wastewater.



(a) Before treatment **(b) After treatment**

Figure 3.6: Morphological and microstructural differences of the structure of IAC detected by SEM and EDS analysis

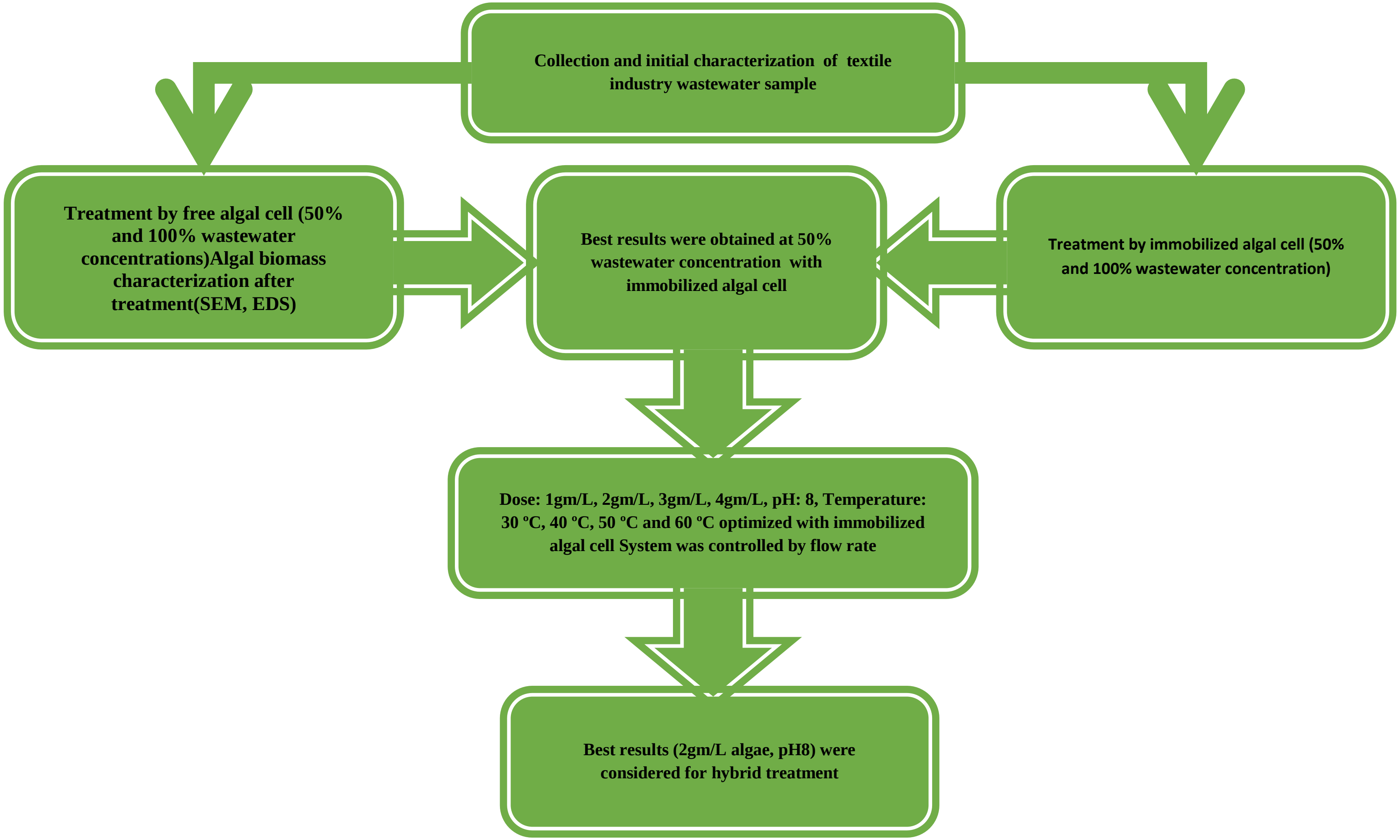


Figure 3.7: flow diagram of the algal-based treatment system

3.6.7 Conclusions

Although algae are easily available in nature and can be cultured cost-effectively, further immobilization of free algae can enhance the efficiency of dye removal. The present experimental study concludes the dye removal with and without optimized conditions. It was confirmed the maximum dye was removed (98%) with the optimized temperature (50ºC) of IAC whereas, 92% of dye was removed at room temperature. The thermodynamics function, as well as pseudo-second-order rate kinetics, were applied to the obtained findings of the present study. From all the above results of the present study, it was concluded that *C. pyrenoidosa* strains are highly efficient for dye removal in free algal cells forms and when the free algal cells are converted into immobilized form, the removal efficiency significantly increases concerning temperature (up to 50ºC). It is because the randomness of the dye molecules increases with the increase in temperature. So, the present study generates strong ideas about the color removal from dye industry wastewater with specific reference with pH and temperature effect and it generated the most adorable ideas as it is a natural as well as low cost based technology.

Chapter-4

Experimental Evaluation of Solar Energy Based Setup for the Treatment of Dye Contaminated Textile Industry Wastewater

4.1 Introduction

The water crisis is a major challenge faced by many regions and is becoming even worse due to the increasing water demand brought by economic growth in developing countries. Meanwhile, the discharge of municipal and industrial wastewater effluent without proper treatment that caused serious pollution on freshwater sources has aggravated the problem. According to the United Nations Environmental Programm (UNEP), 1/3 of the world population live in water-stressed countries, while by 2025, 2/3 of the world population will face water scarcity (Shatat et al., 2013). The scarcity of water strongly limits socio-economic development. Dyes are always critical for humans as they are a part of human lifestyle and culture and have been used in an assortment of industrial sectors for the manufacturing of various textile products. These dyes are chemical compounds that connect themselves to surfaces or fabrics to impart color. Whenever these toxic dyes come in contact with surface water, they pose high challenge for the survival of aquatic organisms. The dye expulsion into the hydrosphere poses a significant source of pollution due to its recalcitrance nature. It provides objectionable color to the water bodies, reduces sunlight penetration, and resists photochemical and biological attacks on aquatic flora and fauna (Pazdzdior et al., 2019)**.** Direct discharge of dye effluents also results in increased alkalinity, BOD, and COD (Pei et al., 2016; Sela et al., 2020). These alterations in the water parameters result from the pre-treatment chemicals used before the dyeing process. As per global estimation, more than 100,000 commercial dyes are known with an annual production of over 7×10^5tonnes/year**.** The total dye consumption in the dye contaminated textile industry worldwide is more than 10,000 tonnes/year and approximately 100 tones/year of dyes are discharged into water streams (Jegatheesan et al., 2016; Yaseen and Scholz, 2017). The dye industrial sector is known as the deliberate factor for most of the water pollution. It is a group of huge industries which uses large amount of water at the same time release a large number of secondary pollutants and wastewater with the manufacturing products. These impurities pollute the hydrosphere as it contains unfavorable substances within it (Holkar et al., 2016; Jegatheesan et al., 2016). These are so much attached with chemical bonding that their treatment needs high-level technologies. Also, they possess the non-breakable substances/molecular structure of these dyes creates more difficulties for their treatment (Yagub et al., 2014; Lellis et al., 2019). These dyes need to be removed to bring the standard water quality. The exact treatment of these toxic dyes has not been proved efficiently considerable. But, so many conventional treatments and advanced treatment options are available for this but fail in many aspects. These methods are able to treat dye contaminated textile industry wastewater, but in realistic perception, they are lacking in some sort of issues like high energy requirements, more sludge generation, *etc*. So, researchers are trying to find out innovative and cost-effective technologies for this purpose. So, the renewable energy-based treatment system is expected from the major research scientists to be accepted. In this context, solar energy for the treatment of dye industry wastewater is gaining attention due to its dual benefits of cost and energy-intensive in nature (Zhai et al., 2021; Tones et al., 2020). It is potentially proficient for the breakdown of toxic chemical compounds and a cost-effective as well as renewable-based approach which provides multidimensional scope to be used. Solar energy is by far the most abundant renewable energy source. It shows the highest technically feasible potential among available renewable energy sources (Blanco et al., 2009). Solar power is very cheap compared to other sources of energy generation. They are also abundant and suitable for several applications (Wilberforce et al., 2019). The technologies like solar desalination technologies, solar photocatalysis technologies, and solar disinfection are the most widely investigated solar-based water treatment technologies (Gong et al., 2021; EL-Mekkawi et al., 2020). Sharon et al (2015) discussed briefly the advantages and disadvantages of each technology as well as the problems existing in solar energy and desalination processes. A very comprehensive review of solar-assisted seawater desalination was given by Li et al., (2013). As per literature, the uses of solar energy-based technologies are mainly two types such as: concentrating solar power (CSP) and photovoltaic (PV) technology. Again CSP technology includes parabolic trough, linear fresnel reflector systems, and central tower receiver.

For the present experiment, the most developed CSP technologies (parabolic trough) have been preferred to be used due to their easy handling technique as well as efficiency in concentrating elevated solar radiations. The fundamental idea behind the technique is the concentration of solar radiation onto an absorptive receiver (pipe) which contains the wastewater to be treated. The parabolic reflecting surface concentrates the direct solar radiations on the receiver tube creating heat and enhancing the wastewater treatment process (Fendrich et al., 2018; Compain. 2012; Kannan and Vakeesan. 2016). This is an innovative and renewable-based low-cost approach where concentrating solar energy-based treatment has been used for textile industry wastewater treatment. To examine the efficiency of Solar Parabolic Trough Reactor (SPTR) for dye industry wastewater treatment the SPTR was built at lab scale and has been discussed in the following sections:

4.2 Material and methods

The experimental setup has been divided into subsections like the collection of wastewater samples and its initial parametric study, designing of the solar energy-based experimental setup, treatment of dye contaminated textile industry wastewater by designed solar energy-based setup. The details of the applied methodologies have been discussed below**:**

4.2.1 Collection of wastewater samples and its parametric study

The wastewater samples collection its parametric study has been described is in the material and method section (chapter-2)

4.2.2 Experimental setup

To examine the pollution reduction efficiency of SPTR with the dye contaminated textile industry wastewater was planned to be treated with solar energy-based setup.

4.2.2.1 Designing of SPTR

It consists of reflective, parabolic surface that focuses solar radiation onto the transparent glass tubes along the parabolic focal line through which the reactant fluid flows. As a result, the collector aperture plane is always perpendicular to the solar radiation reflected by the parabola onto the reactor tube for optimum performance. The concentration factor of the solar collector is defined as the ratio between the collector's "aperture region" and "absorber area." To ensure the highest reflectivity, the trough surface was made of aluminum. The reactor tube is a closed system, so volatile compounds do not vaporize. The aluminum surface was made up of 1.5 mm aluminum metal with two meters in length and the glass tubes are two meters in length with 1.5 mm thickness. Over the reflecting aluminum surface, these three connecting glass tubes have been connected in parallel forms, and connectors of hard plastic joint them so that wastewater could easily flow over the reflector. The wastewater tank is of ten litres capacity with the working volume of eight liters. Electric motor of 0.5-hertz power has been used to flow water through the designed reactor with the plastic regulator to control wastewater flow. The whole designed reactor stands over a woody stand which is designed in such a way that it can track solar radiation manually during the experiment.

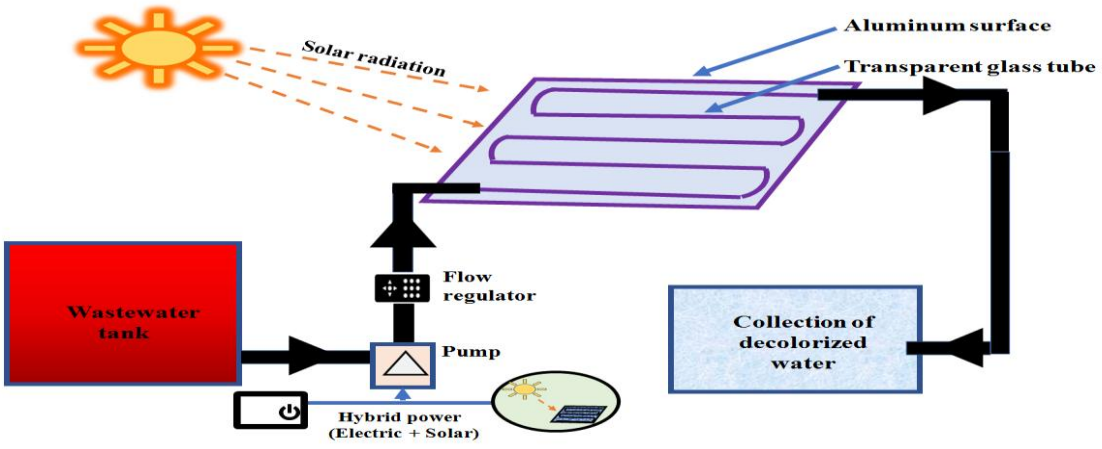


Figure 4.1: Sketch diagram of the designed reactor

The solar intensity was measured by solar intensity measurement device (KM-SPM-530) in W/m^2 on an hourly basis and the mean and standard deviation of each day was calculated in Microsoft Excel 2007. The color absorbance was checked each day by using UV spectrophotometer (HALO-DB 20) and after the experiment, the dye contaminated textile industry wastewater was collected and the COD reduction efficiency was assessed.

The details of the design have been described in the material and methodology section (chapter-2).

4.2.2.2 Flow rate optimization

The flow rate is a key influencing factor in the case of color and pollutant reduction. So, for the present study, the dye effluent was circulated with four different flow rates (0.5, 1.3, 1.95, and 2.6 L/minutes) through the designed setup at solar radiation (mean+ SD). The flow rate of the designed setup was controlled by the regulator made up of hard plastic. Before confirming any standard, the primary analysis of flow rate was conducted where the experiment was made to run with random flow rates to gain the basic idea about the flow rates with the given solar setup. After conducting the preliminary study, the above-mentioned standard flow rates were maintained and run for standard four hours of the experiment and the optimized flow rate was considered for further study of the present experiment.

4.3 Results and discussion

The results of treatment technologies for dye contaminated textile industry wastewater treatment SPTR have been discussed in the following sections:

4.3.1 Characterizations of collected dye contaminated textile industry wastewater

The dye contaminated textile industry wastewater was analyzed by the scientific protocol prescribed by APHA, (2012) before treatment. Physico-chemical parameters of collected textile industry wastewater have been described in chapter-2. After the initial characterization of dye contaminated textile industry wastewater, the experiment was conducted with solar energy-based treatment. The SPTR was run on with natural sunlight. It was observed that the solar intensity was capable to break the toxic chemical bonding of the wastewater water. The reading was taken at each five-day interval to check the efficiency progress.

Table 4.1: Characteristics of wastewater parameters after treatment by SPTR

Sl no	Parameters	Initial characterization
1	Total Solids	5004 ±2.08 MgL^{-1}
2	Total Suspended Solids (TSS)	100.3±0.6 MgL^{-1}
3	Total Dissolved Solids (TDS)	4904± 4.5MgL^{-1}
4	Nitrate	315±1.5 MgL^{-1}
5	Phosphate	3.73±0.57 MgL^{-1}
6	Alkalinity	893 ±1.52
7	BOD	587±2.5 MgL^{-1}
8	COD	997.3 ± 1.52MgL^{1}
9	Chloride	816±0.5 MgL^{-1}

The progress of pollution reduction efficiency of SPTR is positive after every five days of interval. It was observed initially the reduction rate was higher as compared to the final days of the experiment. It was also confirmed that maximum pollution reduction was obtained within five days of experimental work by SPTR. The COD reduction of wastewater and color removal from the textile industry by SPTR has been described in figure 4.2.

4.3.2 Effect of solar radiation on color and COD reduction

The change in flow rate provided so many differences in the color and pollutant loads. The present study was conducted with four different flow rates (0.65, 1.3, 1.95, and 2.6 L/minute) on the basis of the preliminary assessment of flow rates with the solar reactor. This experimental flow rate optimization process was processed for six hours as the prime objective of the present study was to check the best rate of circulation by which it would mostly affect the color and pollution reduction efficiency. The basic objectives behind keeping this experimental limit only for six hours were to catch the high solar intensity usually found at peak during mid-afternoon.

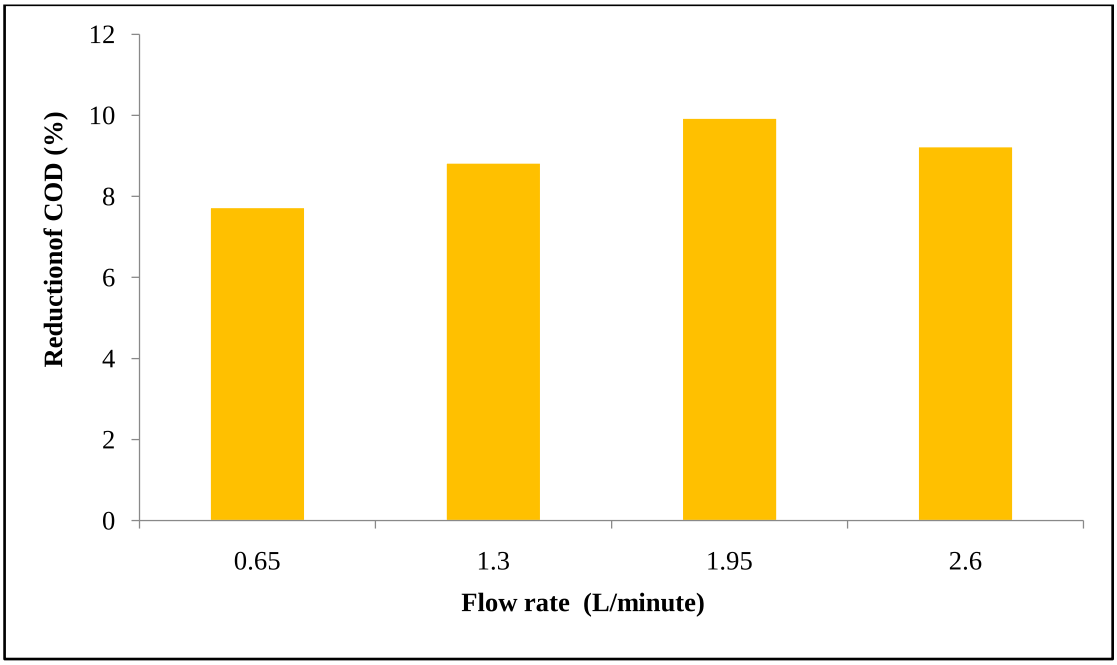


Figure 4.2: Effect of different flow rates on COD reduction (exposure time: six hours with solar intensity (849.3 ± 21.2 W/m^2)

According to literature, when the BOD and COD ratio (B/C ratio) is 0.5, wastewater is quickly biodegradable, when it is 0.4-0.6, it is average biodegradable, when it is 0.2-0.4, it is steadily biodegradable, and when it is less than 0.2, it is non-biodegradable Zhang et al., 2020). The B/C radio of the collected wastewater sample was detected at 0.5, which is most appropriate for wastewater degradation, so the experiment was performed with the current study using a solar-powered built reactor based on more degradability hypothesis. With varying circulation rates, substantial color and COD reduction were observed. The highest COD reduction (10%) and decolorization (13%) were obtained at 1.95 L/minute, while the lowest COD reduction (7%) was obtained at 0.65 L/minute. COD was reduced 8.8% and 9.2% with 1.3 L/minute and 2.6 L/minute respectively. As a result, the flow rate of 1.95 L/minute was considered the most efficient flow rate for the present experiment. Although, on the basis of other used processes of treatment for dye contaminated textile industry wastewater either physical, chemical, or biological the rate of decolorization and COD reduction are at large but poses several drawbacks including use of harmful chemicals, generation of toxic byproducts, and the high-cost necessity for experimental process makes them less impactful (Donkadokula et al., 2020). So, the current experimental reactor was designed to perform up to the limit of six hours per day in the sunlight to treat the dye-contaminated textile industry wastewater.

The flow rate allows the wastewater molecules to move over the reflecting surface, increasing the randomness of the wastewater molecules and reducing the color concentration. However, after a certain flow rate, the contact time decreases, whether the flow rate is very high or very low. In this context, the optimum flow rate for the present designed solar reactor was 1.95 L/minute and further study was conducted with this specific flow rate during the whole experiment. Color removal from dye-contaminated textile industry wastewater was seen significantly higher by this solar energy-based treatment reactor and it was observed ≥76% of color concentration was reduced from the initial concentration. The high-intensity ultraviolet solar radiation is capable of breaking down the toxic chemical bonding and, at the same time, could be highly efficient for color removal from the dye-contaminated textile industry wastewater (illustrated in figure 4.3).

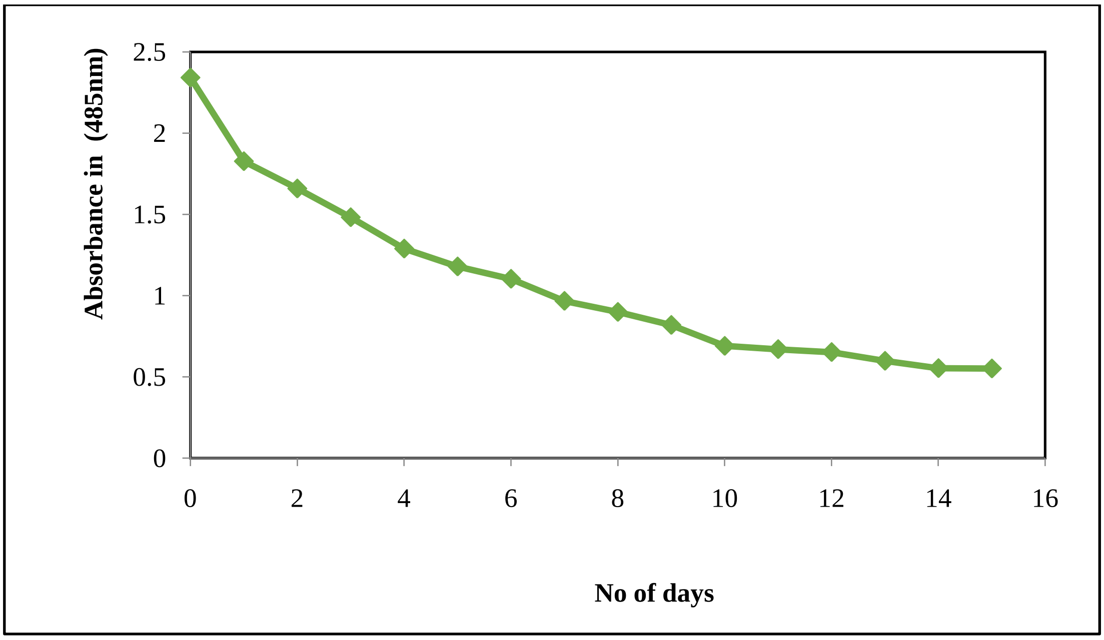


Figure 4.3: Effect of solar radiation on decolorization of dye contaminated textile industry wastewater with optimized flow rate (1.95 L/minute)

Patil et al (2019) reported that the concentrating solar technique is one of the excellent ideas used as a superior tool for wastewater pollution minimization so that the wastewater could get high-intensity solar temperature. The high evaporation rate of wastewater causes color removal more efficiently. The high-intensity solar radiation also causes changes in the chemical oxygen demand of the effluents. The chemical oxygen demand has reduced with the working of solar treatment reactor.

