ADSORPTION OF SELECTED DYES AND SURFACTANTS ONTO FUNCTIONALIZED ADSORBENTS

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Submitted By

Utkarsh Dixit

Enrolment Number: 1049/19

Under the Co-supervision of

Dr. Sudhanshu Mohan

Physical Chemistry Division
National Sugar Institute, Kanpur

Under the Supervision of

Prof. Kaman Singh

Department of Chemistry
BBAU, Lucknow

DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL & DECISION SCIENCES
BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY
(A CENTRAL UNIVERSITY) (NAAC: A++ ACCREDITED)
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The present research work has been divided into the following **seven chapters:**

Chapter 1: Introduction and objectives of the present work

This chapter introduces various classes of dyes and surfactants, their application, toxicity, and environmental implications. The textile industry contributes 7% of the total world exports and it is one of the major contributors to water pollution. The discharge of dyes in water not only affect marine species, land, and plants but humans too. The molecules of dye accumulate on the surface of the water and block the sunlight, which disturbs the process of photosynthesis causing the death of marine animals and plants. Inadequate disposal of dye-related materials can lead to land pollution which can manifest as chemical leaching into soil or groundwater contamination. Certain dyeing additives may contain nutrients that, upon release into water bodies, can contribute to eutrophication. Surfactants create health hazards by finding their way into the drinking water supply. The surfactants in which the alkyl side chain is highly branched, are resistant to biological degradation in sewage discharge and septic tanks. Surfactants can induce excessive foaming in natural water bodies, particularly in areas where they accumulate due to discharge from wastewater treatment plants. Phosphatic additives (STPP) cause water pollution by providing nutritive water for the growth of water plants which can cause oxygen deficiency that results in the death of fish. This chapter also discusses the various methods of dyes and surfactants removal from wastewater. The experimental process of adsorption and theoretical developments in the field of surface chemistry have been also discussed in detail. The theoretical development of adsorption started in 1888 when the so-called Freundlich empirical equation was first proposed by van Bemmelen. It is known in the literature as the Freundlich equation because Freundlich assigned great importance to it and popularized its use. At times, different theories such as Langmuir monolayer adsorption theory, BET surface area theory, etc. have been given for the interpretation of the mechanism of adsorption at various solid-liquid interfaces.

Chapter 2: Review of literature

This chapter discusses the recent developments in the field of the adsorptive removal of dyes and surfactants by different classes of adsorbents. The adsorption capabilities of various adsorbents range from 1 to >1000 mg/g, depending on the adsorbent's surface area, pH, temperature, surface functional group, concentrations, contact time, and other parameters. Carbonaceous adsorbents, clay and natural mineral adsorbents, nanomaterial adsorbents, biosorbents, bio composite and nanocomposite adsorbents are the five classes of adsorbents evaluated for the removal of selected dyes and surfactants. Carbon-based adsorbents, including waste-derived activated carbon and commercially available activated carbon, consistently demonstrated superior performance compared to natural clays and minerals, nanomaterial adsorbents, biosorbents, bio composite and nanocomposite adsorbents in various aspects of effectiveness and efficiency. The significant potential for dyes and surfactant removal and reuse of the adsorbent is a major advantage of adsorption over other applicable methods.

Chapter 3: Materials, methods, and characterization techniques

This chapter describes the materials and experimental methods used throughout the research work. The characterization techniques used for the analysis of adsorbents are as follows:

- UV-vis spectroscopy for concentration determination at a specific wavelength.
- Fourier Transform Infrared (FT-IR) spectroscopy for functional group analysis.
- Powder X-ray Diffraction (XRD) for phase analysis
- Scanning Electron Microscopy (SEM) for surface morphology.
- Brunauer-Emmett-Taylor (BET) surface analysis for porosity and surface area analysis.
- Zeta potential for surface charge measurement
- CHNS analysis to determine the elemental composition of carbon, hydrogen, nitrogen, and sulphur in the adsorbent.
- PZC for the type of surface charge (positive or negative) at a particular pH.