The pollutant load of COD was reduced by 79% from the dye effluents, but other pollutional parameters like BOD, nitrate, and phosphate were reduced very less as compared to COD. The color concentration was reduced by 76.4% after the treatment by the solar parabolic trough reactor. Many researchers and scientists have worked on similar areas related to the present experimental work and also reported their findings, which are essential for this present study to be compared. Rodrigues et al (2013) reported COD removal of 30.1 to 70% while experimenting on optimization and economic analysis of dye contaminated textile industry wastewater under-stimulated and artificial solar radiation. Patil et al (2019) confirmed only 30% of COD reduction while treating wastewater by parabolic trough collector. Chavaco et al (2017) reported 55% COD reduction while evaluating the feasibility of solar pond reactors to carry out degradation of dyes. Bandala et al (2008) reported 63% of COD removal while conducting an individual photocatalytic decolorization technology of textile dye industry wastewater. The mechanism of solar radiation-based treatment is due to the high-intensity ultraviolet radiation which is gathered by the concentrated parabolic collector. The experimental performance of decolorization during low light and without solar radiation is very less impactful. The solar intensity keeps increasing the randomness of the wastewater effluent molecules, so the color concentration drastically changes from highly dark to lightly visible at the same time, the undefined COD value also decreases with the impact of solar radiation. Also, no significant increment was noticed in the BOD of the particular dye-contaminated textile industry wastewater. That is due to the high-intensity solar radiation controlling the pathogenic activities inside the dye-contaminated textile industry wastewater so that the BOD of dye-contaminated textile industry wastewater was not so much different from the initial concentration. The same mechanism was also noticed for nutrients like nitrate and phosphate. Researchers have developed several methods for reducing color and COD in different forms of wastewater by using solar energy-based systems such as solar photovoltaic systems and solar parabolic collectors. However, the majority of them are not significant with real conditions of wastewater treatment because multiple variables (temperature, pH, reflectivity, study area location, and flow) affect the efficiency of the treatment process. The contact time is an important component in any wastewater treatment process and the efficiency of decolorization will eventually increase as the polluted wastewater molecules undergo more time in interaction with electromagnetic heat. However, after a certain period the efficiency of decolorization does not improve anymore and in this case, controlling the flow rate of the developed reactor is necessary for achieving the best performance. So, for the current study, we have optimized the flow rate of the designed solar energy-based reactor to deliver the best possible results in terms of decolorization and COD reduction which is an advanced innovative procedure that researchers and industrialists could implement in terms of decolorization and COD reduction.

The pollutant load of COD was reduced by 79.5% from the dye effluents, but other Researchers have been working on the impact of radiation on any chemical reaction to date. Many of them have clarified that reflecting surface increases the radiation intensity as compared to normal radiation. This high intensity possesses detoxifying nature of pollutants. Rahbar and Esfahani (2012) reported that temperature (air), solar intensity, directly affects the treatment process.The solar radiation-based technique is highly effective against a wide range of pathogens. The impactful effect of sunlight is due to optical and thermal processes and a strong synergistic effect at temperatures over 45(Blanco et al., 2009). In addition to direct killing by UV light, sunlight is absorbed by non-biodegradable compounds present in the wastewater, which then react with oxygen-producing highly reactive oxygen molecules which have a disinfecting effect. Although solar energy-based treatment has only been evaluated for lesser numbers in the research field, the efficiency of solar energy for many viral toxic compounds creates opportunities for long terms future treatment. The major steps current experiments have been graphically illustrated in the figure below.

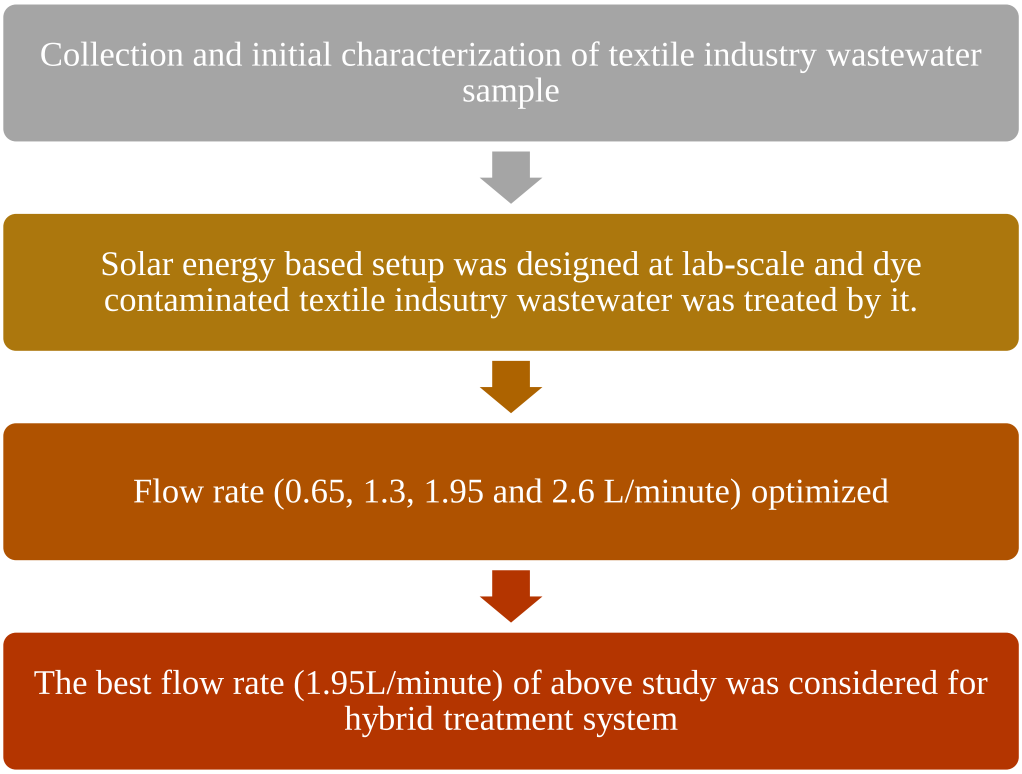


Figure 4.4: Flow diagram of solar energy-based treatment

4.4 Conclusion

Dye industry effluents were treated by designed solar setup with the optimized rate of circulation. It was noticed significant results were obtained in color reduction efficiency from dye wastewater effluents. The pollutional parameters (BOD, nitrate, and phosphate) were also examined before and after the treatment by designed solar energy-based treatment setup. But, more often it was observed that there were more enhancements in COD reduction efficiency from dye industry effluents rather than other pollutional parameters like BOD nitrate and phosphate. The pathogenic growth and activities in the wastewater effluents were reduced by the highly induced ultraviolet radiation that could be the reason for less reduction of BOD, nitrate, and phosphate. This idea of solar energy-based treatment is renewable-based treatments approach with more efficient in terms of cost-effectiveness, generation of secondary pollutants than other conventional treatment methods. Though, there are numerous treatment technologies reported by various authors for color and COD reduction from dye industry effluents, here the authors have examined the color and COD reduction with very low expenditure. So, this study gives ideas about cost-effectiveness, secondary waste minimization, and treatment efficiency of color and wastewater parameters from dye industry effluents. But, complete degradation of dye contaminated textile industry wastewater compounds is not so easy due to the complex bonding of toxic chemicals. Recently, many physical and chemical technologies are being used for dye-contaminated textile industry wastewater treatment, but still few disadvantages make them less impactful. In this context, keeping in mind, the global water scarcity and future energy crisis, water treatment technologies driven by solar energy are sustainable alternatives to address the worldwide water problem and reduce the harmful impacts as well. The selection of solar water technologies can be very site-specific. Among the various technologies, there are simple, low-tech, low investment technologies such as solar still and solar desalination, which are especially suitable for wastewater treatment. But, the need of abundant financial support and access to high technology and skilled workers are required for those. Although some of them are not commercially available, indirect desalination technologies and solar photocatalysis technologies are becoming more reliable and technically mature with the developments and technical improvements in both solar technologies and the water treatment processes. Besides, estimated costs of large-scale solar desalination plants showed that they could be economically comparable with conventional plants although no real large-scale plant has been built yet. Furthermore, there is still much room for the price decline of solar energy-based treatment with the development of solar technologies. Solar-based desalination will be more competitive in the near future. In terms of the current research on different solar water treatment technologies, a serious issue is, most researchers speak highly of the technology of their focus while ignoring the limitations and problems that exist in the area. This makes it even difficult to evaluate and compare different technologies. Meanwhile, most technologies are still under research and development.

Chapter-5

Experimental Evaluation of Novel Solar-Algal Hybrid Reactor for Dye Contaminated Textile Industry Wastewater Treatment: Techno-Economic Assessment

5.1. Introduction

Global threats are increasing day to day on the basis of contamination levels. The contamination level is increasing with furious speed due to unconscious human activities. These unconscious activities emphasize the human lifestyle, at the same time possess uncertain imbalances for the ecosystem to sustain. Besides this, the earth is facing severe environmental crises, particularly water pollution. The dye industrial sector is higher pollutant generator to the environment. These industries fabricate enormous quantities of poisonous substances throughout its handing out of manufacturing (Holkar et al., 2016; Jegatheesan et al., 2016). These toxic compounds are nothing but an assortment of types of carcinogenic colorants that possess confront to civilization to carry on quality life. Because, these dyes are decidedly injurious composite and able to for creating so many diseases like skin reaction, cancer, and mutation in human beings. It is tricky to treat the dye effluents because of the multifaceted fragrant molecular configuration of these composites. The molecular configuration of dyes makes them more unwavering and non-degradable in nature (Yagub et al., 2014; Lellis et al., 2019). These are principally chemical composites that can connect themselves to surfaces or fabrics to convey color. The current handling of dye contaminated textile industry wastewater engages various treatment methods, but the features like dye sewage composition, treatment asking price, and operational practicability conclude the sensible and economic applicability of these treatment techniques. An assortment of physical and chemical techniques together with adsorption, precipitation, coagulation, filtration, ozonolysis, advanced oxidation, membrane separation, and advanced techniques resembling ultra-filtration have been scrutinized for textile effluents (Siddique et al., 2017; Bhatia et al., 2017). This technique comprises prospective for dye elimination but, several stern anxieties like toxicity, elevated power effort, high expenses, and generation of secondary pollutants formulate them unviable for this purpose. For that reason, pioneering and cost-effective skills are required to accomplish cost-effective and efficient treatment of textile industry wastewater. Then, utilization of the renewable energy-based handling coordination with power reduction and price tag-efficient alternatives are in use as a principal intention of this investigational study associated with the pros and cons of existing treatment options. Hence, utilization of algal biomass is a superlative preference for pollution diminution from dye contaminated textile industry wastewater, as the adsorption with algae is a low-cost technology. The algal-based pollution diminution is chemically unwavering with high adsorption capacity as well as inattentiveness towards toxic elements (Siddique et al., 2017). A wide range of algal species are baked for the treatment of this dye industry wastewater (*C. vulgaris*, *C. pyrenoidosa*, *Scenedesmus* sp., *Chara* sp., *Dunaliella* sp., and *Oscillatoria* sp.) have been applied as source of adsorbent or bioaccumulators to remove dye from dye industry wastewater (Chia et al., 2014; Pandey et al., 2019). Chia et al (2014) reported a significant result with 100% dye removal of indigo blue dye by using immobilized *Scenedesmus quadricauda*. Similarly, El-Kassas and Mohamed (2017) also reported the potential of *C. vulgaris* as a bioaccumulator of dye industry wastewater with 75% dye removal efficiency. Rymond and Kadiri (2017) reported 63.89% and 45.7% dye removal by using biological agents i.e. *C. vulgaris* from blue and green dye respectively. In addition, the authors have examined the latent dye elimination effectiveness of *Sphaerocystis schroeteri*, and obtained 63.8% (for blue dye) and 60% (for green dye). The utilization of solar energy for the treatment of wastewater is to gaining attention due to its dual benefits of cost and energy-intensive in nature. It is potentially proficient for the breakdown of toxic chemical compounds and a cost-effective as well as the renewable-based approach which provides multidimensional scope to be used.

At the same time, solar energy-based treatment for the pollution reduction of dye industry wastewater is highly efficient. The major treatment technologies of solar energy-based treatment include solar desalination technology, solar photocatalysis technology, and solar disinfection which is the majority of extensively scrutinized solar-based water treatment techniques. In the midst of them, all the solar energy-based treatment technologies have received significant consideration all over the globe due to their applicability to most of the areas with no cost even in barren or isolated sections. The worldwide applicability and opportunities of solar desalination have been further demonstrated by researchers (Tiwari et al., 2003; Shatat et al., 2013; Pugsley et al., 2016). Sharon et al (2015) discussed briefly the benefits and lacking every technology as well as the predicament obtainable in desalination processes. On the basis of recent literature, the uses of solar power-based technologies are mainly two types such as: concentrating solar power (CSP) technology and photovoltaic (PV) technology. CSP technology includes parabolic trough, linear fresnel reflector systems, and central tower receiver. For our present study, the most developed CSP technologies (parabolic trough) have been preferred to be used due to their easy handling technique as well as efficiency in concentrating elevated solar radiations. The fundamental idea behind the technique is the concentration of solar radiation onto an absorptive receiver (pipe) which contains the wastewater to be treated. In this experiment, this parabolic solar collector has been designed to track (manually) the sun from east to west during the treatment process. The parabolic reflecting surface concentrates the direct solar radiations on the receiver tube creates heat and enhances the wastewater treatments process (Fendrich et al., 2018; Compain. 2012; Kannan and Vakeesan. 2016). Despite significant pollution reduction capacity, nutrient removal with color from dye contaminated textile discharge wastewater is a challenge. Therefore, with the assumption that like as individual, both the treatment technologies (algal and solar) shows the synergetic effect to each other and help in treatments of textile industry wastewater in particular also, is taken as a major objective for the study. The present study focused on the integration of solar-algal-based hybrid systems to examine the increment in the potential of pollution reduction compared with individual treatment systems for the efficient process as an advanced treatment solution.

This chapter has been focused on the treatment of dye contaminated textile industry wastewater with designed Solar Algal Hybrid Reactor (SAHR). This is an innovative and renewable-based low-cost approach where immobilized *C. pyrenoidosa* was used as adsorbent in coupling with concentrating solar parabolic through. This chapter delivers new and innovative scope for the treatment of dye contaminated textile industrial wastewater in an efficient and low cost-effective manner.

5.2 Material and methods

For the treatment of collected dye contaminated textile industry wastewater by hybrid treatment technology, experimental set up was designed at lab scale (details have been described in material and methodology section (chapter- 2). The flow diagram of the hybrid treatment system has been briefly illustrated in figure 5.1 below:

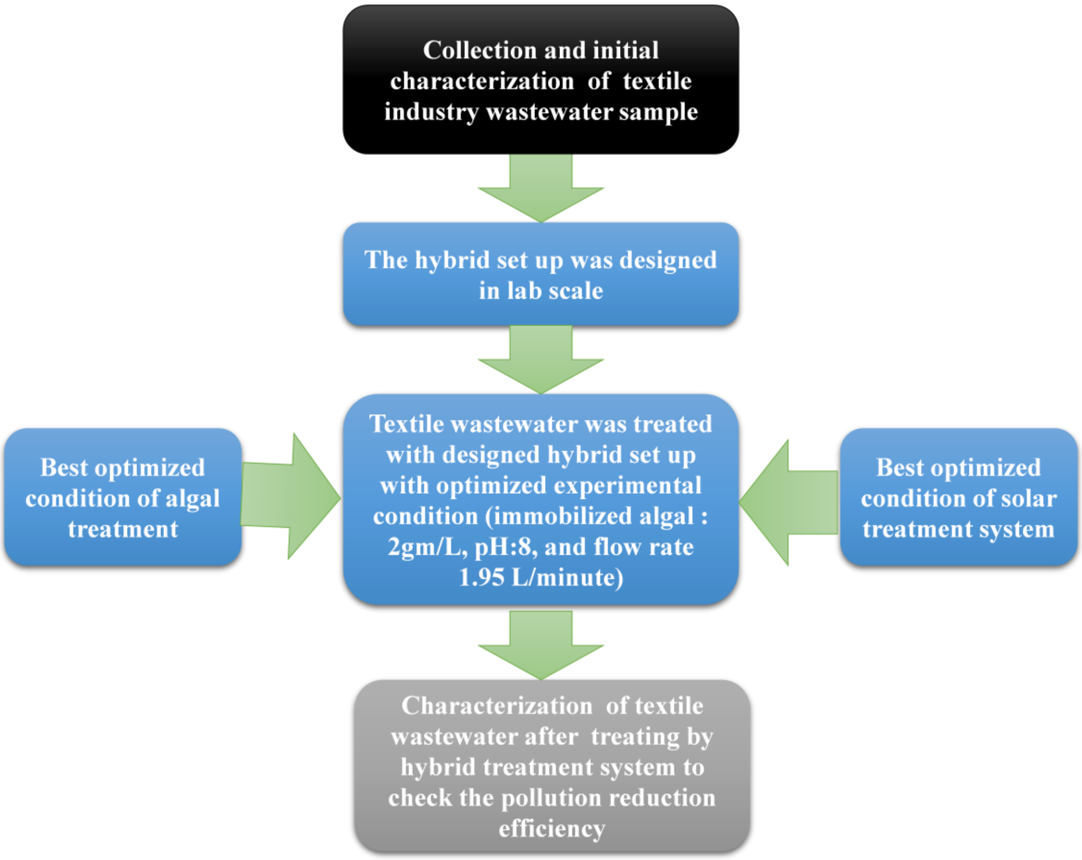


Figure 5.1: Key features of the hybrid treatment system

The materials and methodology section have been divided into several sub-parts and all of them have been briefly described as follows:

5.2.1 Collection of wastewater samples and its parametric study

The collection of wastewater samples and its parametric study has been described in the material and methodology section (chapter-2).

5.2.2 Algal samples collection and growth

Algal samples collection and growth have been described in the material and methodology section (chapter-2).

5.2.3 Experimental setup

To examine the pollution reduction efficiency of SAHR for dye contaminated textile industry wastewater the Solar Energy Based Hybrid setup was built at lab-scale the details of the apparatus requirement have been described in chapter 2.

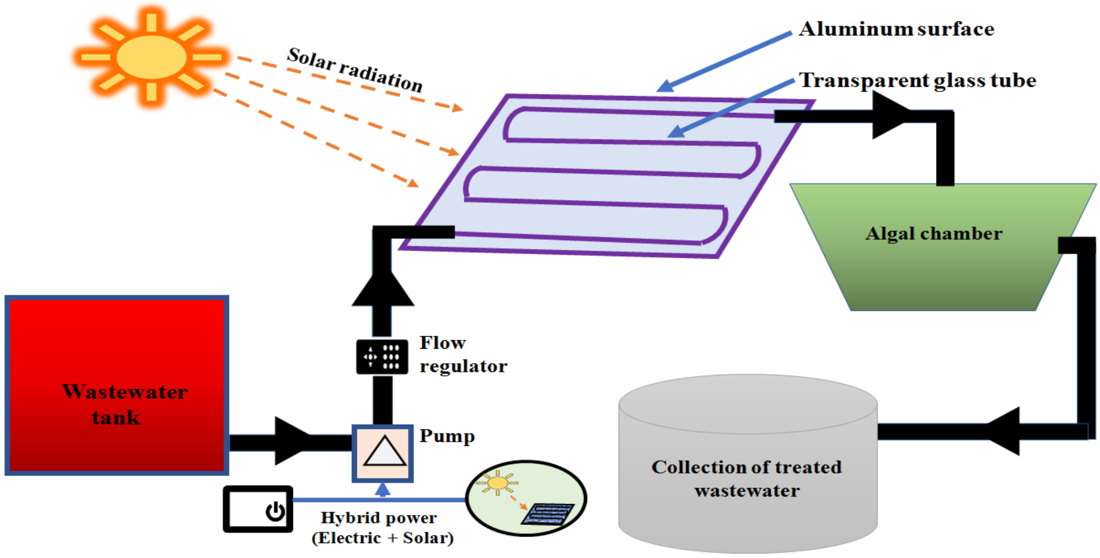


Figure 5.2: Sketch diagram of lab-scale designed SAHR

The parabolic trough collector idea has been derived from the applications of the production of solar thermal energy quite valid idea for the current process.

5.2.4 First order kinetic model for the removal of COD and color

The first-order kinetic model was implemented and validated with the investigated data for the present study. The detailed process of this kinetic model has been described in chapter-2.

5.3 Results and discussion

The results of the current experiment have been divided into different subsections such as characterizations of collected wastewater, pollution reduction with SAHR, the color reduction from dye contaminated textile industry wastewater, cost-effectiveness, and statistical analysis of the investigated data. The detailed findings of the experimental study have been discussed below:

5.3.1 Characterizations of collected dye contaminated textile industry wastewater

To obtain the initial pysico-chemical parameters, the dye contaminated textile industry effluent was evaluated by using the prescribed technique (APHA, 2012) and it was revealed that the textile industry effluent contained a significant nutritional and hazardous load of contaminants. Table 5.1 depicts the specifics of the characteristics of wastewater.

Table 5.1: Characterization of collected wastewater and its final value

Sl no	Parameters	Initial Value	Final Value
1	Total Solids	5004 ±2.08	2566±0.57
2	Total Suspended Solids (TSS)	100.3±0.6	68±1.5
3	Total Dissolved Solids (TDS)	4904± 4.5	2498±0.57
4	Nitrate	315±1.5	91.2±0.34
5	Phosphate	3.73±0.57	1.23±0.005
6	Alkalinity	893 ±1.52	391.5±0.81
7	BOD	587±2.5	135±0.28
8	COD	997.3 ± 1.5	97±0.76
9	Chloride	816±0.5	185±0.28

** All the parameters are in Mg/L*

The collected wastewater was highly polluted with high-value pollutional parameters like COD, BOD, nitrate, and phosphate. The initial COD was 997 Mg/L; BOD was 587 Mg/L and 315 Mg/L nitrates, *etc*. The reduction of these pollutional parameters also depends on the processing parameters of the hybrid treatment system which have been discussed in the following sections.

5.3.2 Effect of process parameter

The process parameters have a substantial impact on the pollution reduction effectiveness of any treatment method, and characteristics such as temperature and flow rate increase the rate of reaction and, in certain cases, mitigate the treatment efficiency. So, the current study has concentrated on flow rate optimization to attain the best potential results. The details of the flow rate study using the designed setup have been provided in Chapter-4, and other processing parameters like pH and temperature have been discussed in chapter-2.

5.3.2.1 Effect of pH and temperature

The pH is important for wastewater treatment in hybrid treatment systems so, the pH for the current experiment was kept constant to avoid experimental biases. The pH of any reactant media can affect the entire experiment; hence the pH of the test solution was kept constant by employing a buffer solution throughout the experiment. At the same time, the effect of temperature is an important aspect of this experiment because the solar intensity raises the temperature of the test solution. The flow of wastewater inside the hybrid setup was maintained by the plastic regulator, but the temperature of the test solution changes with every circulation. The inflow and outflow temperature from the hybrid setup varies every time due to the impact of high-intensity solar refection by the aluminum surface and glass tubes. The average temperature (Mean± SD) of mid-noon time was almost constant for each day of the experiment but, the temperature was varied during the morning and afternoon period. That also affects the pollution reduction efficiency, but for the present experiment, the mean and SD of each day solar flux was recorded for the experiment. Not much significant difference was noticed in each day's solar flux. The recorded solar radiations have been graphically illustrated in figure 5.3 below.