Chapter 4: Surface activity, mechanisms, kinetics, and thermodynamic study of adsorption of malachite green dye onto sulfuric acid-functionalized *Moringa oleifera* leaves from aqueous solution

This chapter describes the preparation of an economical adsorbent, denoted as the ACMOL (activated carbon prepared from H_2SO_4-functionalized *Moringa oleifera* leaves), derived from agricultural waste in the form of *Moringa oleifera* leaves. The objective is to utilize this adsorbent for the efficient removal of hazardous malachite green (MG). Extensive analyses using FTIR, SEM, BET, PZC, Zeta potential, Proximate analysis, CHNS analysis and XRD techniques substantiated the significant adsorption of MG onto the ACMOL material. Examination of the surface topography of the ACMOL exhibited a pronounced irregularity, while BET analysis and Zeta potential data confirmed its mesoporous nature and negatively charged surface. Various experiments were conducted to assess the influence of factors on adsorption capacity such as adsorbent quantity, temperature, pH, contact time, ionic strength, and urea. Notably, an increase in temperature from 303 K to 323 K resulted in a decline in MG adsorption. Under optimal conditions of pH 7.0, ACMOL dose 0.02 g and at 303 K, the maximum adsorption capacity was determined to be 126.40 mg/g. The Langmuir isotherm model emerged as the most fitting explanation for the experimental data, displaying high R^2 values in comparison to other assessed adsorption isotherm models. The pseudo-second-order model was found to provide a satisfactory explanation for the adsorption kinetics. The thermodynamic analysis affirms the spontaneous and chemical nature of the adsorption process, highlighting its exothermic character. The dominant factors governing the adsorption of MG were electrostatic attraction, hydrogen bonding, and the π-π interactions. Adsorption-desorption study confirmed that the ACMOL can be used up to six cycles with almost no loss in adsorption capacity. With these valuable insights from our study, the ACMOL can be effectively employed as an affordable adsorbent for the removal of MG from wastewater streams.

Chapter 5: Surface activity, kinetics, thermodynamics, and comparative study of adsorption of selected cationic and anionic dyes onto H_3PO_4-functionalized bagasse from aqueous stream

This chapter describes the preparation of an economical adsorbent, denoted as the TCAB (Thermochemically activated bagasse), derived from bagasse. The objective is to utilize this adsorbent for the efficient removal of selected cationic [safranin (SF), brilliant green (BG), and malachite green (MG)] and anionic [methyl red (MR), congo red (CR), and bromocresol green (BCG)] dyes. Extensive analyses using FTIR, SEM, BET, PZC, Zeta Potential, Proximate analysis, and XRD techniques substantiated the significant adsorption of these dyes onto the TCAB material. Examination of the surface topography of the TCAB exhibited a pronounced irregularity, while BET analysis and Zeta potential data confirmed its microporous nature and positively charged surface. Various experiments were conducted to assess the influence of factors on adsorption capacity such as adsorbent quantity, initial dye concentration, temperature, pH, ionic strength, and urea. The current study demonstrates that in addition to electrostatic forces, chemical bonds between the adsorbate and adsorbent play a crucial role in adsorption. This is evident from the fact that MR and BCG, both being anionic dyes, exhibit notable differences in their adsorbed quantities onto TCAB. The order of adsorption strength on TCAB for different dyes is MR (185 mg/g) > SF (178 mg/g) > CR (146 mg/g) > BG (139 mg/g) > MG (130 mg/g) > BCG (94 mg/g). Analysis of the adsorption isotherm data confirms the occurrence of multilayer adsorption between the dyes and TCAB. Kinetic data further indicates that the adsorption of all the tested dyes adheres to PSO kinetics. Thermodynamic analysis reveals the exothermic and spontaneous nature of the adsorption process for all dyes onto TCAB. The persistent adsorption of dyes on TCAB even after three cycles suggests its potential as an effective adsorbent for both cationic and anionic dyes. The study highlights TCAB's high affinity for both types of dyes, with a relatively stronger affinity for anionic dyes.