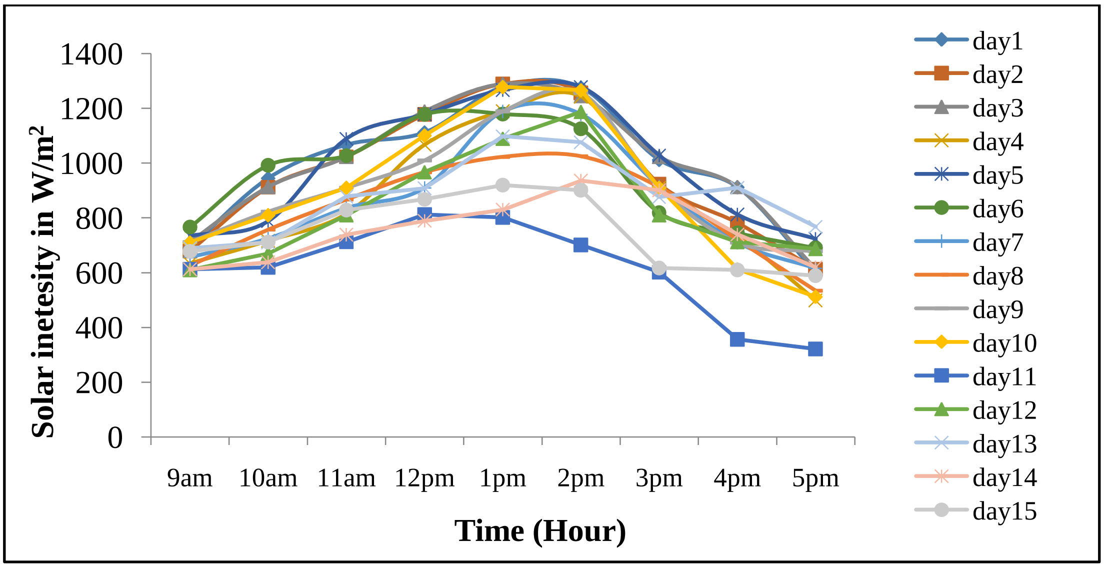


Figure 5.3: The recorded solar radiations (W/m^2) during hybrid treatment

The solar intensity was noted carefully during the experiment and the peak (solar intensity) of the current study was recorded to be between 11 am to 2 pm of each day. So, this statement concludes most of the pollutional parameters as well as the color might have been degraded during that period. The pollution reduction and color removal have been described in the following sections.:

5.3.3 Pollution reduction by designed SAHR

Throughout the experiments, the solar radiations were seen to have fluctuated randomly. However, in order to assess its influence on pollution reduction, the wastewater parameters were examined at regular intervals. Initially, pollutant reductions like COD and BOD were reported to be 68%and 63%, respectively (approximately in the first five days). Similarly, nitrate and phosphate levels were reduced by 56% and 42%, respectively. Gradually, pollutant reduction becomes slower; this could be due to immobilized algal dosages reaching saturation or threshold limitations on a daily basis. The reduction of major wastewater parameters (nitrate, phosphate, BOD & COD) have been illustrated in figure 5.4 below.

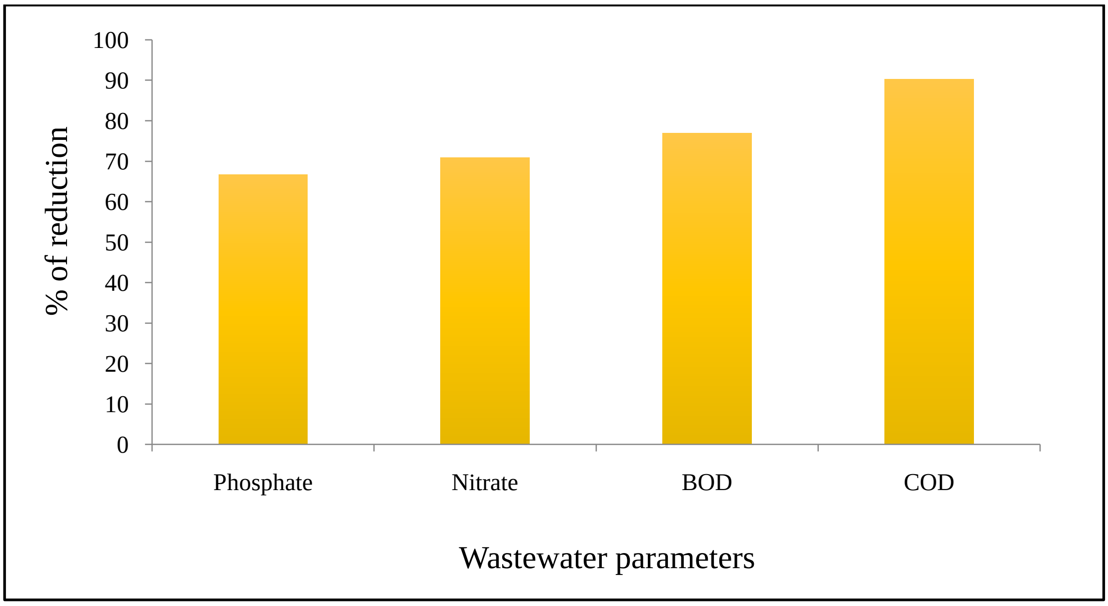


Figure 5.4: Percentages of wastewater parameters reduction

It was noticed that COD reduction was obtained by 90% whereas the COD reduction was obtained only 83% by algal-based treatment and 79% by solar energy-based treatment. This indicates the efficiency of the hybrid treatment than both treatment systems. It was also noticed that the other pollutional parameters like BOD, nitrate, and phosphate were also reduced more efficiently as compared to both the single treatment ones. About 77%, 70%, and 60% of BOD, nitrate, and phosphate were reduced respectively by SAHR whereas in algal and SPTR the reduction potentially lowers for pollutant as well as nutrient load. Moreover, it was also found perceptible color reduction from wastewater by hybrid setup. The maximum color reduction was obtained by solar hybrid setup than single treatment system like solar and algal-based treatment. The details of color removal have been illustrated in figure 5.5 below:

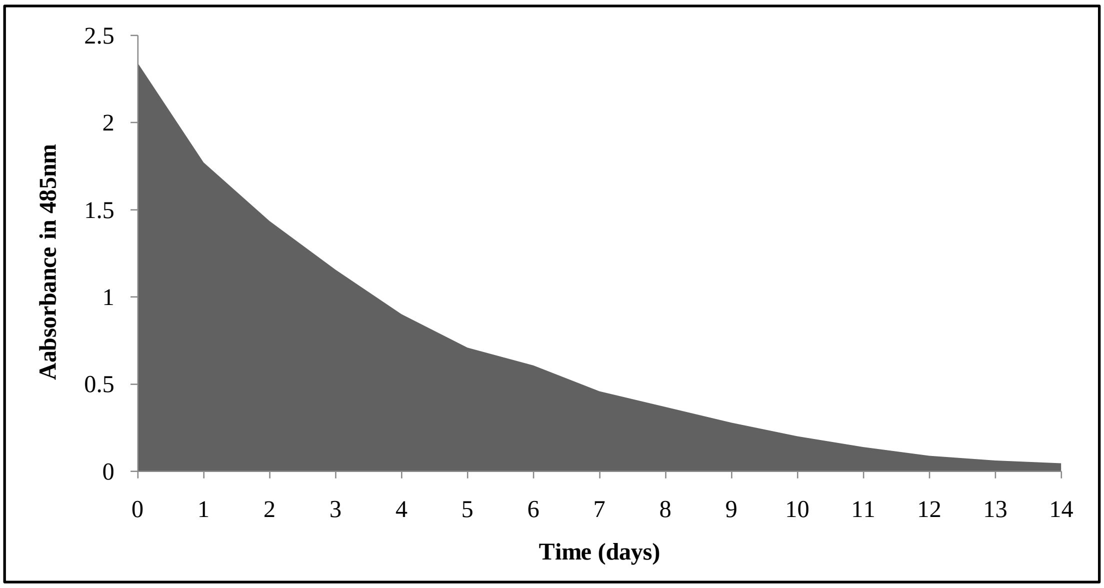


Figure 5.5: Color removal from dye contaminated textile industry wastewater by hybrid treatment

The other physicochemical parameters also showed similar observations. TDS and TSS were reduced by 49% and 47% respectively. It was observed that most of the parameters have been efficiently degraded in hybrid treatment than individual treatment. It is because of the integration technology between algal and solar energy-based treatment.

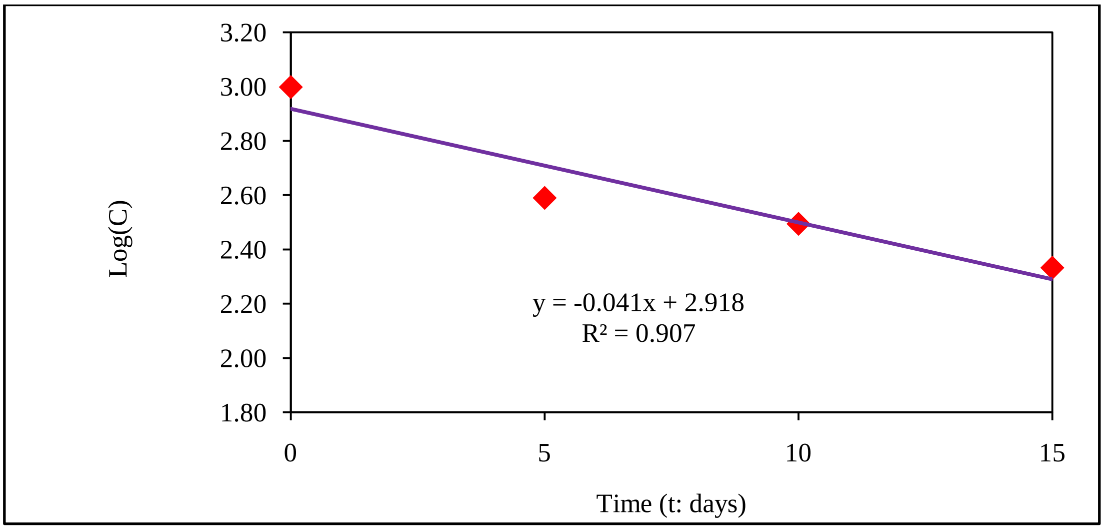
5.3.4 Kinetic modelling of color and COD removal

The first-order kinetic model was utilized over the investigated data of the current experiment, especially on COD reduction. The following equations have been used for the calculation of the kinetic removal rate of COD.

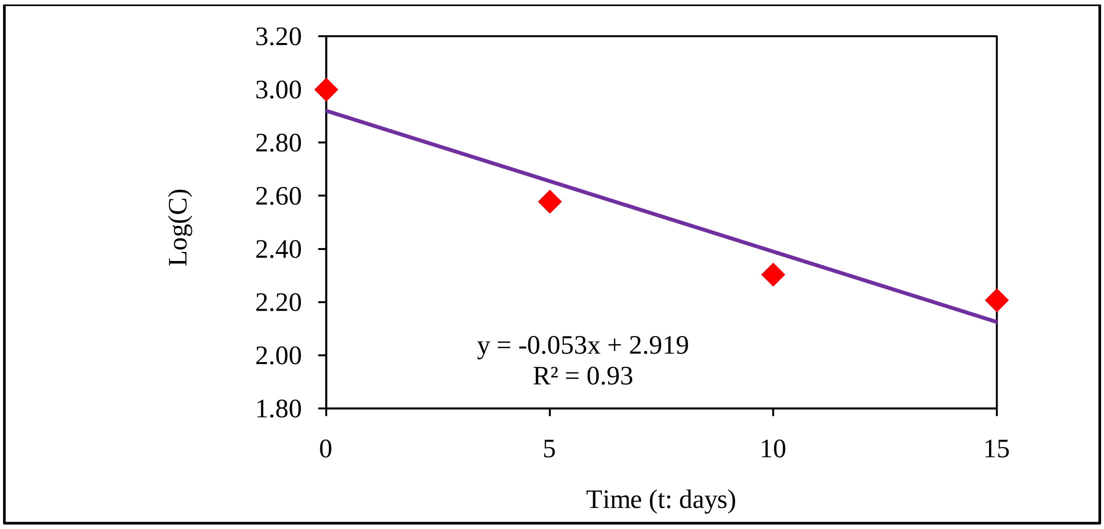
$$\text{Kinetic removal rate } (k) = -\frac{\text{Log}\left(\frac{C_i}{C_0}\right)}{t}$$

$$\text{COD removal rate (Mg/L/d)}: \frac{(C_i q_i - C_0 q_0)}{C_i q_i} \times 100$$

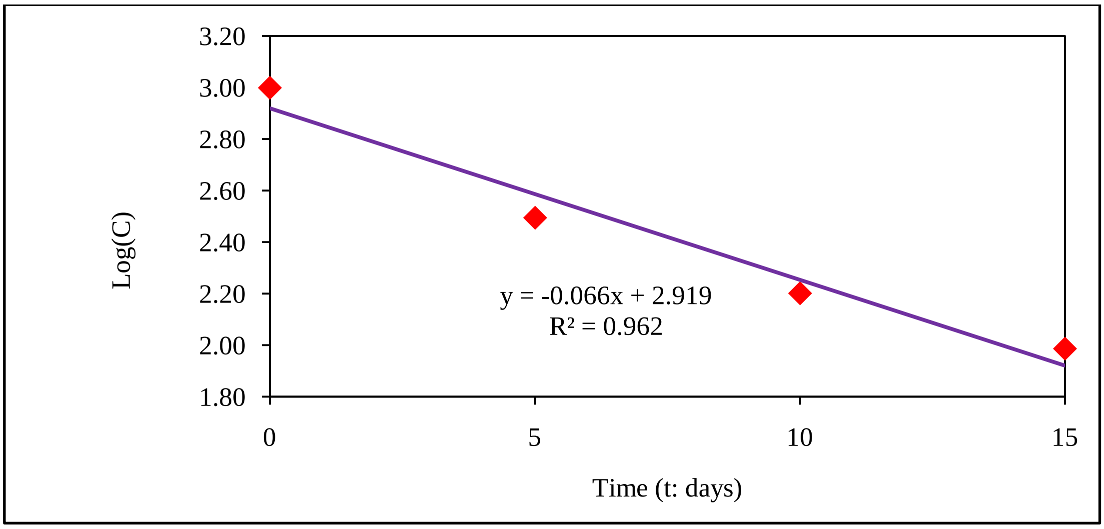
Where C_i and C_0 are the initial and residual COD contents, q_i and q_0 are inlet and outlet hydraulic loading rates (L/day), and t indicates the experimental time (days). The graphical representation has been derived between Log (C) vs. t. The kinetic removal rate (k) and reduction (R^2) have been plotted and described in figure 5.6 below.



(5.6a)



(5.6b)



(5.6c)

Figure 5.6: Log(C) *vs.* t plots for the fitness of first-order kinetic model (5.6a: COD reduction by SPTR, 5.6b: COD reduction by algae, 5.6c: COD reduction by Hybrid treatment)

The first-order kinetic values have been described in table 5.2 below. The kinetic removal rate "k" was very much significant in every treatment system. The values of "k" are 0.04, 0.53, and 0.06 for COD removal in SPTR, algal, and hybrid treatment systems respectively. Similarly, the calculated "R^2" values are 0.9, 0.93, and 0.96 for COD in SPTR, algal, and hybrid treatment respectively. The kinetic model parameters have been described in the table below:

Table 5.2: First order kinetic model parameters for the removal of COD and color

Pollutant	Reactor	Equation	*K*	R^2
COD	SPTR	$y = -0.0419x + 2.918$	0.0419	0.9072
	Algal	$y = -0.053x + 2.919$	0.053	0.93
	Hybrid	$y = -0.0666x + 2.9195$	0.0666	0.9620

The parametric values indicate that the rate of COD reduction is directly proportional to the time. As the time of the experiment increases the reduction efficiency also increases. But, at the threshold point, the reduction efficiency gradually comes to a certain range. Similar trend was also observed for color reduction during the experiment and the color reduction rate was much higher during the initial phase of the experiment, but, after a certain period of time, the rate of color degradation decreases, which may be due to the effect of the threshold limit of adsorption by algal cells.

5.4 Comparative discussion of solar, algal, and hybrid treatment for dye contaminated textile industry wastewater

It is well known that conventional treatment technologies have the potential for the treatment of any wastewater which could be tannery, dairy, or textile industry wastewater. But, some sort of disadvantages like secondary pollutant generation, treatment efficiency, and cost-effectiveness make them less preferable. Here two separate treatment options have been utilized for the dye contaminated textile industry wastewater treatment at the same time both the treatment technologies have been coupled to check where they are best capable for pollution minimization. And the conclusion is very interesting and valid as it was discussed in the literature and review section (chapter 2). The effect of conventional algal-based treatment was observed quite proficient on pollution as well as color removal. In the same way, the implication of solar parabolic through reaction over the toxic dye contaminated textile industry wastewater should the same result. Though it can be hypothesized that the algae-based treatment is a typical process of adsorptive so that the reduction of all the pollutional parameters like nitrate, phosphate, and BOD are higher due to more pathogenic activities. But in SPTR due to the strong radiance effect of ultraviolet radiation keeps minimizing the impact of pathogens on the text solution therefore, reduction of all the pollutional parameters is very less in comparison to algal-based treatment. But the color concentration was reduced by each treatment technology and at the same time, the COD values were also reduced at a significant value. The values have been discussed result section. The application of hybrid treatment reduced the nutrient load like nitrate and phosphate by 52% and 63% respectively at the same time color concentration by ≥ 98%. It was seen the reduction values of color concentration by designed hybrid setup was more as compared to both the separate treatment technology. The estimated value of color reduction by solar energy-based treatment was 76%, similarly <=98% by algal-based treatment but it >98% when we merge both the treatment system means by hybrid treatment system (illustrated in figure 5.7).

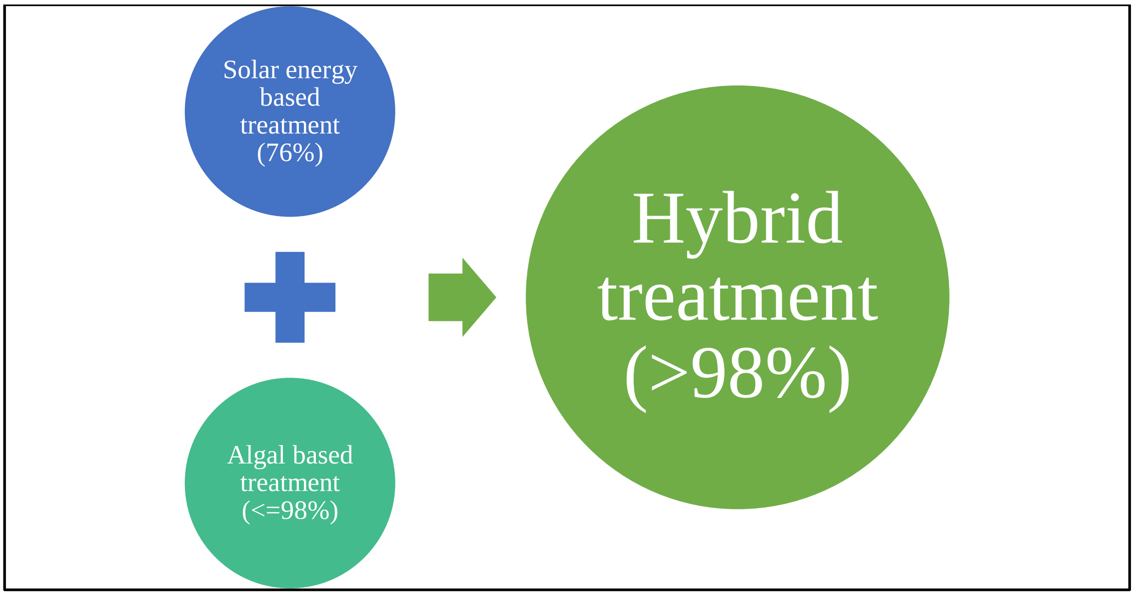


Figure 5.7: Color removal by solar, algal, and hybrid treatment

The main mechanism of pollution reduction by hybrid treatment is due to both adsorption and solar radiation. The *C. pyrenoidosa* has been used for the same purpose where it will process the adsorption process of the highly toxic compounds, which have been broken down by high-intensity solar radiation. The high-intensity solar radiation is capable to break the toxic chemical bonds of non-biodegradable dye wastewater flowed by algal-based chamber which is the best fit and capable for the pollution and nutrient load reduction from wastewater (Siddique et al., 2017; Sharon et al., 2015). It was observed that the efficiency of pollution reduction is higher at the initial stage (at the beginning of the experiment) which gradually slows down. Due to differences in the pathogenic activities, the reduction values of pollutional parameters differ in each treatment technology. Mostly in solar energy-based treatment, the pathogenic activities are very less so the pollutional parameters like nitrate, phosphate, and BOD are degraded in very less amounts. But the COD reduction efficiently occurred in all three treatment technologies adopted for experimental investigation. The comparisons of all the COD values have been illustrated in figure 5.8:

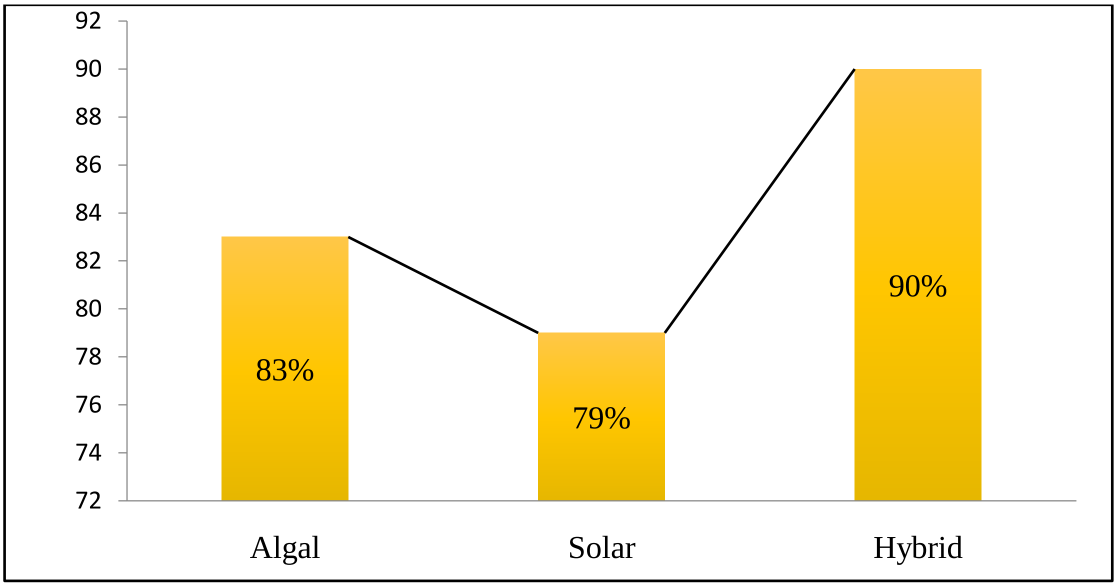


Figure 5.8: COD reduction by algal, solar, and hybrid technology

It was noticed that 79% of COD reduction was obtained by solar energy-based treatment whereas 83% of COD reduction was obtained by algal-based treatment but 90% of COD was obtained by hybrid treatment. So many researchers have detected COD and color reduction by separate algal and solar energy-based treatments. Aragaw and Asmare (2018) studied the phycoremediation process with indigenous algae in textile industry wastewater and reported 91.50% and 82.6% of COD and color removal respectively. Pathak et al (2014) checked the efficiency of *C. pyrenoidosa* and reported 62% and 87% of nitrate and phosphate removal respectively, from dye contaminated textile industry wastewater. Anandhan et al (2018) investigated the potential of algae for treatment of dye contaminated textile industry wastewater and reported only 19% and 15% of color removal with *Chlorococcum vitiosum and Dactylococapsis* sp. respectively. Similarly, Ahmad et al (2013) reported the reduction of nitrate and phosphate up to 98.3% and 98.6%) from wastewater with *C. vulgaris* species. Singh et al (2010) reported 44–45%, 33–33, and 38–62% nitrate, phosphate and COD were reduced respectively while applying *C.*

vulgaris for pollution reduction of textile industry wastewater. Vijayaraghavana and Shanthakumara (2018) reported 92.7% of color removal from dye contaminated textile industry wastewater using algal alginate. *They also confirmed the removal of color concentration was only 41% to 50%.* The experimental data revealed from our study suggest that immobilized algal biomass (C. pyrenoidosa) also has potential for color removal in integration with pollutant and nutrient removal both. It has been also noticed that relevant researchers' maximum used free algal biomass but in terms of utilization of maximum efficiency of the process best with is immobilized algal biomass due to large surface area to react with wastewater as a media.

Rodrigues et al (2013) reported COD removal of 30.1 to 70% while conducting experiment on optimization and economic analysis of textile industry wastewater under-stimulated and artificial solar radiation. Patil et al (2019) confirmed only 30% of COD reduction while treating wastewater by parabolic trough collector. Chavaco et al (2017) reported 55% COD reduction while evaluating the feasibility of solar pond reactors to carry out the degradation of textile dyes. Bandala et al (2008) reported 63% of COD removal while conducting an individual Photocatalytic decolorization technology of textile industry wastewater. The reason may be the shape of parabolic through the collector, which can focus sun at 30 to 1000 times of its normal intensity, which will help in detoxification of wastewater from textile industry wastewater.

5.5 Techno-economic assessment of hybrid treatment system

Though the hybrid treatment was conceived and created at the lab scale, and it is also known as renewable-based technology, it does have certain real-world costs associated with its design and manufacture. As with any treatment technique, there are costs associated with the process, however, the costs and management, in this case, are far lower than other traditional treatment methods. Table 5.3 summarizes the primary needs and their associated costs:

Table 5.3: The requirements with the approximate cost for hybrid setup

Requirements	Approximate cost (INR)
The parabolic aluminum reflective surface	200
Transparent glass tube	300
Wastewater tank	50
The plastic connector between glass pipes	30

The reflective aluminum surface was chosen rather than alternative metal surfaces due to its higher reflectivity and ease of availability at a lower cost. It was within the experiment's budget, and a two-meter-long aluminum sheet with a thickness of 1 mm cost only Rs. 200. The transparent glass tubes were available on a lab-scale, but their cost is still being considered in order to calculate the entire expenditure. A single transparent glass tube costs Rs. 100. So, the three glass tubes cost is Rs. 300 in total. The wastewater tank and algal chamber were simply recovered from the laboratory's waste products, which may cost around Rs.50 in the local market. Plastic connectors cost Rs. 30. All of the required chemicals were available at the departmental laboratory Except for sodium alginate which could be generally available from thermal scientific chemical vendors at a very cheap price. The total estimated cost of the fabricated setup is approximately Rs. 500 also the overall cost could be managed and reduced by arranging through waste or unnecessary products from the society like broken aquarium glasses could be used for the wastewater or algal chamber after joining them with the help of proper glass jointing gum at the same time the small plyboard pieces could be used as the hybrid treatment system stands. Thus, it is justified that it is a very low-cost treatment system. However, it is also evident that an increase in water quantity will have no effect on treatment costs because the same hybrid design could well be utilized for wastewater treatment several times. The cost of an algal culture is quite low because it was obtained from NCIM Pune, however, the cultures had to be cultivated numerous times before they could be collected and used in the experiment.

The conventional handling technologies necessitate supplementary energy input for treatment progression, at the same time these techniques discharge enormous quantity of the poisonous substance to the surroundings. They are costly to hand out and difficult for researchers to utilize. Though, the pollution diminution capability of those methods is reasonably fine but, the serious factors like high sludge production, supplementary time consumption, high requirement of manpower, and additional time requirement for final manufacturing product generation make them unviable. A single treatment system is capable to demean dye-contaminated textile industry wastewater but, in many aspects, it fails. Comparing conventional treatment technology with hybrid treatment options on the basis of cost-effectiveness generates plenty of optimistic scopes for hybrid ideas. The hybrid technologies are exceedingly professional for contamination remediation from dye contaminated textile industry wastewater also derives ideas on the lesser need of operational resources. The maintenance cost, operating cost, capital cost and energy requirement, manpower need are lesser (comparing ratio of two treatment technology) in comparison with a single treatment system. The assumption of hybrid treatment options sometimes changes in specific cases with the manufacturing process being utilized, nature of raw materials, and complexity of used chemicals, the capacity of external power being imposed, and expertise of the operator. As these process parameters change the major impact of cost-effective analysis. The foremost explanation behind the hybrid treatment option is more preferred are it shows immense opportunities for industrialists and researchers on the ground of treatment cost. This hybrid treatment option is more valid, reliable, and specific on the basis of cost-effectiveness.

Table 5.4: Assessment of different factors of hybrid treatment

Parameters	**Algal**	**Solar**	**Hybrid**
Cost-effectiveness	High	Medium	Medium
Generation of sludge/secondary pollutants	Medium	Medium	Medium
Professional than conventional treatment methods	Medium	Medium	High
Maintenance cost	High	Medium	Medium
Energy input requirement	Medium	Medium	Low
Trouble-free handling technique	Medium	Medium	Medium
Environmental friendly solution	Medium	Medium	High

Any treatment technology is considered novel and widely accepted when the used resources are a lesser amount cost consuming than its relative treatment technology. On the basis of the textile manufacturing process, wastewater generation, sludge production, and available treatment options for its treatment, solar-algal-based preferences are economically stable and create immense opportunities for pilot scale compatibility.

5.6 Eco-friendly approach

Environmental degradation and its restoration preferences should be looked forward by modern scientists. The coupling of two or more than one treatment system is favorable from environmental perspectives as it consumes less energy and labor at the same time it is more efficient for pollution remediation from dye contaminated textile industry wastewater. Recent sciences need more certified treatment technologies favorable for ecosystem balance as well as pollution minimization. In this context, the hybrid treatment option is new innovative, cost-effective, less energy-consuming, and environmentally friendly treatment technology which is much needed for the recent environmental pollution scenario. This recent global scenario is fully dependant on new, novel treatment options where the expectation for high load pollutants could be easily minimized at the same time the hydrosphere imbalance could be avoided. The eco-friendly treatment system has been emerged by various scientists for years but, the success rate of these methods is very rare and in some specific cases these methods were unable to gain attention for implementation. The suggested option for dye contaminated textile industry wastewater is an advanced option for textile industry wastewater treatment and is capable of the full fill of such expectations. Finally, to carry out the recent process on long-term basis, proper importance/ preferences should be taken over this approach.

5.7 Conclusion

The present study is one of the brief comprehensive assessments of three different treatment options for the treatment of dye contaminated textile industry wastewater. As it is well known every treatment option is highly capable of its separate role of pollution minimization from this specific wastewater. Both solar treatment and algal treatment technologies have separate limitations as well as advantages. For the present study, the hybrid treatments system was implemented to overcome these limitations from each separated treatment at the same time to increase the pollution reduction efficiency. From the experimental study, it was proved that the pollution reduction efficiency was more in hybrid treatment systems than individual treatment technology. But, complete degradation of dye contaminated textile industry wastewater compounds is not so easy due to the complex bonding of toxic chemicals.

The recent physical and chemical technologies like coagulation, ozonolysis, advanced oxidation, membrane separation, and advanced method like ultra-filtration are being used for dye contaminated textile industry wastewater. But, serious issues like cost-effectiveness, generation of secondary pollutants make them unfeasible. Again, single treatment technology is incapable of full degradation of this highly polluted textile industry wastewater. So, the combination of two or more this treatment options can enhance the potential of pollution reductions. From the result and discussion, it can be concluded that the present study (hybrid treatment system) is the best possible approach which can degrade the high load pollutants as well as fulfill the gaps remaining in single treatment technology.

Chapter-6
Conclusions and Future Recommendations

6.1 Conclusion

Dye expulsion into the hydrosphere is a substantial source of pollution Due to its recalcitrance, while also providing an unappealing color to water bodies, reducing sunlight penetration, and inhibiting photochemical and biological activities of aquatic flora and fauna. Textile dye wastewater has distinct characteristics depending on the industry because each industry has its manufacturing process guidelines. As a result, treating this wastewater raises numerous challenges for researchers. Though, a number of technologies are used in the various manufacturing industries but, some serious concerns like the way of resource utilization, the timing of machine running, and way of instrument handling create the parametric differences in the wastewater. The typical dye industry wastewater disturbs the balance of basic water parameters like Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Suspended Solids (SS), Dissolved Solids (DS), pH, Chloride, Sodium, *etc*. On the basis of toxic chemical compounds, its treatment poses immense challenges to environmental experts. The treatment system of dye wastewater can be broadly classified into (i) conventional treatment technologies which include all the traditional (physical, chemical & biological) methods. These technologies offer more dye removal potential, but they are unsuitable for commercial use due to a number of issues such as toxicity, high energy input, high cost, and the formation of secondary pollutants. (ii) Modern treatment technologies include advanced applications of recently developed techniques such as the use of nonmaterial, treatment through ion exchange, reverse-osmosis, biomass-based treatment, solar-energy-based treatment system, *etc*. The current research is the comprehensive assessment of three alternative dye-contaminated textile wastewater treatments including solar energy, algal, and hybrid treatment. It is known that each treatment approach is capable of minimizing pollutants from this specific wastewater at the same time it is also clear that each treatment option has several limitations. In this context, the hybrid treatments system was used to fulfill these limitations left by both solar and algal treatment, also increasing the pollution reduction efficiency. On the basis of objectives, the current research work was divided into three phases; algal-based treatment, solar energy-based treatment, and hybrid treatment (combination of both solar and algal-based treatment technology). In algal-based treatment, the phytoremediation treatment process was implemented for pollution reduction and decolorization of dye contaminated textile industry wastewater where *C. Pyrenoidosa* was used as an adsorbate in both free and immobilized form. In solar energy-based treatment, the fabrication of solar parabolic setup was made in the department and experimental analysis was performed with the textile industry. The hybrid setup was the combination of both solar and algal-based treatment.

Specific concluding remarks of the results are given below:

- The pollution reduction was more efficient by immobilized algal cells than free algal cells; it's due to the availability of more surface area in immobilized alga in comparison to free algal biomass. The larger surface area enhances the adsorption process as it is directly proportional to the surface area of the adsorbate.
- The immobilized algal biomass reduced 46.7% of nitrate, 59.4% of phosphate, 83.1% BOD, and 83.0% of COD whereas; free algal biomass cell reduced 43.2% of nitrate, 56.7% of phosphate, 71.4% of BOD, and 78.0% COD.

- It was observed that with the increase in flow rate the pollution reduction increases, it's because the no of passes per unit time inside the reactor increases.

- There was a non-ideal flow behavior due to collision with immobilized algal cells while flowing in horizontal directions. But, this obstacle benefited the treatment efficiency. Because the contact time between immobilized algal cells and wastewater effluents increased due to such collisions which enhanced the pollution and color reduction efficiency.

- The estimated color reduction by solar energy-based treatment was 76%, and <98% by algal-based treatment.

- The application of hybrid treatment reduced the nutrient load like nitrate and phosphate by 52% and 63% respectively, at the same time color concentration by $\geq$ 98%. It was seen the reduction values of color concentration by designed hybrid setup was more as compared to both the individual treatment technologies.

- The COD reduction was 90% by using hybrid treatment whereas; 79% and 83% of COD reduction were obtained by solar energy and algal-based treatment respectively.

Though the pollution reduction and decolorization of dye wastewater were highly significant, complete degradation of dye contaminated textile industry wastewater compounds is not so easy due to the complex bonding of toxic chemicals. The recent physical and chemical technologies like coagulation, ozonolysis, advanced oxidation, membrane separation, and advanced methods like ultra-filtration are being used for dye contaminated textile industry wastewater. But, serious issues like cost-effectiveness, generation of secondary pollutants make them unfeasible. Again, single treatment technology is fully incapable of the degradation of this highly polluted textile industry wastewater. So, combination of two or more of these treatment options can enhance the potential of reductions. It can be concluded that hybrid treatment system is the best possible approach which can degrade the high load pollutants as well as fulfill the gaps remaining in single treatment technology.

6.2 Future recommendations

Though the hybrid treatments system is one of the highly advanced treatment systems for wastewater treatment, it also has certain limitations. One of the major disadvantages of this treatment system is that the hybrid treatment system is dependent on electricity for its functions. So, longtime use of this system could demand high electricity. In this context, to fulfill this energy demand solar power could be one of the ideal options. Solar power-based electricity generation is so important and feasible these days that the hybrid setup could be designed in such a way so that solar energy-based electricity could be the best fit in that system. Thus, the whole hybrid system could be renewable energy-based cost-effective green technology. Besides this, the immobilized algae used for this study could be utilized for further experimental purposes. The algae used for the experiment could be collected and further used for multipurpose scientific studies like biodiesel production rather than merely leftover in the environment. Finally, it is recommended to deeply and carefully analyze all the process parameters (pH, temperature, dose and flow rate, *etc*) of the hybrid treatment system while implementing it on pilot scale.

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Appendix

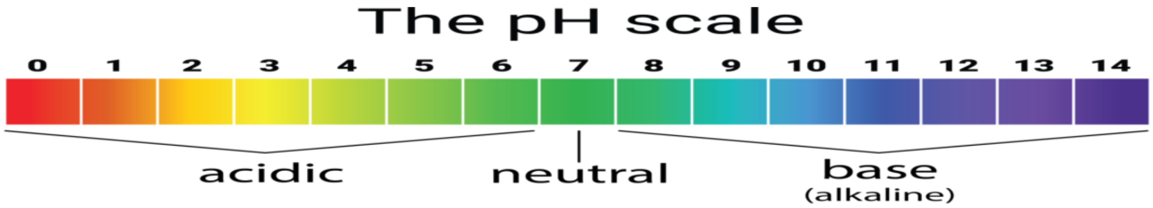
The methodology adopted for the analysis of physicochemical parameters analysis (APHA, 2012), process parameters (Loewus, 1952; Maiti, 2004, Wang 2010; Reiner, 2012), and instruments used (Daniel et al., 1997) was followed as the prescribed in the particular protocols is given in details:

1. pH

The pH unit measures the degree of acidity or basicity of a solution. the pH of the most natural waterfall within the ranges of 4 to 9. The majority of waters are slightly basic (i.e. generally over 7.0) because of the presence of carbonate and bicarbonates. The pH increases (acidic) during daytime due to photosynthesis activity. By definition, pH is the negative logarithm of hydrogen ion concentration, more precisely hydrogen ion activity.

$$pH = -\log10\ [\ H^{+}]\ \text{or}\ pH = \log10\ 1/[H^{-}]$$

The concentration range suitable for the existence of most biological life is quite narrow and critical (typically 6 to 9). Wastewater with an extreme concentration of hydrogen ions is highly affecting the discharge point and if the concentration is not altered before discharge to the environment, it generates some adverse conditions to the flora and fauna of the discharge point. The allowable pH range usually varies from 6.5 to 8.5. The hydrogen ion concentration in water is connected closely with the extent to which water molecules dissociate.



Estimation of pH

Estimation of pH can be done by two methods:

(i) By using paper: simple, inexpensive, and inaccurate.

(ii) (ii) By using electronic pH meter: accurate and free from interferences, gives reading with accuracy of ± 0.05 pH.

2. Total dissolved solids (Mg/L)

Total dissolved solids of filterable residue are those solids left after evaporation of the filtered sample.

Procedure

100 ml washed and dried crucible was taken and weighed, immediately before use. 100 ml of well-mixed sample was poured and filtered through filter paper.

Collected the filtrate in the 100 ml weighed crucible. Evaporated the sample in an oven at 105ºC ±1 for 4 to 6 hrs and cooled the crucible and weight.

Calculation

$$TDS\ (mg/l) = \frac{(A - B)}{V} \times 10^6$$

Where, A = Final weight of crucible in gm, B = Initial weight of crucible in gm, and

V = Volume of sample.

3. Total suspended solids (Mg/L)

Total suspended solids are the retained material on Whatman no. 42 filter paper after filtration TSS was determined by taking difference between the total solids and total dissolved solids.

Calculation

$$TSS\ (Mg/L) = TS - TDS$$

4. Total Solids

Total solids can be determined as the residue left after evaporation at 103 to 105°C of the unfiltered sample.

Apparatus

1. Evaporating dishes: Dishes of 100 ml capacity made up of either porcelain or platinum.

2. Desiccator, provided with a desiccant containing a color indicator of moisture ($CuS0_4.5\ H_2O$).

3. Drying oven or hot air oven, for operation at 103 to 105°C.

4. Analytical balance, capable of weighing to 0.1 Mg.

Procedure

1. Take an evaporating dish or clean beaker (400 m capacity) of suitable size and dry at 103 to 105°C for 1 h. Store and cool the dish in a desiccator until needed. Weigh immediately before use. Note the initial weight (Wi) in Mg.

2. Put 250-300 ml unfiltered well-mixed sample in it.

3. Put in a hot air oven from 103°C to 105°C for 2 h up to dryness.

4. Cool in desiccators and take the final weight (Wt) in Mg.

5. Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained, or weight change is less than 4% of the previous weight or 0.5 Mg, whichever is less. When weighing the dried sample, be alert to the change in

weight due to air exposure and sample degradation. Duplicate determination should be within 5% of the average.

Calculation

$$TS\ (Mg/l) = (Wf - Wi) \times 1000/\text{Volume of sample, ml}$$

5. Biochemical oxygen demand (Mg/L)

Principle:

The principle of the method involves measuring the difference of the oxygen concentration in the samples and after incubation for 5 days at 20°C.

Apparatus and reagents

a). BOD bottles

b). BOD incubator (at 20°C)

c). Phosphate buffer: 2.1gm H_2SO_4, 5.43gm KH_2PO_4, 8.35 gm $Na_2HPO_4.7H^2O$, and 0.42gm NH_4Cl were dissolved in distilled water to prepare 250 ml of solution.

d). Magnesium sulfate: 8.25gm $MgSO_4$ was dissolved in distilled water to prepare 100 ml of solution.

e). Calcium chloride: 2.75gm of anhydrous $CaCl_2$ was dissolved in distilled water to prepare 100 ml of solution.

f). Ferric chloride: 0.25gm $FeCl_3.6H_2O$ was dissolved in distilled water to prepare 1 liter of solution.

g). Sodium sulfite solution: 1.57gm Na_2SO_4 was dissolved in 100 ml distilled water and diluted to 1000 ml.

Procedure

Dilution water was prepared in a glass container by bubbling compressed air in distilled water for about 30 minutes.

Added 1 ml each of phosphate buffer, magnesium sulfate and calcium, calcium chloride, and ferric chloride solutions for each liter of dilution water and mix thoroughly. Neutralize the sample to a pH of around 7.0.

Prepared dilutions in a large glass bottle mix the content thoroughly. Fill 2 sets of the BOD bottle. Kept one set of the bottles in BOD incubator at 20°C for 5 days, and determine the DO content in another set immediately.

DO in the sample bottle was noted immediately after the completion of the 5days incubation period. Similarly, a blank was run for dilution water.

Calculation

$$\text{BOD (Mg/L)} = (D_0 - D_5) \text{ dilution factor}$$

Where, D_0 = initial DO in the sample and D_5 = DO after 5 days.

6. Chemical Oxygen Demand (COD)

The COD test is used to measure the oxygen equivalent of the organic material in wastewater that can be oxidized chemically using dichromate in an acid solution. It would be expected that the value of the ultimate carbonaceous BOD would be as high as the COD, this is seldom the case, some of the reasons for the observed differences are as follows:

1. Many organic substances which are difficult to oxidize biologically, such as lignin, can be oxidized chemically.

2. Inorganic substances that are oxidized by the dichromate increase the apparent organic content of the sample.

3. Certain organic substances may be toxic to the microorganisms used in the BOD test.

4. High COD value occurs because of the presence of inorganic substances with which the dichromate reacts.

Reagents

1. Standard potassium dichromate solution (0.250 N) – dissolve 12.259 gm. of K2Cr2O_7 in dissolved in 1000 ml distilled water.

2. Ferroin indicator- Dissolve 1.485 gm., 1, 10 phenolphthalein monohydrate, and 695 Mg $FeSO_4$. $7H_2O$ is dissolved in 100 ml distilled water.

3. Standard ferrous ammonium sulphate titrant (0.25 N) – dissolve 98 gm. $Fe(NH_4)$ 2 (SO_2) $2.6H_2O$ (FAS) in distilled water and add 20 ml concentration H_2SO_4, cool it, and dilute in 1000 ml 4 Mercuric sulphate

Procedure

1. Take a 20 ml sample in a conical flask.

2. 10 ml $K_2Cr_2O_7$ in each sample and add 1 pinch Mercuric sulphate then add 1 pinch silver sulphate in the sample.

3. Add 30 ml concentration H_2SO_4 in each sample.

4. And then put all samples in a COD digester for 2 Hours in 150oC.

5. After digestion of the sample, add the ferroin indicator in 1-3 drops.

6. Titrate with 0.25 N FAS

7. Then color changes from green to wine red.

Calculation

$$COD\ (Mg/L) = \frac{(A - B) \times \mathrm{N} \times 8000}{Ml\ of\ sample}$$

A = vol. of FAS used for blank concentration B = Vol. of FAS used for sample N = Normality of FAS

7. Nitrate

Reagents

1. Stock solution of KNO3: 0.1gm KNO_3 dissolved in 100 ml distilled water.

2. 5 % Salicylic acid: 5 gm salicylic acid dissolved in 100 ml conentration H_2SO_4.

3. 2N NaOH: 20 gm NaOH dissolved in 250 ml distilled water.

Procedure

Standard with KNO_3

Reference: 0.1 ml of distilled water + 0.4 ml of 5 % salicylic acid + 9.5 ml 2N NaOH.

1. Take 0.1 ml of sample in the test tube.

2. Add 0.4 ml 5 % salicylic acid and then add 9.5ml 2N NaOH.

3. Orange-yellowish color appeared after 20 minutes.

4. Take OD at 410 nm.

Calculation

Nitrate (Mg/L) = K- factor x Absorbance (O.D.)

K- Factor = Absorbance (O.D.) / Concentration

8. Phosphate

Phosphate in the extract is measured by the reaction of phosphate with ammonical molybdate in an acid medium to form molybdohpsphoric acid .the molybdophosphoric acid is then reduced to a pink colored complex and these blue-colored compounds are detected through at absorbance 640 nm using a spectrophotometer.

Reagents

1) Ammonium molybdate $(NH_4)_2MoO_4$

2) SnCl2

Procedure

1. Take 10 ml sample in a test tube.

2. Add 0.4 ml ammonium molybedate $(NH4)_2MoO_4$ in a test tube

3. Then add 2 drops $SnCl_2$

4. Take OD at 680 nm.

Calculations Phosphate (Mg/L) = K-factor x Absorbance (O.D.)

K- Factor = Absorbance (O.D.) / Concentration

9. Scanning electron microscope

Surface characteristics of the algal cell were analyzed by using SEM facility. The algal samples used for SEM analysis were fixed with osmium tetroxide (OsO4). A

10% working solution of osmium tetroxide in distilled water was used. Samples were fixed for 10-30 minutes with a final concentration of 1-2% of osmium tetroxide. Following steps were followed for sample preparation:

1. 1. A volume of 200-500 µL of culture was filtered by applying the light pressure on the plunger of the syringe to avoid damage to the sample.