Chapter 6: Comparative study of adsorption, kinetics, and thermodynamics of selected cationic and anionic surfactants on ultrasound-assisted bagasse

This chapter describes the preparation of an economical adsorbent, denoted as the USAB (ultrasound-assisted bagasse), derived from bagasse. There is no use of chemicals in the formation of USAB, hence, it can be observed as a green adsorbent. The objective is to utilize

this adsorbent for the efficient removal of selected cationic (N-cetyl-N,N,N trimethyl ammonium bromide) [CTAB] and anionic (sodium dodecyl benzene sulfonate) [SDBS] surfactant. Extensive analyses using FTIR, SEM, BET, PZC, Zeta Potential, and Proximate analysis techniques substantiated the significant adsorption of these surfactants onto the USAB material. Examination of the surface topography of the USAB exhibited a pronounced irregularity, while BET analysis and Zeta potential data confirmed its mesoporous nature and negatively charged surface. Various experiments were conducted to assess the influence of factors on adsorption capacity such as adsorbent quantity, initial concentration of CTAB and SDBS, temperature, pH, contact time, and urea. The adsorption strength on USAB differs for anionic surfactant (SDBS) at 25.6 mg/g and cationic surfactant (CTAB) at 36.2 mg/g. The adsorption isotherm data indicates that monolayer adsorption has occurred between the surfactants and USAB. Kinetic analysis demonstrates that both SDBS and CTAB adhere to PSO kinetics during adsorption. Thermodynamic assessment reveals that the adsorption of both surfactants onto USAB is exothermic and spontaneous. As there is no significant reduction in surfactant adsorption on USAB for up to two cycles, it suggests its potential as an effective adsorbent for both cationic and anionic surfactants. However, it exhibits relatively higher affinity for the adsorption of cationic surfactants.

Chapter 7: Conclusion & future prospects

This chapter describes the conclusions and future prospects of the present research work. The efficiency of removing selected dyes by ACMOL and TCAB from an aqueous solution is notably influenced by the solution's pH, impacting both the surface charge of the adsorbent and the ionization level of the adsorbate. It was observed that in the case of cationic dyes BG and SF, equilibrium adsorption increased gradually with an increase in pH while in the case of MG, it increased from pH 4.0- 8.0 and became highest at pH 8.0, after pH 8.0, it decreases sharply to pH 10.0. In the case of anionic dyes, MR, CR and BCG equilibrium adsorption decreases gradually with an increase in pH, however, pH has no vital role in the adsorption of the SDBS and CTAB onto USAB because there is no significant change in the adsorption of surfactants with a change in pH. The binding of MG to ACMOL occurs through a combination of electrostatic interactions resulting from oppositely charged groups, hydrogen bonding, and π-

π interactions, which involve the overlapping π electron clouds of the MG and ACMOL molecules. Due to the opposing charges on the dyes and adsorbent, a significant electrostatic interaction between TCAB and negative dyes (CR, MR, and BCG) has occurred. Except for BCG, intermolecular hydrogen bonding has happened during the adsorption of both cationic and anionic dyes. In particular, π-π interactions have only happened between SF and MR dyes and the π electron systems of TCAB. Notably, electrostatic forces have been the only driving force behind the interaction in the case of BCG adsorption. The binding of CTAB to USAB occurs through a combination of electrostatic interactions along with hydrogen bonding. The desorption study concludes that ACMOL, TCAB and USAB can be used up to six cycles, three and two cycles with an almost negligible decrease in adsorption capacity.

The usage of low-cost adsorbents has introduced a new area of research for wastewater treatment, and it also brings more opportunities to produce a better way of management. The future perspectives of low-cost adsorbents can be determined to explore the possibilities, functionalization/modifications/pre-treatment of agriculture-waste-based materials to improve their adsorption potential.