2. Wash the samples about 3 times to remove the salt.

3. Dehydrate the samples by passing through a series of alcohols in increasing concentrations (25%, 50%, 75%, 95%, 100% V/V).

4. The dried material was processed for critical point drying (CPD), in which ethanol is replaced by liquid carbon dioxide under control conditions of pressure and temperature. Pressure is reduced to evaporate the carbon dioxide without causing surface tension on the algal cell. Then samples were dried under atmospheric conditions.

5. Before the SEM analysis samples were coated with a metal coating.

List of Publications

List of publications

- Majhi, P. K., Kothari, R., Pandey, A., & Tyagi, V. V. (2020). Adsorptive behavior of free and immobilized Chlorella pyrenoidosa for decolorization. *Biomass Conversion and Biorefinery*, 1-14.
- Majhi, P. K., Kothari, R., Arora, N. K., Pandey, V. C., & Tyagi, V. V. (2021). Impact of pH on Pollutional Parameters of Textile Industry Wastewater with Use of Chlorella pyrenoidosa at Lab-Scale: A Green Approach. *Bulletin of Environmental Contamination and Toxicology*, 1-6.
- Majhi, P. K., Azam, R., Kothari, R., Arora, N. K., Tyagi, V. V. (2022). Impact of Flow Rate in Integration with Solar Radiation on Color and COD Removal in Dye Contaminated Textile Industry Wastewater: Optimization Study. *Energy Engineering, 119(1)*, 419–427.
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- Pradeep K Majhi, Richa Kothari, Shubham Raina, Gagandeep Kour, V.V. Tygai (2021) Hybrid approaches for textile industry wastewater treatment: an innovative solution, *International Journal of Bioresource Technology (Elsevier).*
- Pradeep K Majhi, Richa Kothari, V.V. Tyagi (2021) Design and experimental evaluation of novel solar hybrid reactor for wastewater treatment, *International Journal of Solar Energy (Elsevier).*

Biomass Conversion and Biorefinery (2021) 11:3023–3036
https://doi.org/10.1007/s13399-020-00770-6

ORIGINAL ARTICLE

Adsorptive behavior of free and immobilized *Chlorella pyrenoidosa* for decolorization

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Received: 11 December 2019 / Revised: 20 April 2020 / Accepted: 14 May 2020 / Published online: 5 June 2020

Abstract

In the present work, the potential adsorptive behavior of algal cells (*Chlorella pyrenoidosa*) for decolorization of dye industry wastewater has been studied in the form of free algal cells (FAC) and immobilized algal cells (IAC). Effect of concentrations of real dye industry wastewater (50 and 100%), temperatures (30, 40, 50, and 60 °C) at controlled pH, and equal amount of algal cells (2 g mL^{-1}) have been studied. Adsorption isotherms (Langmuir and Freundlich) with kinetic and thermodynamic equations were applied to experimental data; 52–87% of decolorization was noticed with both algal cells and concentrations at room temperature. But, maximum (98%) decolorization was obtained at 50 °C with immobilized form of algal cell. Results were analyzed by Langmuir and Freundlich equations at different temperatures and were found to be more significant ($R^2 = 0.99$) with Langmuir isotherm for adsorption with IAC. The pseudo-second-order kinetic model was also found significant ($R^2 = 0.90$) to explain the kinetics of adsorption more efficiently. Endothermic nature reaction has been in adsorption process and thermodynamic parameters (ΔG, ΔH, and ΔS) also have been calculated. It has been concluded from the results that adsorption of the dye in wastewater that follows a pseudo-second-order kinetics provides a low-cost approach solution for treatment.

Keywords Dye industry wastewater · Immobilized algal cell · Adsorption isotherm · Kinetic and Thermodynamic functions

1 Introduction

Among the different types of contaminants, like organic- and inorganic-dissolved solids and colors, colors are the most prominent and undesirable feature of wastewater. Dyes are the chemically synthesized water-soluble colorants, which are responsible for colors in water sources and mostly utilized in textile industries. Wastewater from these industries is considered the source of serious environmental problems and is harmful for fragile ecosystems. It stops the penetration of sunlight in water bodies [1, 2]. Global estimation stringently clarifies that, more than 100,000 commercial dyes are identified with an annual production of 7×10^5 tons $year^{-1}$. The total dye consumption in the textile industry worldwide is more than 10,000 tons $year^{-1}$, and approximately 100 tons $year^{-1}$ of dye are discharged into water streams [3–5]. According to the World Bank, 17 to 20% of textile industry water pollution comes from dyeing and finishing treatments that apply to the fabric [4, 5]. It has been researched that wastewater discharged from textile dyeing industry contains a total of 72 toxic chemicals out of which 30 chemicals cannot possibly be removed by advanced waste treatment processes or conventional treatment options[1]. Characteristics of dye industry wastewater vary from industry to industry depending upon the processes used. This wastewater from the industries can be treated by a number of treatment processes such as: photo-catalytic degradation in advanced oxidation process, poly-electrolyte promoted osmosis-membrane distillation, nano-filtration, biological treatment, coagulation/

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s13399-020-00770-6) contains supplementary material, which is available to authorized users.

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flocculation, electrochemical treatment, ozonation treatment, etc. [6]. Pirkarami et al. [7] reported the removal of dye, emphasizing on the degradation mechanism as well as economic efficiency. Singh et al. [8] conducted the study with diesel exhaust emission soot as an adsorbent for the removal of dye. Rajabi et al. [9] observed the potential of magnetic nano-particles in a modified form with cetyltrimethyl ammonium bromide, being a superior adsorbent for dye removal. Hassan et al. [10] studied various advanced oxidation processes for the degradation of direct blue 86.

Among the various advanced processes of removal of dye from wastewater, ion exchange, reverse osmosis, nano-filteration, etc. are considered to be with high operating cost, but adsorption process is the best option for the decolorization of dyes and provides potential results to remove various types of dissolved coloring materials [11]. Thus, the use of biological organisms/materials for accumulation of concentrated pollutant load including color from aqueous solutions, offer a technically attractive approach. These methods have a potential for dye removal, but some serious concerns like toxicity, high-energy input, high expenditure, and generation of secondary pollutants make them unviable/unfeasible for this operation (dye removal). Bacteria [12, 13], fungi [14–16], and algae as biochar [17] are used as biological agents for the adsorption of pollutants as cited by various recent researches, either in living or dead cell forms [18, 19].

Thus, the use of algal cell can be the ideal option for dye removal, as the adsorption with algae is a low-cost technology [5, 20]. It is well known that algae are photosynthetic microorganisms, present in almost all parts of the world. Therefore, alga-based decolorization is chemically stable with high adsorption capacity, as well as inattentiveness toward toxic elements. A wide range of algal species (*Chlorella vulgaris*, *Chlorella pyrenoidosa*, *Scenedesmus* sp., *Chara* sp., *Dunaliella* sp., and *Oscillatoria* sp.) have been applied as source of adsorbent or bioaccumulators to remove dye from dye industry wastewater [21]. Foroutan et al. [22] studied the effect of cultivated algal carbon Fe_3O_4 and reported more than 98% of cationic decolorization from the aqueous solution under optimal condition. Similarly, El-Kassas and Mohamed [23] also reported the potential of *Chlorella vulgaris* as a bioaccumulator of dye industry wastewater with 75% decolorization efficiency. Behl et al. [24] one time cultivated *Chlorella* species in supplemented biochar aqueous solution and reported 80% of decolorization in 180 min of contact time.

Chlorella species is a fresh water microalga, rich in chlorophyll content, and easily available, which helps in sunlight capturing for energy conversion. Presently, it is part of active research due to its excellent efferent characteristics. It has a potential to bind most of the toxic heavy metals from wastewater and in remediation of organic pollutant load. It has favorable surface area, which makes it suitable to remove dye molecules from the textile wastewater [25]. Unfortunately, there are very few studies on real dye industry wastewater treatment using *Chlorella pyrenoidosa* as an adsorbent and particularly as an immobilized cell. Hence, the use of *Chlorella pyrenoidosa* was selected for immobilizing cell for wastewater treatment with novel approach as an adsorbent for color removal from real industrial wastewater. Immobilization is based on the principle of keeping the *Chlorella* cell metabolically active in gel matrix, with limited mobility. The cells are immobilized (trapped) alive within the polymer because its pores are smaller than the microorganisms, while the fluid flows through it and sustains their metabolism and eventual growth which enhances the contaminants, as well as nutrient removal efficiency of more than 60% [26]. Therefore, the objective of this study is to compare the efficiency of decolorization between free algal cells (FAC) and immobilized algal cells (IAC) via the process of adsorption. The experiment was conducted with respect to dye industrial wastewater concentration and temperature in a batch experiment process at controlled pH. In this study, selected IAC are also evaluated for their biosorption kinetics with adsorption isotherms (Langmuir and Freundlich isotherms with pseudo-second order) and process thermodynamics.

2 Materials and methods

Here, for the present study, we have preferred real dye industry wastewater rather than synthetic wastewater, to make the process practically applicable. To study the innovative behavior of immobilized *Chlorella pyrenoidosa* cell with real-type dye industry wastewater experimentally, it was investigated with two concentrations of test solution (50 and 100%). Entrapment method of cell immobilization in polymers is used in this study. Alginate, natural polymer derivative of algal polysaccharides, is used here instead of synthetic polymer derivatives for immobilization of cell, which is also an eco-friendly step in this investigation. Decolorization efficiency of the process for wastewater is compared between immobilized and free algal cells. This section is divided into the following subsections, i.e., Sects. 2.1, 2.2, 2.3, and 2.4. Detailed process of the experimental setup study has been given below:

2.1 Wastewater: sample collection and characterization

To carry out the experiment for the study of adsorptive behavior of *Chlorella pyrenoidosa*, the dye industry wastewater samples were collected from the local textile industry (Handloom Bhandar, Unnao, Uttar Pradesh, India (26.55° N, 80.49° E)). Plastic cans (20 L) were used to collect dye industry wastewater samples and afterwards stored in the laboratory at 4 °C (to suppress/avoid any microbial activity) for further experimental use. The initial physico-chemical characterizations were accomplished by following the standard analytical procedures prescribed by the American Public Health Association [27]. The detected dye industry wastewater parameters are as follows: color, blackish red; order, pungent smell; pH 8.2 ± 0.1; alkalinity, 893 ± 1.52 mg L^{-1}; temperature, 27 ± 0.81 °C; conductivity, 28 ± 0.51 μS; total solid, 5004 ± 2.08 mg L^{-1}; total suspended solid (TSS), 92 ± 2.08 mg L^{-1}; total dissolved solid (TDS), 4904 ± 4.5 mg L^{-1}; nitrate, 315 ± 1.5 mg L^{-1}; BOD, 587 ± 2.5 mg L^{-1}; and chloride, 816 ± 0.5 mg L^{-1}. Afterwards, to precede the batch experiment, the desired concentrations (test solution) of the dye industry wastewater were maintained by diluting with distilled water to investigate the adsorptive behavior of algal biomass. The UV-visible spectrophotometer (HALO-DB 20, Thermo Scientific) was used to detect the optical density of dye industry wastewater (485 nm, λ_{max}) after scanning the wastewater sample.

2.2 Algal species: culture and growth

The culture of *Chlorella* sp. was collected from the NCIM, Pune, India. The BG-11 medium is best suitable for the growth of *Chlorella* sp. So, the *Chlorella* sp. was grown in the freshly prepared BG-11 media for a period of 15 days. The symphonies of the BG-11 medium as prescribed by NCIM are the composition of (for 100 mL) $NaNO_3$ (150 mg), $K_2HPO_4 \cdot 3H_2O$ (4 mg), $MgSO_4 \cdot 7H_2O$ (7.5 mg), $CaCl_2 \cdot 2H_2O$ (3.6 mg), citric acid (0.6 mg), ammonium ferric citrate (0.6 mg), Na_2EDTA (0.1 mg), Na_2CO_3 (2 g), trace metals mix A_5 + Co (0.1 mL), and distilled water (99.9 mL). The trace metal mix A_5 + Co were prepared using H_3BO_3 (256 mg), $MnCl_2 \cdot 4H_2O$ (181 mg), $ZnSO_4 \cdot 7H_2O$ (22.2 mg), $Na_2MoO_4 \cdot 2H_2O$ (3.9 mg), $CuSO_4 \cdot 5H_2O$ (7.9 mg), $Co(NO_3)_2 \cdot 6H_2O$ (4.9 mg), and distilled water (100 mL). Afterwards, the cultured algal species were harvested and used for the batch experiment in immobilized as well as free algal cell [28, 29]. The culture was exposed under florescent cool light for 12:12 h day and night cycle with approximate temperature of 23–25 °C. Algal cultures were agitated homogenously by mixing nutrients equally to avoid lumping of sediments. Growth of algal biomass has been measured at 480 nm optical density.

2.3 Immobilization of algal cells: process and mechanism

The immobilization of algae is an advanced industrial procedure for pollution minimization [26, 30]. For the conversion of algae into immobilized form, equal volumes of algal cell suspension and sodium alginate (viscous in nature) are assorted and added drop by drop to calcium chloride solution (illustrated in Fig. 1). The algal strain used for the inoculation is a highly dense culture whose optical density is 3.27. Calcium ions have the potential to link together the alginate monomers to form a gel form of calcium alginate. It is not involved in the adsorption process. But, sodium salt of alginic acid $(C_6H_8O_6)_n$ is selected here due to its inherent gelatinous nature, bio-adhesiveness for algal cells, and low toxicity. The strength of alginate gel is totally dependent on the number of crosslinked forms, the length of blocks by links, and the types of bivalent ions used. Gel stabilization ability depends on the intermolecular hydrogen bonds. Here, when sodium alginate is dropped into calcium chloride solution, gel beads formed and cations are diffused to sodium alginate solution droplets, binding to the polymers. Calcium alginate here acts as an enzyme, inert, and insoluble material which provides the resistance power to bind algal cell toward pH and temperature. Thus, the live algal cells are trapped and immobilized into the small beads and collected for experimental uses [30–32]. The above said mechanism as per protocol was applied for algal immobilization procedure for the present study. The immobilization of algal cells with sodium alginate was performed using an aqueous solution of alginate in a batch process; 1.5% sodium alginate solution and 2% $CaCl_2$ solution were prepared in the laboratory. Then, the prepared sodium alginate solution was mixed with the healthy algal cell suspension in a

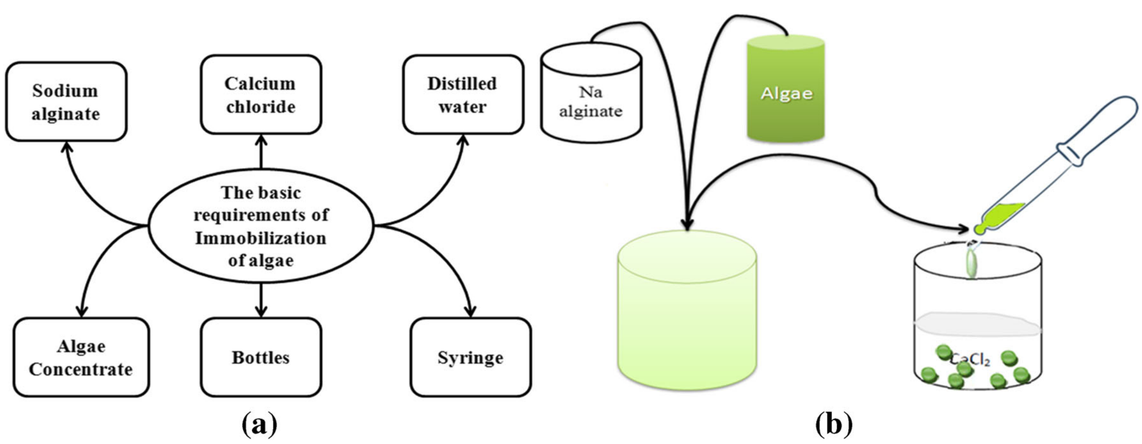

Fig. 1 Processing steps for immobilized algal cell. **a** material required; **b** steps for Lab-scale process

ratio of 1:1. A uniform mixture was prepared by gently mixing the algae and alginate (natural polymer derivative of algal polysaccharide). The algae-alginate mixture was added to 2% $CaCl_2$ solution using a syringe pump (TRUTH glass surgical size: 20 mL, luerlok tip with 30 mm needle size) to get a uniform and circular surface. When the mixture comes in contact with the $CaCl_2$ solution, the alginate solidifies into uniform circular algal beads by entrapping them. Alginate is a hydrophilic polymer, allowing wastewater to diffuse into the bead. These algal beads were rinsed and kept in distilled water before being used as an adsorbent for decolorization (as illustrated in Fig. 2) experiment.

2.4 Experimental set-up

The present experimental set-up was alienated simultaneously into two co-joint phases, such as: impact of (a) FAC and (b) IAC with wastewater. On comparative analysis, best cells were further investigated with different temperatures, discussed in detail in further sections of this study. We have selected real wastewater rather than artificial/synthetic wastewater for the present study, which was studied by a very few number of researchers with immobilization process. So, to know the exact decolorization efficiency with real wastewater conditions, only two specific concentrations were selected; otherwise, the use of other concentration of wastewater cannot produce the exact potential due to dilutions by distilled water in selected samples.

The decolorization progress was read using UV spectrophotometer (HALO-DB 20) at every 20 min intervals of the experiment by reading absorbance at maximum wavelength to know the possible dye colors in wastewater. HALO-DB 20 UV-visible spectrophotometer showed the maximum wavelength at 485 nm supports the possibility of blue color dyes in wastewater according to literature. Reading scan was taken on the day the experiment was set-up as the initial (Day 0).

2.4.1 Impact of algal cells on decolorization

The FAC and IAC were processed with a fixed amount (2 g L^{-1}) of algae, which are exposed into two different concentrations of dye industry wastewater (test solutions of 50 and 100%). The experiment was performed for 180 min in a series of batch processes after preparing the desired test solutions followed by the experimental conditions such as: dye concentration at room temperature (30–35 °C) and at maintained pH 7. To investigate the decolorization, the samples were checked with UV-visible spectrophotometer at 485 nm (HALO-DB 20). Then, the best result obtained from IAC was further considered to study the temperature impact on cell with 50% concentration of wastewater.

2.4.2 Impact of temperature with IAC on decolorization

Four different ranges of temperatures (30, 40, 50, and 60 °C) were applied to the test solution, to make the study findings globally applicable with ambient temperature ranges with best possible efficiency of decolorization in real wastewater. The temperatures of the batch experiment were balanced with the help of a thermostat (Digital Thermostat AC 220 V, 1500 W temperature controller switch, Amici Smart AC) and performed for 180 min. pH maintained for this study is 7. After conducting the experiment with the desired ranges of temperature, decolorization removal (%) was monitored with UV-visible spectrophotometer at (HALO-DB 20) 485 nm at every 20 min intervals of the experiment. After maintaining the batch experiment for the desired period of time, the percentage (%) of decolorization and specific uptake were calculated using Eqs. (1) and (2):

$$\text{Specific uptake} = \frac{c_0 - c_1}{x} \quad (1)$$

$$\text{Decolorization efficicncy } (\%) = \frac{c_0 - c_1}{c_0} \times 100 \quad (2)$$

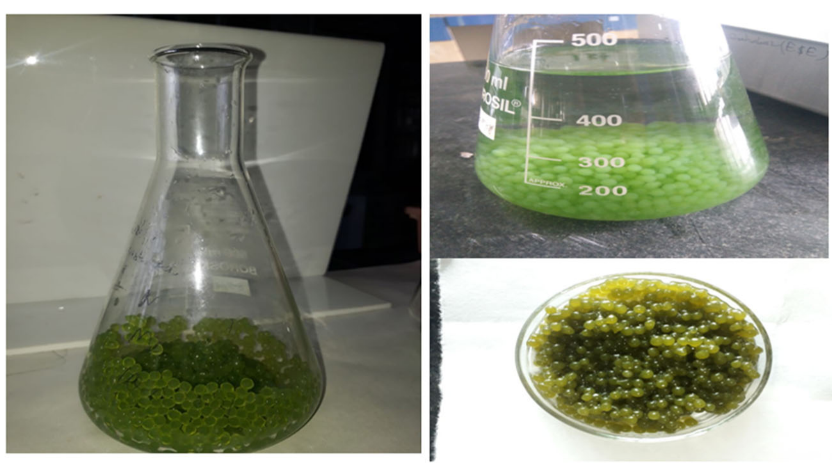

Fig. 2 Prepared fresh immobilized algal cells at lab scale

where C_0 is the initial dye concentration (mg L^{-1}); C_1 is the dye concentration after adsorption (mg L^{-1}); and x is the adsorbent doses (g L^{-1}).

2.5 Adsorption isotherm study

Adsorption mechanism was studied using adsorption isotherms (Langmuir and Freundlich) and kinetic model (pseudo-second order). Langmuir isotherm was used to study the sorption process of dye uptake with the use of an adsorbent. The uptake of dye was calculated by Eq. (3) given by [33]

$$q = \frac{(C_i - C_f)*V}{1000*m} \tag{3}$$

where q is the amount of dye uptake (mg g^{-1}), C_i and C_f represent the initial and final concentration of dye (mg L^{-1}), V is the volume of dye solution (ml), and m is the amount of adsorbent (g).

To analyze the kinetics of the sorption process, linear form of Langmuir isotherm is obtained by plotting $1/q$ versus $1/C_f$, which can be obtained from Eq. (4).

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \tag{4}$$

where q_e represents the amount of dye adsorbed at equilibrium by adsorbent (mg g^{-1}), C_e is the concentration of adsorbate at equilibrium in solution after adsorption (mg L^{-1}), and q_{max} is the Langmuir constant which represents the maximum adsorption capacity. The values of q_{max} and constant b are calculated by using the intercept and slope. The maximum monolayer sorption capacity was obtained from Eq. (4), and the essential feature of Langmuir isothermic model may be expressed in terms of equilibrium parameter or separation factor R_L dimensionless constant [34, 35].

The value of R_L indicates the adsorption nature unfavorable if $R_L > 1$, for a favorable nature of adsorption R_L, value ranges between 0 and 1 and the irreversible nature of adsorption is expressed by $R_L = 0$. The value of R_L is calculated using Eq. (5):

$$R_L = \frac{1}{1 + bC_i} \tag{5}$$

Similarly, Freundlich isothermic model also investigate to study the effectiveness of adsorbent. It is non-ideal and reversible which is not restricted to monolayer when applied to the multilayer model. The isotherm is expressed by Eq. (6):

$$q_e = K_f C_e^{1/n} \tag{6}$$

q_e and C_e are previously defined, and K_f is expressed as Freundlich adsorption coefficient (mg g^{-1}).

The linear form of Freundlich can be logarithmically expressed by Eq. (7):

$$\log q_e = \left(\frac{1}{n}\right)\log C_e + \log K_f \tag{7}$$

Thus, a plot established between q_e and C_e is a straight line, and the values of K_f and n can be calculated from the slope and intercept of the plot. If the slope ranges in between 0 and 1, the surface is more heterogeneous and process is favorable, but a value above 1 indicates that the adsorption process is uncooperative in nature and unfavorable [36, 37].

2.6 Adsorption kinetics

Besides the Langmuir and Freundlich isothermic models of study for kinetics, this study also determines the pseudo-second-order kinetic model for the adsorption of dye with algae [5, 38, 39]. This kinetic is widely used for many purposes due to its accuracy. So, the surface binding with the decolorization with respect to time can be calculated by pseudo-second-order kinetics, which has been expressed in Eq. (8):

$$\frac{d_q}{d_t} = k_2(q_e - q)^2 \tag{8}$$

where k_2 represents the second-order rate constant (g mg^{-1} min^{-1}) integrating Eq. (8) at the initial condition (t = 0 and q = 0), and after some time ($t = t$ means $q = qt$) which gives the expression of Eq. (9):

$$t/q_t = 1/K_2 q_e^{\,2} + t/q_e \tag{9}$$

where K_2 is the equilibrium rate constant (g mg^{-1} min^{-1}); q_e is the amount of dye removed at (mg g^{-1}) equilibrium; q_t is amount of dye removed at time t (mg g^{-1}). q_e and q_t are the initial variables and quantified for Eq. (10), as represented:

$$q = (C_0 - C_1) \times \frac{V}{M} \tag{10}$$

where q is the adsorbent capacity; C_0 is the initial dye concentration; C_1 is the dye concentration after adsorption; V is the total volume of the solution (L); and M is the amount of algae used (mg L^{-1}). A straight plot is derived with the help of pseudo-second-order kinetic model between t/q versus t. With the help of this straight line plot, different variables such as K_2 (rate constant), h (initial adsorption rate which was calculated by the formula: $h = K_2 \times q_e^2$), and q_e (calculated adsorption capacity) were calculated.

2.7 Thermodynamic functions

The feasibility of adsorption over different temperatures can be calculated by developing Eyring and Arrhenius equations.

2.7.1 Eyring equation

The adsorptive behavior of adsorbents has been studied by the application of thermodynamic parameters. The thermodynamic parameters, i.e., Erying-type plot was obtained by the graph plotted between $\ln K_2/T$ versus $1/T$ to calculate the thermodynamic variables. Erying equation is used for many purposes like, to express the variance of the rate of reaction in chemical reaction with temperature. The Van't Hoff equation was used to calculate the change in enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) after adsorption with different temperatures [40, 41]. Further, other thermodynamic parameters such as, standard free energy changes (ΔG), the standard enthalpy changes (ΔH), and the standard entropy change (ΔS) was obtained from various temperatures with Eqs. (11) and (12):

$$Intercept = \left[ln\ (kb/h) + \Delta S\right] \tag{11}$$

$$Slope = \left[-\Delta H/R\right] \tag{12}$$

where kb is the Boltzmann constant; h is the Plank's constant; and R is the gas constant. The slop and intercept of the straight-line equation is used to calculate the thermodynamic parameters, i.e., ΔH and ΔS. The ΔG (Eq. 12) has been calculated by the obtained values of ΔS and ΔH for different temperatures in Kelvin.

$$\Delta G = \Delta H – \mathrm{T}\Delta \mathrm{S} \tag{13}$$

where ΔG is the Gibb's free energy; ΔH is the enthalpy; and ΔS is the entropy.

The above-mentioned equation was applied to investigate the mathematical relationship between dye adsorption by the algal adsorbent with different temperatures and time. Thermodynamic parameters obtained from Van't Hoff graph.

2.7.2 Arrhenius equation

The Arrhenius equation is an exponential function which derives a relationship among temperature, rate constant, and activation energy. It provides a clarification on the dependency of the rate constant on absolute temperature during a chemical reaction. The activation energy (E_a) is a key factor for adsorption in dye removal. The E_a is that a minimum amount of energy is required to start any chemical reaction. It confirms that adsorption is a function of temperature, which can be expressed as:

$$\mathrm{Slope} = E_a/R \tag{14}$$

where E_a is the Arrhenius activation energy and R is the gas constant (8.314 J mol^{-1} K^{-1}).

2.7.3 Statistical analysis

For experimental validation, the statistical analysis of adsorption isotherms (Langmuir and Freundlich) as well as pseudo-second-order kinetics and thermodynamics study were investigated by using Microsoft Excel 2010 developed by Microsoft Corporation, USA. Mean of the triplicate of data was used for this process, and validation of model was determined by the sum of error square (SSE %) test. It determines the percent error in the proposed model, and several authors also report this to determine the error [5, 42, 43] which can be expressed by Eq. (15):

$$\sum_{i=1}^{n} (q_e - q_i)^2 \tag{15}$$

2.7.4 SEM-EDS study

To characterize the surface structure and morphology of algal cell (both FAC (before treatment) and IAC (with 50% test solution after treatment)), SEM (JEOL, JSEM-6490LV) was used as like other researchers to support the findings [44]. For sample preparation of SEM-EDS, algal cells were collected from the BG-11 media and wastewater sample (50 °C from 50% concentration) and dried to remove moisture.

3 Results and discussion

The findings of the present study were highly significant in the perspective to color removal from dye industry wastewater. But, it was observed that IAC was more effective in comparison with FAC for this process. The details of obtained findings from the study have been discussed in the following subsections.

3.1 Effect of selected adsorbents (FAC and IAC) on decolorization in wastewater

This section of the paper has been focused on the effect of *Chlorella pyrenoidosa* (both IAC and FAC form) on decolorization removal efficiency from dye industry wastewater. The significant effects of this study have been discussed in the following subsection.

3.1.1 FAC

The experimental data showed a significant decolorization efficiency from the dye industry wastewater by applying FAC as an adsorbent, i.e., 74% removal efficiency was obtained from 50% test solution and 67.6% removal efficiency was obtained from 100% test solution. The specific uptakes of

Table 1 Percentages of decolorization efficiency and specific uptake with FAC in 50 and 100% concentration of dye industry wastewater

Time (min)	Percentages of decolorization		Specific uptake	
	50% test solution	100% test solution	50% test solution	100 % test solution
60	57.2	52.2	0.81	1.50
120	73	66.7	1.03	1.92
180	74	67.6	1.04	1.94

pollutants from dye industry wastewater were calculated, i.e., 1.04 and 1.94 with 50 and 100% test solution, respectively, as described in Table 1.

3.1.2 IAC

The investigation by applying IAC as adsorbent concluded that the decolorization efficiency gradually becomes less significant by increasing the concentration of test solutions, i.e., between 50 and 100% test solutions, the 50% test solution has more possibilities for high removal rate by IAC dosages. Therefore, 87% dye was removed from 50% test solution; whereas, only 77% of dye was removed from 100% test solution. The specific uptakes of the pollutants from the dye industry wastewater were calculated, i.e., 1.23 and 2.22 in 50 and 100% test solution, respectively, as described in Table 2.

From the above comparative study between IAC and FAC as an adsorbate, it was confirmed that maximum decolorization removal was obtained at IAC (87%) in 50% test solution whereas lowest removal was obtained at FAC (67%) in 100% test solution.

The adsorption mechanism and factors which mainly creates the difference in removal efficiencies are surface area between FAC and IAC. Biosorption surface capacity of immobilized algal cell is found to be more comparative with free algal cell surface. More surface area provides more contact space between dye molecules and algal cells; in that case, the dye molecules get more opportunities to be attached with the immobilized algal cells. According to Satiroglu et al. [45], cell wall properties of algal biomass impart an important role for biosorption influenced by electrostatic attraction. IAC of *C. pyrenoidosa* supports the maximum removal efficiency, which may be due to less intervention in physical-chemical condition changes during the immobilization process. This entrapment promotes a permeability, null toxicity, and favorable environment in transparent matrix for immobilized cell. Most research findings cited with immobilized algal cells focused on heavy metal removal, but here, we support its use for decolorization purposes. Other advantages of using the immobilized algal cells are its ability for desorption and reusability of algal cells for experimental investigations.

The experiment showed that, initially, the rate of decolorization was excessively high as compared with later phase and more than 50% of color was removed rapidly within 60 min from both the test solutions (50 and 100%) using both FAC and IAC as an adsorbent. But, gradually, it becomes slower with time because it depends on the availability of dye molecules or volume of the adsorbate, adsorbent, and the potential charge difference. Therefore, once the dye molecules are attached on the surface of the adsorbent, the freedom of movement of dye molecule becomes lesser due to the entropy factor as well as the unavailability of surface area. Hameed et al. [46] and Karagoz et al. [47] also reported similar findings, i.e., the adsorption rate to be higher at the initial stage as compared with later stages. Furthermore, the use of alginate, in IAC, helps in the enhancement of sorption of dye molecules onto the surface of the polymer during the decolorization process because it is an extracellular polymer that consists of surface functional groups. This may be due to the release of metabolic intermediates with excellent coagulation capacity along with the dye that remains in the wastewater which tends to be adsorbed onto the surface of the polymers and settle (biocoagulation) [48]. Figure 3 depicts the effect of algal biomass as adsorbents in two different forms (IAC and FAC) on decolorization in wastewater.

Table 2 Percentages of decolorization efficiency and specific uptake with IAC in 50 and 100% concentration of dye industry wastewater

Time (min)	Percentages of decoulorization		Specific uptake	
	50% test solution	100% test solution	50% test solution	100% test solution
60	58.9	56.9	0.83	1.63
120	78.1	69.9	1.10	2.01
180	87.1	77.1	1.23	2.22

3.2 Effect of temperature with IAC on decolorization in wastewater

To study the effect of temperature on the decolorization efficiency, a specific experiment was conducted with four different temperature ranges (30, 40, 50, and 60 °C) and the adsorbent dosages (IAC) were maintained at a constant (2 g mL^{-1}) for 180 min in the laboratory using 50% test solution (Fig. 4). The present study confirmed that at 30 °C, the decolorization was 92% and when the temperature increased to 40 °C, it was 94%. The maximum decolorization was obtained (98%) at 50 °C and with increasing more temperature (60 °C), the decolorization efficiency declines from 98 to 97.5% (described in Table 3). This may be due to the thermal stability of algal cells which increased with alginate binding and provides an alternative monolayer for adsorption. According to available literature, most of the adsorption studies experimentally investigated with non-living biomass for dye removal and decolorization. But, here, the use of living cell entrapped with gel structure, i.e., algal-alginate bead provides a novel finding with high temperature because with free living algal cell, adsorption studies take place at maximum with 32–35 °C only, after that, the cell starts degenerating at high temperature of aqueous media. This thermal stability in between immobilized cell and dye molecules is due to electrostatic attraction, hydrogen bonding, and hydrophobic interaction.

The mechanism works behind this phenomenon is the randomness or entropy of dye molecules with IAC. The randomness of the dye molecules is directly proportional to the adsorption process. When the randomness increases, the dye molecule attachment possibility of dye molecules over the adsorbent surface increases. The adsorption isotherm with kinetic and thermodynamic functions has been applied to the experimental data to be more reliable and valid (discussed in Sect. 3.5). Al-Degs et al. [49] and Saravacos et al. [50] reported that with the increase in temperature, the rate of adsorption increases but optimized temperature with other influencing parameters always affects the rate of sorption.

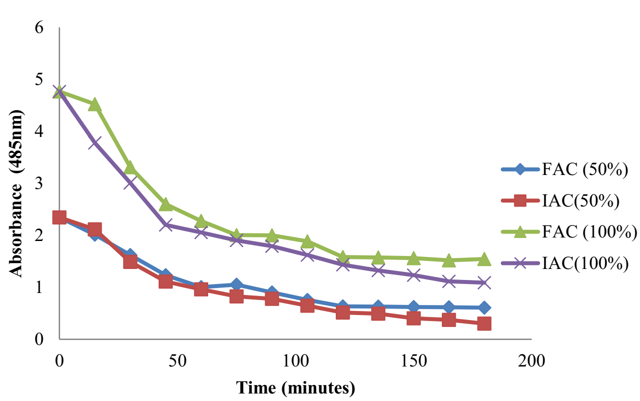

Fig. 3 Sorption with IAC (50 and 100%) and FAC (50 and 100%) at room temperature for decolorization

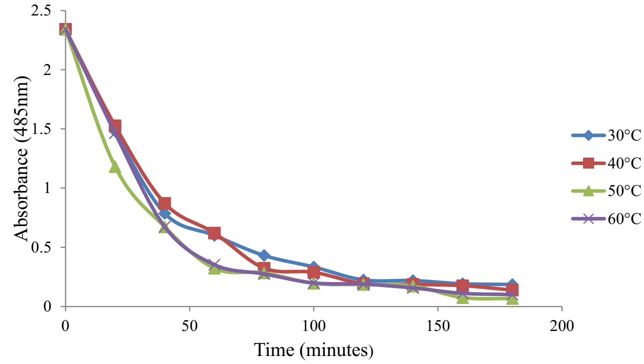

Fig. 4 Impact of IAC with 50% concentration of dye industry wastewater at different temperatures for decolorization efficiency

3.3 Effect of pH on adsorption

The pH of any industrial wastewater is the influencing factor, and its variability can directly affect the uptake of dye as well as the adsorption process. Similarly, functional groups on the algal cell wall components (i.e., functional groups carrying polysaccharides and proteins) are also responsible determining the extent of biosorption [51]. When the pH of the reaction media changes at a regular or irregular basis, the mechanism of the process also varies. It is estimated that the textile industry wastewater discharge thresholds is in between pH values of 6 and 9 [52]. In our study, the initial pH of the wastewater was measured at pH 8. But, as per researchers' citation, optimized pH values for dye removal/decolorization required is between 6 and 10 as optimum [53–55]. So, a pH value of 7 was maintained during the whole experimental procedure with IAC by using 1 M of HCL solution because the removal efficiency with strong acid or alkaline pH values noticeably drops. Mohan et al. [51] utilized the *Spirogyra* sp. for azo dye sorption at various pH values and support that very low and very high pH values directly affect the biosorption phenomena for protonation or un-protonation of functional groups present on the surface of the algal cell and increase of hydroxyl ion leading to the formation of aqua-complexes thereby retarding the sorption for decolorization, respectively. Hence, pH 7 is the best with algal species for wastewater treatment to avoid any influences due to the high/low pH values of aqueous media in the sorption process.

Table 3 Impacts of various temperature on decolorization with IAC in 50% concentration of dye industry wastewater

Temperature (°C)	Decolorization (%)
30	92
40	94.5
50	98
60	97.2

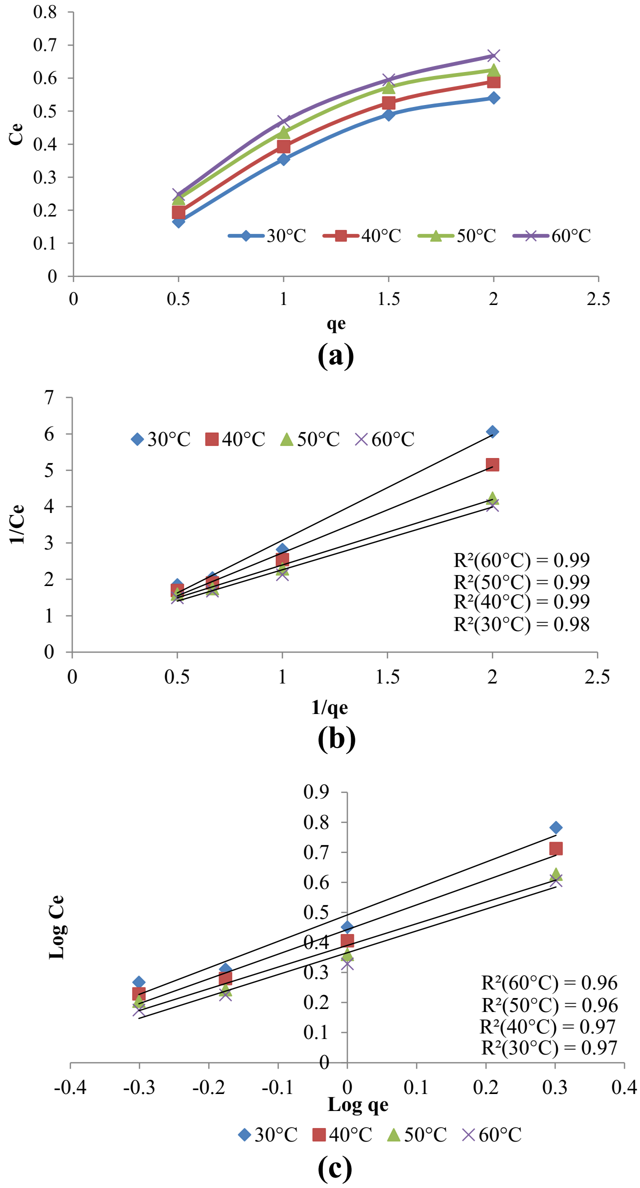

Fig. 5 Adsorption isotherm for the decolorization of dye from IAC in wastewater: **a** relation between q_e and C_e, **b** linear form of Langmuir isotherm, and **c** linear form of Frendulich isotherm

3.4 Adsorption isotherm study

In the present study, two different isotherms Langmuir and Freundlich are used to describe the mechanism of biosorption which is widely used in adsorption mechanism. Figure 5a, b shows the Langmuir isotherm, and Fig. 5c shows the Freundlich isotherm for uptake of dye on biosorbent (IAC). The maximum biosorption capacity (q_{max}) 15.66 mg g^{-1} with energy of binding (K_b) 0.71 L mg^{-1} and correlation coefficient (R^2) 0.99 is achieved for this study. The figure of Langmuir isotherm can be articulated by calculating R_L factor (separation factor) as shown in Table 4 and obtained value found in between 0 and 1, which favors the sorption by biosorbent. The Freundlich isotherm explains the adsorption coefficient (K_f) at 0.39 mg g^{-1} with an adsorption intensity of dye uptake (n) of 1.384 and correlation coefficient (R^2) at 0.97 in this study. In the Freundlich isotherm, the value of n found in between 0 and 1 describes the good indication of uptake of dye by biosorbent. Langmuir isotherm (R^2 = 0.99) described the dye uptake better than Freundlich isotherm (R^2 = 0.97) with all selected temperatures.

3.5 Kinetic model and thermodynamic function

Thermodynamic pseudo-second-order kinetic model was applied over the experimental data. Figure 6a–d illustrates the plot derived between t and t/q, which implies a significant correlation among the temperatures (R^2 > 0.98, 0.99). This plot also confirms that the rate constant increases with increase in temperature, with ranges of 0.012–0.047 (Table 5). So, it is clear that the rate of decolorization can be increased with the increase in temperature. The same observation was seen for the initial adsorption rate, i.e., "H." The initial adsorption rate increased with the increase in temperature. The highest adsorption rate was obtained (0.047 mg g^{-1} m^{-1}) at 50 °C; whereas, the lowest adsorption rate was obtained (0.012 mg g^{-1} min^{-1}) at room temperature (30 °C). To investigate the feasibility of the decolorization at various temperature ranges, the thermodynamic

Table 4 Values of constants for Langmuir and Freundlich isotherms for IAC in dye industry wastewater

Temperature (°C)	Langmuir isotherm constant				Frendulich isotherm constant		
	Maximum adsorption capacity q_{max} (mg g^{-1})	Energy of adsorption b (L mg^{-1})	Correlation coefficient (R^2)	Separation factor (R_L)	Adsorption intensity (n)	Adsorption coefficient K_f (mg g^{-1})	Correlation coefficient (R^2)
30	10.34	0.58	0.98	0.033	1.11	0.23	0.96
40	12.54	0.68	0.99	0.028	1.32	0.34	0.96
50	15.66	0.71	0.99	0.027	1.38	0.39	0.97
60	15.94	0.74	0.99	0.026	1.41	0.43	0.97

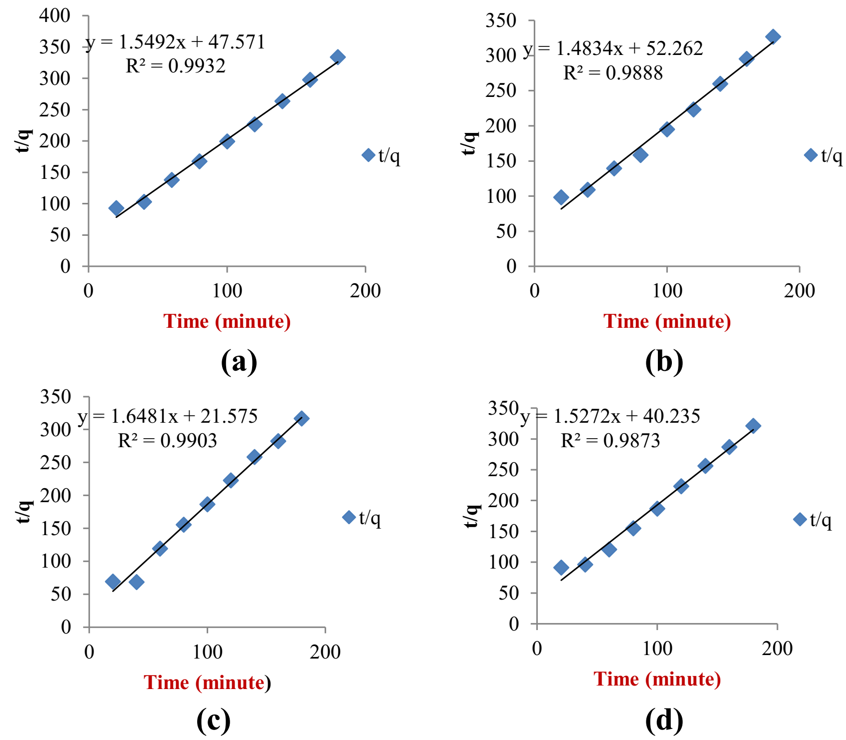

Fig. 6 Pseudo-second-order rate constant at different temperatures: (**a**) 30 °C, (**b**) 40 °C, (**c**) 50 °C, and (**d**) 60 °C

variables (illustrated in Fig. 7) were calculated with the help of Erying plot (lnK_2/t versus $1/t$) and Arrhenius plot (ln$K$ versus $1/t$). ΔH and ΔS have been calculated with the intercept and slop of Eyring plots and the ΔH value was found positive which clearly signifies that the adsorption is endothermic in nature. So, there are possibilities of physical adsorption. Mittal at el. [56] reported that with the increase of temperature, the rate of physical adsorption increases. The same positive observation was found in ΔS indicating that entropy is directly proportional with temperature and ΔG value is found to be negative, but it does not affect the rate of adsorption. Nuhoglu and Malkoc [40] said the positive value of ΔH indicates that the reaction is endothermic whereas, ΔS signifies the increase of randomness with the increase in temperature. The calculated activation energy is 29.07 kJ mol^{-1}, which was derived with the help of Arrhenius plot (ln$K$ versus $1/t$) as described in Fig. 7.The activation energy possesses an essential role in chemical reaction, as it is the minimum amount of energy required to start a chemical reaction. The study pointed 50 °C as an ideal temperature for dye removal, because the maximum efficiency was observed at this temperature with IAC.

3.6 SEM-EDS analysis

The SEM images of algal cell of free cell (before treatment) and immobilized algal cell (after treatment) are presented in Fig. 8 in favor of decolorization of dye industry wastewater. It can be noted from the figure that there are a number of cavities and pores found on the surface of *Chlorella pyrenoidosa* cell, whereas immobilized cells after treatment (50 °C in 50% concentration of wastewater) of these pores were filled with unknown molecules of colored compounds and calcium present in the wastewater. After, completion of the sorption process with temperature and binding alginate provides morphological changes that are easily seen in the cell wall matrix. These changes may be due to the cross-linking between the ionic chemical groups in the cell wall and unknown colored molecules of dye in wastewater. Nautiyal et al. [6] also confirmed similar morphological pores and cavities on the algal surface in their study. The molecules attached on the surface of algal cell were analyzed by EDS (Fig. 8). The EDS mapping analysis shows Ca, Mg, Na, Zn, S, Cl, C, S, and O are present on the surface with immobilized surface. The structural and morphological analysis reveals that IAC has a capability to remove elemental waste from dye industry wastewater in greater

Table 5 Pseudo-second-order kinetic variables for IAC with different temperatures

Temperature (°C)	K_2 (g mg^{-1} min^{-1})	q_e (mg gm^{-1})	H	R^2
30	0.047	0.666	0.012	0.99
40	0.048	0.714	0.024	0.98
50	0.121	0.625	0.047	0.99
60	0.056	0.666	0.025	0.98

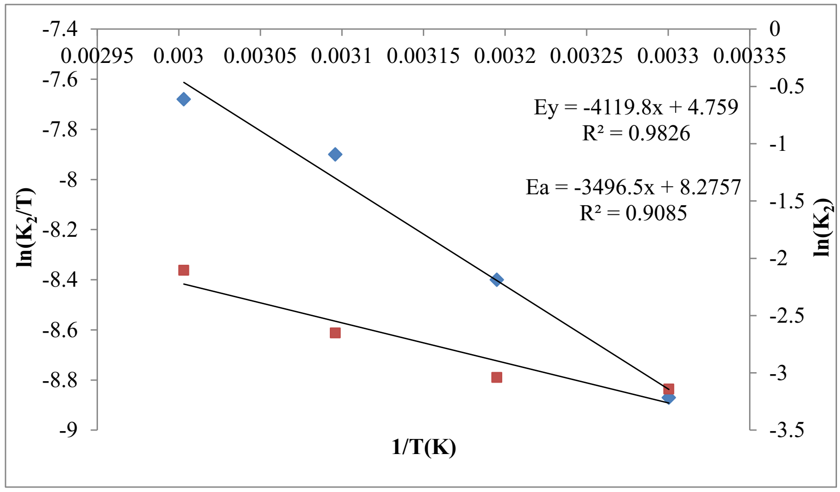

Fig. 7 Thermodynamic variable functional plot at various temperatures (°C) with Eyring (Ey) and Arrhenius plot (Ea)

Thermodynamic function	kJmol^{-1}
ΔH	34.24
ΔS	0.039
$\Delta G_{(30°C)}$	-46.23
$\Delta G_{(40°C)}$	-46.63
$\Delta G_{(50°C)}$	-47.03
$\Delta G_{(60°C)}$	-47.42
Ea	29.07

proportion than FAC. The EDS analysis of IAC shows higher elements than FAC. Therefore, it is clear from the SEM and EDS images that IAC has a significant potential for decolorization of industrial wastewater.

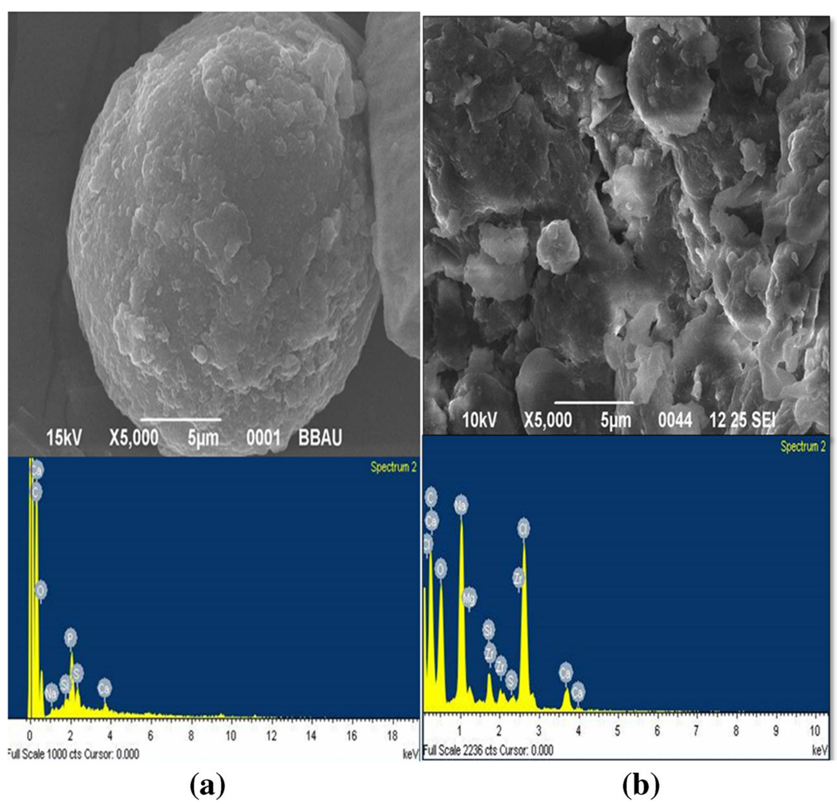

Fig. 8 SEM-EDS of the (**a**) adsorbent before adsorption (free algal cell), (**b**) after adsorption (immobilized algal cell)

4 Conclusions

The present study revealed the potential of *C. pyrenoidosa* to decolorized the real dye industry wastewater with unknown colored molecules in the form of immobilized cells as an adsorbent, and the results are compared with free algal cell's sorption capacity. Results obtained from this work showed that algal species also has thermal stability with high decolorization efficiency (98%) in immobilized form; 50 °C was determined as optimized temperature for decolozation in immobilized algal cell with 50% concentration wastewater. The results obtained are well fitted with the linear forms of Langmuir and Freundlich isotherms. Furthermore, thermodynamic parameters as well as pseudo-second-order rate kinetics indicated the spontaneous, endothermic process and significant adsorption which support the physical sorption of dye-based colored molecules on immobilized algal cell surface. Due to the high removal efficiency with dye industry wastewater, the use of immobilization process instead of free forms of algal cell can be considered a low-cost bio-treatment approach in comparison with expensive physical and chemical treatment options.

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Bulletin of Environmental Contamination and Toxicology
https://doi.org/10.1007/s00128-021-03208-5

Impact of pH on Pollutional Parameters of Textile Industry Wastewater with Use of *Chlorella pyrenoidosa* at Lab-Scale: A Green Approach

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Received: 7 December 2020 / Accepted: 22 March 2021

Abstract

The current study focused on the pollution remediation of textile industry wastewater by using *Chlorella pyrenoidosa* in two different physical forms: free algal biomass and immobilized algal biomass. The hypothesis behind the present study was to analyze the pollution reduction efficiency of immobilized algal biomass and free algal biomass on comparative scale on the basis of the adsorption process which is directly proportional with the surface area of the adsorbate. So, in this context the immobilized form of algae could enhance the pollution reduction efficiency due to availability of more surface area. So, the textile industry wastewater was treated by both free algal biomass and immobilized algal biomass and the major wastewater contributors like nitrate, phosphate, Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were assessed before and after the treatment process. To conclude the optimum comparative results, the pH of wastewater was maintained constant, as it can capitalize or moderate the adsorption process (initial pH of was 8.2 ± 0.1, but it was maintained to 8). The contamination remediation was found to be effective with immobilized algal biomass (46.7% of nitrate, 59.4% of phosphate, 83.1% BOD and 83.0% of COD) than free algal biomass (43.2% of nitrate, 56.7% of phosphate, 71.4% of BOD and 78.0% COD).

Keywords Textile industry wastewater · Immobilized algal biomass · Pollution remediation · Green technology

Introduction

Contaminations in environmental sectors are prime issues in global scale. These contaminations degrade the ecological sustainability of environment, as it is linked with each aspects of ecosystem like soil, air and water resources. Among all environmental issues, water pollution is considered as one of the most important one. The textile industrial sector is considered as one of the major culprit for pollution generation into water bodies. These textile industries produce huge amount of toxic compounds during its manufacturing processes (Paździor et al. 2018; Hynes et al. 2020; Pathak et al. 2020). Many industrial sectors release untreated/partially treated wastewater to the fresh water body which directly/indirectly harms the parameters of hydro as well as lithosphere. These toxic chemicals are nothing, but various types of carcinogenic dyes. Statistically, it is estimated that the consumption of total dyes in global sector is more than 10,000 tonnes/year and approximately 100 tonnes/year of dyes are being released into water bodies (Jegatheesan et al. 2016; Yaseen and Scholz 2018; Lellis et al. 2019). But, till date as per the literature, the exact quantitative data is lacking, because only large discharges of wastewater from dye or textile industries are counted at industrial sector part but, medium and small scale data still needs a strict observation and data compilation. But, the discharge of vital amount of dyes to the water bodies has created dispute to society to sustain a quality life. Because, these dyes are highly harmful compounds and can cause allergy, dermatitis,

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skin irritation and very sever diseases like cancer and mutation in humans. The toxic aromatic molecular structures of these compounds possess challenges for its treatments. Due to its molecular structure, the textile wastewater compounds are biologically non-degradable (Yagub et al. 2014; Lellis et al. 2019). These are mainly chemical compounds that can connect themselves to surfaces or fabrics to impart color. Recent treatments of textile dye effluents involve physical, chemical and biological methods, but the factors like dye effluent composition, treatment cost and operational feasibility determine the practical and financial applicability of these treatment methods. Various physical and chemical methods including adsorption, precipitation, coagulation, filtration, ozonolysis, advanced oxidation, membrane separation and advanced methods like ultra-filtration have been scrutinized for effluents (Bhatia et al. 2017). These methods have potential for pollution reduction, but some major issues like toxicity, maximum energy requirement, high cost demand, and release of high load toxic pollutants cause them less impactful. So, innovative and cost-effective technologies are required to achieve efficient treatments of textile dye wastewater. Therefore, uses of environmental friendly treatment system with energy saving and cost effective options are taken as a prime objective of this experimental study associated with pros and cons of existing treatment options. Hence, use of algae is an ideal option for pollution remediation from dye based textile effluents, as the process adsorption requires very less energy and at the same time it is an eco-friendly treatment technology too. The alga morphology belongs to without vascular system of vegetative structure with a diverse group of photosynthetic organisms (Nguyen et al. 2020).The alga, whenever are used in adsorption process is highly stable chemically and shows numerous potential for adsorption of highly toxic elements (Wang et al. 2016; Wollmann et al. 2019). The alga such as, *Oscillatoria* sp., *Dunaliella* sp., *Chara* sp., *Chlorella pyrenoidosa*, *Scenedesmus* sp., *Chlorella vulgaris*, have potential for pollution reduction and have been used as bioaccumulators for the treatment of textile industry wastewater (Pandey et al. 2019). Chia et al. (2014) reported a significant result with 100% dye removal of indigo blue dye by using immobilized *Scenedesmus quadricauda*. El-Kassas and Mohamed (2014) investigated the efficiency of *C. vulgaris* for dye removal and confirmed its 75% dye removal efficiency with textile industry wastewater. The authors have also examined the potential dye removal efficiency of *S. schroeteri* and obtained 63.8% (for blue dye) and 60.0% (for green dye). The algal based wastewater treatment is considered as the most promising technology in wastewater treatment sector in recent times. Many researchers have proven the feasibilities of using algal based treatment as a supplement of tertiary wastewater treatment due to its high efficiency in nutrient removal from industrial, municipal and agricultural wastewaters (Cai et al. 2013; Gikonyo 2013; Lee et al. 2015; Whitton et al. 2015; Li et al. 2019). With the assumption that, immobilized algal based treatment technology will be highly effective for the dye based textile industry wastewater, due to availability of large surface area for adsorption, is taken as major objective for this study and implemented here at lab-scale for investigation. Bouabidi et al. (2018) also reported that immobilization process is an advanced process in industrial sectors on the part of treatment options. Hence, use of *C. pyrenoidosa* proposed in this study for treatment of textile industry wastewater in the form of immobilized cell. Though, the present experimental analysis is a small scale treatment process with less sample size, but it possesses elevated possibilities for the treatment of industrial wastewater in pilot scale. The requirements, sources, mechanisms and standard implementations of this treatment process could generate major scopes in industries, sciences and advanced research fields.

Materials and Methods

The "Materials and Methods" section has been divided into three phases like: collection of wastewater samples and its parametric study; selection of algal strain and designing of experimental set-up with both free algal biomass and immobilized algal biomass. The free algal biomass is normal form of algae as such it is available in nature and the immobilization algal biomass is lab-scale change in its external surfaces to improve the pollution reduction efficiency. For the present study, the textile industry wastewater was treated by free algal biomass and immobilized algal biomass. The details of the applied methodologies have been discussed below.

To perform the experiment, the textile industry wastewater was collected from a local textile industry which is situated at Unnao (district), India (26.55°N 80.49°E). The plastic containers of 05 L capacity were used for the collection of textile industry effluents samples. The microbes are generally inactive/ less efficient in very low temperature. So, to avoid any kind microbial growth, infection or activity in the wastewater samples, which could change the pollutional parameters, the wastewater samples were stored at 4 ºC in the laboratory. Then, the standard analytical procedures were followed (prescribed by American Public Health Association 2012) to detect the initial physico-chemical characterization (described in Table 1). The chemicals used for this experiment were supplied by Merck analytical grade with $<99\%$ purity.

Chlorella pyrenoidosa was selected to conduct this experiment due to its easy availability and high potential of pollution reduction. The micro alga was collected from National Collection of Industrial Microorganism (NCIM, Collection-ID: 2738), Pune (India) and grown with BG11 media. The specific media consists of various micro as

Table 1 The initial characteristics of collected textile industry wastewater

Physico-chemical parameters	Observations	Physico-chemical parameters	Observations
Color	Dark blackish	Total solid	5004 ± 2.08 mg L^{-1}
Order	Bad smell	Total suspended solid (TSS)	100 ± 0.57 mg L^{-1}
pH	8.2 ± 0.1	Total dissolved solid (TDS)	4904 ± 4.5 mg L^{-1}
Alkalinity	893 ± 1.52	Nitrate	315 ± 1.5 mg L^{-1}
Temperature	27 ± 0.81 °C	Phosphate	3.73 ± 0.57 mg L^{-1}
Chloride	816 ± 0.5 mg L^{-1}	BOD	587 ± 2.5 mg L^{-1}
		COD	997.3 ± 1.52 mg L^{-1}

well as macro nutrients. The composition of BG11 media described by NCIM, Pune is: (for preparation of 100 mL fresh media) $NaNO_3$ (150 mg), $K_2HPO_4.3H_2O$ (4 mg), $MgSO_4.7H_2O$ (7.5 mg), $CaCl_2·2H_2O$ (3.6 mg), Citric Acid (0.6 mg), Ammonium Ferric Citrate (0.6 mg), Na_2EDTA (0.1 mg), Na_2CO_3 (2 mg), trace metals mix A_5 + Co (0.1 mL), distilled water (99.9 mL). The trace metal mix $A_5{}^+Co$ are the compositions of H_3BO_3 (256 mg), $MnCl_2·4H_2O$ (181 mg), $ZnSO_4·7H_2O$ (22.2 mg), $Na_2MoO_4·2H_2O$ (3.9 mg), $CuSO_4·5H_2O$ (7.9 mg), $Co(NO_3)_2·6H_2O$ (4.9 mg) and distilled water (100 mL). The alga was allowed to grow in glass conical flask of 1 L capacity and proper lighting facilities was maintained with an optimum temperature of 25 ± 2 °C (Kothari et al. 2017). To avoid sticking of algae with the walls of conical flask the conical flacks were manually shaked at regular intervals. Then, the alga was harvested and immobilized by standard scientific protocol. To convert free algal cell into immobilized form, equal volume of algal suspension and sodium alginate (mixture) was added drop by drop to calcium chloride solution. The calcium ions have capacity to form the jelly of calcium alginate. Thus, the algal cells are collected and used for experimental purposes (De-Bashan and Y Bashan 2010; Pathak et al. 2015; Pandey et al. 2019; Majhi et al. 2020).

The experimental sections of the present study have been categorized into three phases such as: (a) pH balance (b) pollution reduction with free algal biomass, and (c) pollution reduction with immobilized algal biomass. pH is considered as a key aspect of pollution reduction from wastewater. When the pH of any chemical composition changes, every mechanism related to it also changes. Hence, it is an essential measure of any kind of chemical reaction. In this study, the initial pH of real textile industry wastewater was 8.2 ± 0.1. It was slightly more or less than the actual estimated number. It was due to handling or technical errors in the laboratory. A slight variation in pH can affect the pollution reduction efficiency in both free and immobilized algal biomass. So, it was kept constant. To make the pH unchanged while running the experiment, it was balanced to 8 with the help of buffer solution. Then, free algal biomass was used for the treatment of textile industry wastewater. The experiment was run for 14 days and after that, the pollutional parameters such as: nitrate, phosphate, BOD and COD were assessed. The analysis of every sample was repeated thrice to avoid any kind of experimental/ handling errors and the mean values of these results were considered for this present study. As discussed in above section, the pH was kept constant. Again, the adsorption mechanism is variable with surface area of adsorbent. It plays a key role in influencing the pollution reduction as both are directly proportional to each other. When the surface area is more, the toxic textile molecular components will locate subsequent space to be attached with it. Hence, the rate of reduction will increase. For the justification of the above statements, the textile industry wastewater was treated with immobilized algal biomass as the surface area is more in immobilized algal biomass rather than free algal biomass.

Results and Discussion

The "Results and Discussion" section have been divided into two phases on the basis of pollution reduction by free and immobilized algal biomass. Initially, the free algal biomass was used for pollution reduction. It shows its efficient nature towards reduction of high loaded nutrients as well as other wastewater parameters. It was observed that nutrients like nitrate and phosphate were reduced by 43.2% and 56.7%

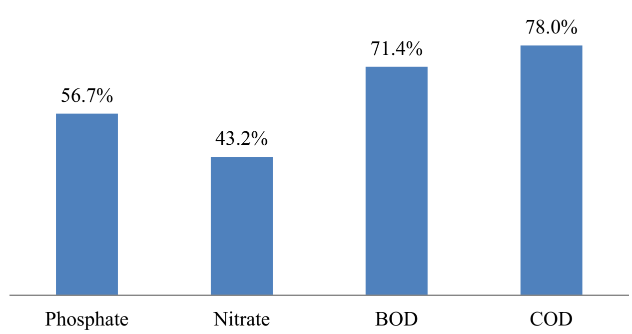

Fig. 1 Percentages of pollution reduction with free algal biomass

respectively. COD was reduced by 78% and similarly BOD was reduced by 71.4%. This reduction capacity of free algal biomass was occurred at a constant pH as described in the above section. The details have been given in Fig. 1.

Another connecting experiment was conducted after investigating the pollution reduction with free algal biomass at a balanced pH. For this experiment, the free algal biomass was converted into immobilized algae by using standard scientific protocol as described in "Materials and Methods" section. To check the comparative efficiency of pollution reduction between free algal biomass and immobilized algal biomass equal quantity of the algal biomass was used for the preparation of immobilized algae that used in free algal biomass experiment. So that, proper justification of differences between free and immobilized algae could be established. The details of the findings have been discussed below:

The result shows significant enhancement in the reduction of major textile wastewater parameters (nitrate, phosphate, COD and BOD). The algal biomass was used for pollution reduction in immobilized algal biomass form as the application of immobilized algal biomass is drastically capable to remove the undesired substances like organic pollutants, metals and nutrients etc. Kaparapu et al. (2016) studied the immobilization process of algal biomass with the help of carrageenan and alginate and reported that the algal biomass was immobilized is more efficient to remove the nutrients like nitrogen and phosphorous than free algal biomass. De-Bashan et al. (2010) mentioned that the algal immobilization technology is a highly improved biotechnological approach for the reduction of nutrients as well as pollutants. Again, this process is an advanced cost effective process where, it can be easily applied in industrial sector as well. During the present study, similar enhancement results were observed with balanced pH and immobilized algal biomass (illustrated in Fig. 2). It was observed 56.7% of phosphate was reduced with free algal biomass and 59.4% of phosphate was reduced with immobilized algal biomass. Similarly, 43.2% of nitrate, 71.4% of BOD, 78.0% COD and 46.7% nitrate, 73.3% BOD and 83.0% of COD were reduced with free algal biomass and immobilized algal biomass respectively.

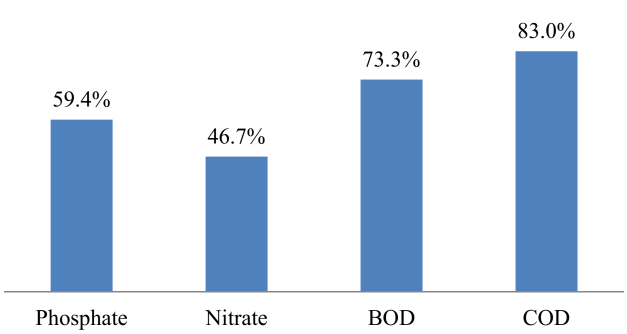

Fig. 2 Pollution reduction with immobilized algal biomass

From the above discussion it is confirmed that immobilized algae is more efficient in nutrients as well as pollutants reduction than free algal biomass. Wu et al. (2020) used immobilized *Chlorella* sp. Wu-G23 (G23) and 70.8% of COD removal efficiency from textile industry wastewater. Ei Kassas and Mohamed (2014) studied the remediation of textile effluents with the algal species (*C. vulgaris*) and reported 69% of COD removals. Lim et al. (2010) studied the pollution reduction of textile industry wastewater with the help of *C. vulgaris* and reported 44.4%–45.1% of nitrate, 33.1%–33.3% of phosphate and 38.3%–62.3% of COD reduction respectively. Brar et al. (2019) studied the potential of *C. pyrenoidosa* and *S. abundans* for the treatment of textile industry wastewater by growing in different wastewater concentrations and concluded more than 85% of COD removal. Aragaw et al. (2018) studied on the textile industry wastewater treatment by using indigenous algae and reported 91% of COD removal from this study. The mechanism behind the high rate pollution reduction of immobilized algal cells may be due to its surface area. When the free algal cells are reformed into immobilized form, it gets more surface area for reaction with reactant media. So, there is ultimate enhancement in area that came in contact with reaction media. So, pollution reduction ultimately will increase. Further, pH of any reaction media is an essential factor. It is a rate limiting factor in pollution remediation. It is due to the transfer of dye molecules across the cell membranes (Saratale et al. 2011). The optimum pH for pollution reduction as well as dye removal ranges between 6 and 10 (Chen et al. 2003; Guo et al. 2007; Kilic et al. 2007). The pollution reduction rate is high in alkaline medium and low in acidic medium, but in very alkaline medium it is also low. For the present study, the fluctuation of pH was stopped by maintaining a constant pH, so that it could be more effective for the treatment process.

Conclusions

Chlorella pyrenoidosa in the form of free and immobilized algal biomass were experimentally used towards the contamination remediation of textile industry wastewater. It was concluded that the reduction of major pollutional parameters were increased by a noticeable range with immobilized algal biomass than free algal biomass due to availability of more surface area. When the surface area increases, the number of adsorbing sites on the adsorbing surface also increases. This mechanism of adsorption influenced the pollution reduction efficiency of immobilized algal biomass than free algal biomass. The present experiment was to establish the difference of pollution reduction efficiency between free algal biomass and immobilized algal biomass. Further, this immobilization based wastewater treatment is a novel technology, where the surface area of the adsorbate increases which catalyses the rate of adsorption. It is a cost effective technology which requires very less external energy inputs also less in secondary pollutant generation. It is also highly efficient treatment option than conventional treatment technologies in terms of waste generation like sludge with chemical mixed. Thus, these findings could motivate researchers and industrialists also to incorporate and introduce with green and clean approaches in the field of wastewater treatment. Green approaches are the demand of today for sustainable water use and reuse by society.

Acknowledgement Mr. Pradeep Kumar Majhi, Senior Research Fellow (SRF) likes to acknowledge National Fellowship for Schedule Caste-University Grant Commission, Government of India for providing financial support. The authors would also like to acknowledge Laboratory of Bio-energy and wastewater treatment from Department of Environmental Sciences and University Sophisticated Instrumentation Centre (USIC) of Babasaheb Bhimrao Ambedkar University, Lucknow, India for conducting the present work.

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Energy Engineering

Tech Science Press

DOI: 10.32604/EE.2022.016973

ARTICLE

Impact of Flow Rate in Integration with Solar Radiation on Color and COD Removal in Dye Contaminated Textile Industry Wastewater: Optimization Study

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Received: 16 April 2021 Accepted: 13 August 2021

ABSTRACT

Dyes are an integral part of the dying industry and have significantly resulted in environmental pollution by altering the standard water quality after their discharge into the water bodies. The culprits behind the altered water quality are the pretreatment chemicals used during dying manufacturing processes. Various advanced treatment methods using conventional and advanced treatment options including solar energy have been put forth by researchers for the treatment of the dying effluents but, these methods have not proved significantly considerable. Therefore, the present study intends to check the efficiency of solar parabolic trough collector for treating the dying effluents in terms of color and COD. However, other wastewater parameters (BOD, nitrate and phosphate) have also been considered for this experimental analysis. Four standard flow rates (0.5, 1.3, 1.95 and 2.6 L/M) were maintained during the experiment for six hours at solar intensity (849.3 ± 21.2 W/m^2) and the optimized flow rate (1.95 L/M) was detected and considered for further study during the present experiment. The color concentration showed a significant reduction (≥76.4%) by treatment with the designed solar reactor. Similar significant results were also noticed in terms of COD (79%). In this context, the current experimental study provides ideas on the decolorization and COD reduction efficiency with optimal flow rate in terms of cost-effectiveness with designed experimental reactor which could be further used and implemented for advanced scientific purposes.

KEYWORDS

Dye industry effluents; decolorization; renewable energy-based treatment; lab-scale experiment

1 Introduction

Dyes are always critical for humans as they are a part of human lifestyle and culture and have been used in an assortment of industrial sectors for the manufacturing of various textile products. These dyes are chemical compounds that adhere to surfaces or fabrics to display color and when come in contact with surface water, pose high challenges for the survival of aquatic organisms [1]. Because of their recalcitrance, dye expulsion into the hydrosphere is a major source of contamination as it gives water bodies an undesirable shade, restricts penetration of sunlight and prevents aquatic flora and fauna from photochemical and biological activities [2]. Direct discharge of dye effluents also results in increased alkalinity, BOD, and COD [3,4]. These alterations in the water parameters result from the pre-treatment chemicals used prior to the dyeing process. According to estimates, there are over 100,000 commercial dyes in the global sector, with an annual production of over 7×10^5 tonnes. The dye industry consumes more than 10,000 tonnes of dye per year, and approximately 100 tonnes of dye are dumped into water bodies every year [5,6]. These dyes need to be removed in order to bring the standard water quality. The exact treatment of these toxic dyes has not been proved efficiently. Several conventional treatment and advanced treatment options are available for this but fail in several aspects. These methods can minimize pollution from dye-contaminated textile industry wastewater, but in realistic perception, they are lacking in several sectors, like high energy requirements and more sludge generation. So, researchers are trying to find innovative and cost-effective technologies for this purpose. So, the renewable energy-based treatment system is expected by the major research scientists to be accepted and, in this context, solar energy for treatment of dye contaminated textile industry wastewater is gaining attention due to its dual benefits of cost and energy-intensive in nature [7,8]. Solar energy is the most abundant renewable energy source, capable of degrading toxic chemical compounds and providing a cost-effective as well as renewable-based strategy with a wide range of applications scopes [9,10]. It is also easily accessible and could be used for a number of purposes [11]. The most widely investigated solar-powered water treatment technologies are solar desalination, solar photocatalysis, and solar disinfection [12,13]. Sharon et al. [14] briefly addressed the benefits and drawbacks of each technology, as well as the challenges of solar energy and desalination processes. Li et al. [15] conducted a very thorough study of solar-assisted seawater desalination. According to the literature, there are two forms of solar energy-based technologies: concentrated solar power (CSP) and photovoltaic (PV) technology and the parabolic trough, linear fresnel reflector systems, and central tower receiver are all part of CSP technology. For the present study, the most developed CSP technology (parabolic trough) has been preferred to be used due to its easy handling technique as well as efficiency in concentrating elevated solar radiation. The fundamental idea behind the technique is the concentration of solar radiation onto an absorptive receiver (pipe) that contains the wastewater flow. The parabolic reflecting surface concentrates the direct solar radiation on the receiver tube, creates heat, and enhances the wastewater treatment process. For the current analysis, the emphasis was held on flow rate optimization so that the impact of contact time and the effect of solar intensity on wastewater treatment could be assessed. As a result, a specific experiment focusing on the wastewater flow/circulation rate through the developed solar parabolic reactor was carried out. The wastewater molecules get contacted and influenced by solar radiation, and color and COD reduction are dependent on the way they are being influenced at the same time. The threshold limit of circulation rate plays a key role in this process. On the basis of the optimized flow rate, the present experiment was further connected. This is an innovative and renewable-based low-cost approach where concentrating solar energy-based treatment has been used for dye-contaminated textile industry wastewater treatment. To examine the efficiency of the solar parabolic trough for decolorization and COD reduction, the solar parabolic trough-reactor was built at lab-scale.

2 Materials and Methods

The experimental setup plan has been divided into subsections like the collection of wastewater samples and its initial characterization, designing of the solar energy-based experimental reactor, optimization of flow rate with the designed reactor, treatment of dye contaminated textile industry wastewater with optimized flow rate.

2.1 Collection of Wastewater Samples and Analysis

The dye-contaminated textile industry wastewater samples were collected from Unnao (Uttar Pradesh), India (location: 26.55°N 80.49°E), which is known as the industrial hub of India for textile industries and their products. The effluents were collected in 20-liter capacity plastic containers and subsequently, to avoid microbe infection and contamination, kept at 4°C. Then, the standard analytical procedures were followed (prescribed by American Public Health Association, 2012) to detect the initial physicochemical characterization.

2.2 Fabrication of Solar Energy-Based Reactor at Lab-Scale

The solar energy-based treatment reactor was fabricated for the color and pollution reduction of dye-contaminated textile industry wastewater. This reactor is principally based on the CPS principle where the parabolic solar collector has been designed in such a movable way so that it could manually track the solar radiation during the treatment process. Table 1 is describing the detailed specifications of the fabricated reactor.

Table 1: Specifications of solar energy-based reactor

Requirements	Measurement
Parabolic aluminum reflective surface	Thickness:1.5 mm, length: 2 meter
Transparent glass tube	Thickness: 1.5 mm, length: 1.5 meter
Wastewater tank	Capacity: 10 liter, working volume: 8 liter
Water holding capacity of glass tube	4.5 liter
Electric motor/pump	Power rating: 0.37 kw/0.5 hp, voltage range: 180 to 240 volts
Plastic connector between glass pipes	Number: 2, length: 35 cm

It consists of reflective, parabolic surface that focuses solar radiation onto the transparent glass tubes along the parabolic focal line through which the reactant fluid flows [16–18]. As a result, the collector aperture plane is always perpendicular to the solar radiation reflected by the parabola onto the reactor tube for optimum performance. The concentration factor of the solar collector is defined as the ratio between the collector's "aperture region" and "absorber area". To ensure the highest reflectivity, the trough surface was made of aluminum. The reactor tube is a closed system, so volatile compounds do not vaporize [19]. The aluminum surface was made up of 1.5 mm aluminum metal with two meters in length and the glass tubes are two meters in length with 1.5 mm thickness. Over the reflecting aluminum surface, these three connecting glass tubes have been connected in parallel forms, and connectors of hard plastic joint them so that wastewater could easily flow over the reflector. The wastewater tank is of ten liters capacity with the working volume of eight liters. Electric motor of 0.5-hertz power has been used to flow water through the designed reactor with the plastic regulator to control wastewater flow. The whole designed reactor stands over a woody stand which is designed in such a way that it can track solar radiation manually during the experiment. The detailed schematic representation with the designed reactor given in Fig. 1.

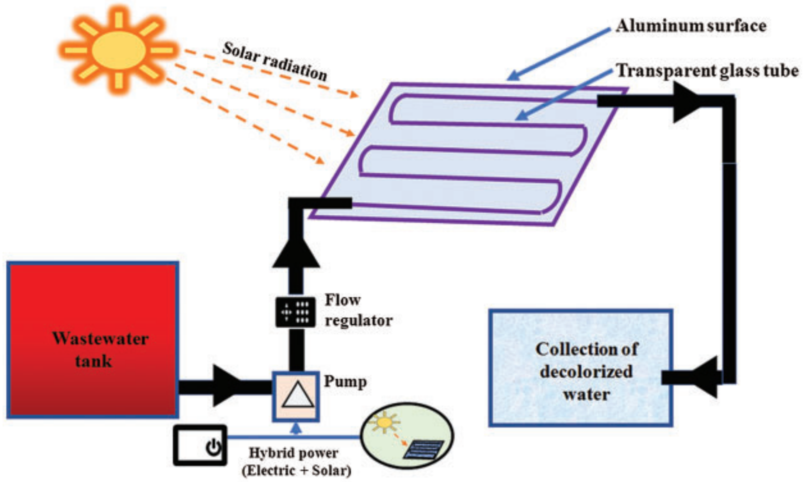

Figure 1: Sketch diagram of the designed reactor

The solar intensity was measured by solar intensity measurement device (KM-SPM-530) in W/m^2 on an hourly basis and the mean and standard deviation of each day was calculated in Microsoft Excel 2007. The color absorbance was checked each day by using UV spectrophotometer (HALO-DB 20) and after the experiment, the dye contaminated textile industry wastewater was collected and the COD reduction efficiency was assessed.

2.3 Flow Rate Optimization

The flow rate is a key influencing factor in the case of color and pollutant reduction. So, for the present study, the wastewater effluent was circulated with four different flow rates (0.5 L/M, 1.3 L/M, 1.95 L/M, and 2.6 L/M) through the designed reactor at solar radiation (849.3 ± 21.2 W/m^2). The flow rate of the designed reactor was controlled by the regulator made up of hard plastic. Before confirming any standard flow rate, the primary analysis of flow rate was conducted where the experiment was run with random flow rates to gain the basic idea about the flow rates with the designed solar reactor. After conducting the preliminary study, the above-mentioned standard flow rates were maintained and run for the standard six hours of the experiment and the optimized flow rate was considered for further study of the present experiment.

3 Results and Discussion

The results and discussion section has been divided into three sections like characterizations of collected dye contaminated textile industry wastewater, effects of flow rate with the solar reactor, decolorization by solar radiation, and COD reduction by solar radiation. The details of the findings have been described below:

3.1 Characterizations of Collected Dye Contaminated Textile Industry Wastewater

The collected wastewater samples were initially analyzed by standard scientific protocol prescribed by American Public Health Association (APHA, 2012) [20]. As per the initial characterization, the dye-contaminated textile industry wastewater was highly polluted with high COD value, very bad smell, and dark blackish color with 27 ± 0.81°C (details have been described in Table 2).

Table 2: The initial characteristics of collected dye contaminated textile industry wastewater

Physico-chemical parameters	Observations	Physico-chemical parameters	Observations (mgL^{-1})
Color	Dark blackish	Total solid	5004 ± 2.08
Temperature	27 ± 0.81°C	Total suspended solid (TSS)	92 ± 2.08
Order	Bad smell	Total dissolved solid (TDS)	4904 ± 4.5
pH	8.2 ± 0.1	Nitrate	315 ± 1.5
Alkalinity	893 ± 1.52 mgL^{-1}	Phosphate	3.73 ± 0.57
Chloride	816 ± 0.5 mgL^{-1}	BOD	587 ± 2.5
		COD	997.3 ± 1.52

The initial value of COD was very high which may be due to the high nutrient load. After getting the initial characterization the flow rate was optimized for the present study. The optimized flow rate and the findings have been discussed in the upcoming section of the article.

3.2 Effect of Solar Radiation on Color and COD Reduction

The change in flow rate provided so many differences in the color and pollutant loads. The present study was conducted with four different flow rates (0.65, 1.3, 1.95, and 2.6 L/M) on the basis of the preliminary assessment of flow rates with the solar reactor. This experimental flow rate optimization process was processed for six hours as the prime objective of the present study was to check the best rate of circulation by which it would mostly affect the color and pollution reduction efficiency. The basic objectives behind keeping this experimental limit only for six hours were to catch the high solar intensity usually found at peak during mid-afternoon.

According to literature, when the BOD and COD ratio (B/C ratio) is 0.5, wastewater is quickly biodegradable, when it is 0.4–0.6, it is average biodegradable, when it is 0.2–0.4, it is steadily biodegradable, and when it is less than 0.2, it is non-biodegradable [21]. The B/C radio of the collected wastewater sample was detected at 0.5, which is the most appropriate for wastewater degradation, so the experiment was performed with the current study using a solar-powered built reactor based on more degradability hypothesis. With varying circulation rates, substantial color and COD reduction were observed. The highest COD reduction (10%) and decolorization (13%) were obtained at 1.95 L/M, while the lowest COD reduction (7%) was obtained at 0.65 L/M. COD was reduced 8.8% and 9.2% with 1.3 and 2.6 L/M, respectively. As a result, the flow rate of 1.95 L/M was considered as the most efficient flow rate for the present experiment. The Fig. 2 is illustrating the effect of flow rates on COD reduction with specific time exposure. Although, on the basis of other used process of treatment for dye contaminated textile industry wastewater either physical, chemical, or biological the rate of decolorization and COD reduction are at large, but posses several drawbacks including use of harmful chemicals, generation of toxic byproducts, and the high-cost necessity for experimental process makes them less impactful [2,22]. So, the current experimental reactor was designed to perform up to the limit of six hours per day in the preference of sunlight to treat the dye-contaminated textile industry wastewater.

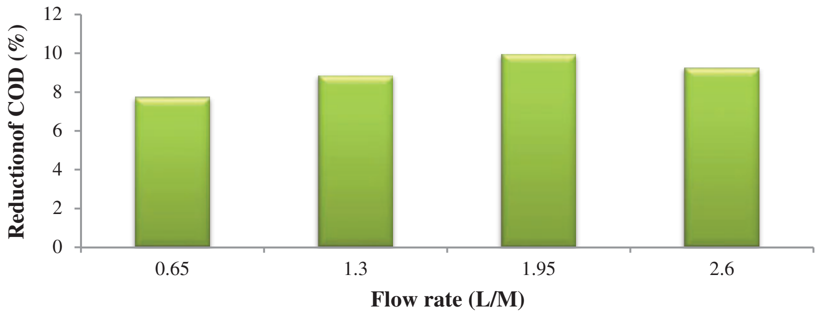

Figure 2: Effect of different flow rates on COD reduction (exposure time: six hours with solar intensity (849.3 ± 21.2 W/m^2)

The flow rate allows the wastewater molecules to move over the reflecting surface, increasing the randomness of the wastewater molecules and reducing the color concentration. However, after a certain flow rate, the contact time decreases, whether the flow rate is very high or very low. In this context, the optimum flow rate for the present designed solar reactor was 1.95 L/M and further study was conducted with this specific flow rate during the whole experiment. Color removal from dye-contaminated textile industry wastewater was seen significantly higher by this solar energy-based treatment reactor and it was observed ≥76% of color concentration was reduced from the initial concentration. The high-intensity ultraviolet solar radiation is capable of breakdown the toxic chemical bonding and, at the same time, could be highly efficient for color removal from the dye-contaminated textile industry wastewater (illustrated in Fig. 3).

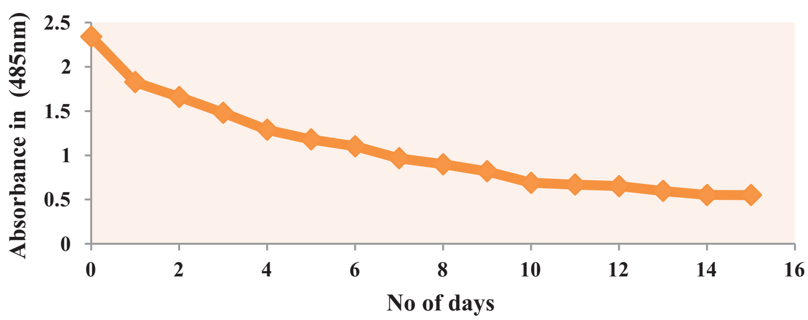

Figure 3: Effect of solar radiation on decolorization of dye contaminated textile industry wastewater with optimized flow rate (1.95 L/M)

Patil et al. [23] reported that the concentrating solar technique is one of the excellent ideas used as a superior tool for wastewater pollution minimization so that the wastewater could get high-intensity solar temperature. The high evaporation rate of wastewater causes color removal more efficiently. The high-intensity solar radiation also causes changes in the chemical oxygen demand of the effluents. The chemical oxygen demand has reduced with the working of solar treatment reactor.

The pollutant load of COD was reduced by 79% from the dye effluents, but other pollutional parameters like BOD, nitrate, and phosphate were reduced very less as compared to COD. The color concentration was reduced by 76.4% after the treatment by the solar parabolic trough reactor. Many researchers and scientists have worked on similar areas related to the present experimental work and also reported their findings, which are essential for this present study to be compared. Rodrigues et al. [24] reported COD removal of 30.1% to 70% while conducting experiment on optimization and economic analysis of dye contaminated textile industry wastewater under-stimulated and artificial solar radiation. Patil et al. [23] confirmed only 30% of COD reduction while treating wastewater by parabolic trough collector. Chavaco et al. [25] reported 55% COD reduction while evaluating the feasibility of solar pond reactors to carry out degradation of dyes. Bandala et al. [26] reported 63% of COD removal while conducting an individual Photocatalytic decolorization technology of textile dye industry wastewater. The mechanism of solar radiation-based treatment is due to the high intensity ultraviolet radiation which is gathered by the concentrated parabolic collector. The experimental performance of decolorization during low light and without solar radiation is very less impactful as getting of ultraviolet radiation is minimum which minimizes the process efficiency. The solar intensity keeps increasing the randomness of the wastewater effluent molecules, so the color concentration drastically changes from highly dark to lightly visible at the same time, the undefined COD value also decreases with the impact of solar radiation. Also, no significant increment was noticed in the BOD of the particular dye contaminated textile industry wastewater. That is due to the high-intensity solar radiation minimizes the pathogenic activities inside the dye-contaminated textile industry wastewater, so that the BOD of dye-contaminated textile industry wastewater was not so much different from the initial concentration. The same mechanism was also noticed for nutrients like nitrate and phosphate. Researchers have developed several methods for reducing color and COD in different forms of wastewater by using solar energy-based systems such as solar photovoltaic systems and solar parabolic collectors. However, the majority of them have not found to be significant with real conditions of wastewater treatment because multiple variables (temperature, pH, reflectivity, study area location, and flow) affect the efficiency of the treatment process. The contact time is an important component in any wastewater treatment process and the efficiency of decolorization will eventually increase as the polluted wastewater molecules undergo more time in interaction with electromagnetic heat. However, after a certain period the efficiency of decolorization does not improve anymore and in this case, controlling the flow rate of the developed reactor is necessary for achieving the best performance. So, for the current study, we have optimized the flow rate of the designed solar energy-based reactor to deliver the best possible results in terms of decolorization and COD reduction which is an advanced innovative procedure that researchers and industrialists could implement in terms of decolorization and COD reduction.

4 Conclusion

Dye contaminated textile industry wastewater was treated by designed solar reactor with an optimized rate of circulation and noted to have remarkable decolorization and COD reduction. The pollutional parameters (BOD, nitrate, and phosphate) were also examined before and after the treatment by designed solar energy-based treatment reactor. But, more often, it was observed that there seen more enhancement in COD reduction efficiency rather than other pollutional parameters. The pathogenic growths and activities in the wastewater effluents were reduced by the highly induced ultraviolet radiation that could be the reason for less reduction of BOD, nitrate, and phosphate. This idea of solar energy-based treatment is a renewable-based treatment approach that is more efficient in terms of cost-effectiveness, generation of secondary pollutants than other conventional treatment methods. Though there are numerous treatment technologies reported by various authors for color and COD reduction from dye-contaminated textile industry wastewater, here the authors have examined the color and COD reduction with very low-cost expenditure. The main objective of the current study was to focus on the flow rate of the designed reactor and its impact on color and COD reduction by varying it at different rates, because it provides the relationship of contact time between wastewater molecules and solar radiation that makes the current study novel and realistic valid, while also increasing treatment efficiency. So, the research seeks to estimate cost-effectiveness, secondarily reducing waste, treatment costs, and coloration/enhancement effectiveness.

Acknowledgement: The authors acknowledge the Departmental Laboratory, Department of Environmental Sciences, and University Sophisticated Instrumentation Centre (USIC) of Babasaheb Bhimrao Ambedkar University, Lucknow (U.P.), India for providing laboratory facilities to perform the experimental work.

Funding Statement: The authors would like to thank the National Fellowship for Scheduled Caste-University Grant Commission, Government of India for providing financial support.

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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Chapter 10
Industrial Wastewater Footprinting: A Need for Water Security in Indian Context

Shamshad Ahmad, Pradeep K. Majhi, Richa Kothari, and Rajeev Pratap Singh

Abstract The continued population expansion with limited resources on the planet earth deteriorated the quality of the environment. To manage the water resources at regional, national and global level, the input-output models of water footprinting (WFP) in relation to the water use and consumed are taken as an objective for this chapter. Types of WFP, assessment for industrial wastewater footprinting (IWFP), associated risks with WFP and water security for sustainable growth and economy with social impacts are critically reviewed and assessed here in this chapter. Furthermore, water polices in an Indian context are also delineated to impact its role in sustainable green water footprinting (GrWFP).

Keywords Freshwater · Water footprint · Environmental impact · Sustainability

10.1 Introduction

Freshwater resources have depleted over the last 5–6 decades from all over the world due to the snowballing of population and urbanization, which amplifies the demand of agriculture for food items with an increase in shifting of consumption patterns (De-Fraiture and Wichelns 2010). Today the scarcity of freshwater due to an exponential growth of pollution is a serious issue. In the near future, there will be

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V. Shukla, N. Kumar (eds.), *Environmental Concerns and Sustainable Development*,
https://doi.org/10.1007/978-981-13-5889-0_10

Conducting Polymer Based Nanoadsorbents for Removal of Heavy Metal Ions/Dyes from Wastewater

Gagandeep Kour, Richa Kothari, Rifat Azam, Pradeep Kumar Majhi, Sunil Dhar, Deepak Pathania, and V. V. Tyagi

Abstract Decline in the availability of potable water due to introduction of enormous contaminants including heavy metals and dyes paves way for the introduction of new and advanced water treatment technologies that ensures suitability of water for drinking purpose and at the same time eliminate pollutants or contaminants present in water. Adsorption based on nanoadsorbents is promising because of cost effectiveness and ease of operation. Therefore, this chapter intends to provide comprehensive detail about the adsorption process which is considered as the best method for heavy metal and dye removal along with the factors affecting the adsorption process. Different types of nanoadsorbents showing greater efficiencies in terms of heavy metal and dye removal are also discussed in detail. Much consideration is being given to conducting polymers. An insight about the synthesis of certain conducting polymer based nanoadsorbents is provided. The excellent properties of conducting polymers have enabled them to be used in remediation of toxic contaminants. Recommendations for future research in the area of conducting polymer based nanoadsorbents for improving the heavy metal and dye removal potentials are also put forth.

Keywords Adsorption · Conducting polymers · Nanoadsorbents · Heavy metals · Dyes · Wastewater

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Submitted by	O. P. Saini
Submitter email	gbl.bbau@gmail.com
Similarity	8%
Analysis address	gbl.bbau.bbau@analysis.urkund.com

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