Synthesis, Characterization and Application of new Adsorbents for Removal of Specific Heavy metals from their Aqueous Solutions

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Water is one of the most significant chemicals of our surrounding and essential for human survival. Safe and readily available water is important for human life; it is used for drinking, household activities, domestic use, agricultural, industrial, food production or recreational purposes.

Commercial activated carbon is the most commonly used adsorbent because of its great capacity for adsorbing diverse compounds such as heavy metals, dyes, pesticides, pharmaceuticals and surfactants. However, taking into account the high cost involves in the preparation and regeneration in carbon adsorption, research has diverted towards non-renewable based potential alternate adsorbents (agricultural as well as industrial by products) [E. Padilla-Ortega *et al.* 2014; T. Calvete *et al.* 2010; K. Singh *et al.* 2011; 2012; F.A. Caliman, 2009; K.L. Wasewar, 2009].

Agricultural waste is one of the rich sources of low-cost adsorbent besides industrial by-product and natural material because- availability and low cost, low inorganic matter content, ease of activation, low degradation upon storing, expected role of surface functionalities for desired application

Agricultural carbonaceous material such as wood, nutshells, fruit stones, peat, char- coal, soft coal, lignite, bituminous coal and petroleum coke etc. (high carbon content materials) may be used as a precursor for the preparation of activated carbons [A. Dabrowski *et al.* 2005].

Adsorption is customary process for water decontamination applications [F. Fu and Q. Wang, 2011]. It is better than any other water treatment methods because of its simplicity of design, ease of operation, economically, flexibility and efficiency for toxic pollutants. Harmful, toxic and unwanted chemical reagents also do not generate during water decontamination. Adsorbent are easily recycled by suitable recovery agent and required a very little space for water treatment.

Among a range of heavy metal ions as arsenic (V), lead (II), cadmium (II) and mercury (II) have gained considerable attention of researchers due to their adverse effects on the environment, their solubility over a wide range of pH, human health and their presence in several industrial wastewaters. These ions with higher concentrations in certain areas are very dangerous for human as well as the environment.

A detailed study of the synthesis, characterization and application of new adsorbents for removal of specific heavy metals from their aqueous solutions have been carried out and presented in the thesis. The organization of the thesis is given below:

Chapter 1: Introduction and review of literature

Chapter 2: Experimental methods and characterization techniques

Chapter 3: Adsorptive removal of As(V), Pb(II), Cd(II) and Hg(II) metal ions by activated carbon derived from *Terminalia arjuna* fruits (ACTA)

Chapter 4: Development of inexpensive adsorbent from mustard cake for effective removal of As(V), Pb(II), Cd(II) and Hg(II) ions from their aqueous solutions

Chapter 5: Synthesis of biosorbent (TBC) from *Trapa Bispinosa* peels and its use for effective removal of As(V), Pb(II), Cd(II) And Hg(II) metal ions from their aqueous solutions

Chapter 6: Removal of As(V), Pb(II), Cd(II) And Hg(II) ions from their aqueous solutions using Balam khira (*Kigelia africana*) as an eco-friendly biosorbent

Chapter 7: Conclusion

The study will broadly follow the scheme as given above. The summary of research work carried out is as follows:

Chapter 1

Heavy metal contamination is the greatest concern among all kinds of environmental pollution because they are highly toxic and transportable. The presence of toxic metals in ground water sources is an important topic of wastewater treatment because their consequences on human health have been well established [J.G. Huang and J.C. Liu, 1997]. Various industries such as electroplating, metal-processing, paint, plastics alloy, batteries, ammunition and the ceramic glass industries, etc generate large quantities of contaminated water containing various types of heavy metals. Studied heavy metal ions that are found in contaminated water, their sources and potential health effects to human are listed in Table 1. Water-related contamination is a global problem from last few decades. It is reported that approximately 1,600 peoples die per day in India (most of them children) due to diseases caused by water contamination [NCERT, 2014]. It is the caused by addition of an organic, inorganic, biological and radioactive substance to pure water which alters its physiochemical properties.

Table 1: Specific metal ions, their sources and potential health effects to human

Metal Ions	Sources	Human Health Effects	References
As(V)	Leaching, Weathering process, Volcanic eruption	Dermal pigments, Skin and lung cancer, Vascular diseases	[I. Bodek *et al.* 1988; T. Dey, 2012]
Pb(II)	Battery industry, Paints etc.	Affects nervous and renal system, Headache, Constipation, Cancer	[WHO, 2000; L.A. Smith *et al.* 1995]
Cd(II)	Coal combustion, Metal plating, Water pipe, Phosphate fertilizers etc	Cardiovascular disease, Cancer kidney damage	[L.A. Smith *et al.* 1995; Y. Chervona *et al.* 2012]
Hg(II)	Coal combustion, Electrical batteries, Chlor-alkali industry	Nerves damage, Death, Kidney and brain damage.	[EPA, 1998; L.A. Smith *et al.* 1995]

According to certified public health organizations, maximum permissible limits of these aforesaid metal ions have specified [C.N. Sanyer *et al.* 2003; I. Hespanhol and A.M.E. Prost, 1994; ISI.IS:10500; ISI, 1983; BIS, 1994] in drinking water, which are listed below in Table 2.

There are several reported technologies for waste water treatment, broadly classified into: chemical (oxidation, thermal oxidation, chlorination, and ozonation, solvent extraction, irradiation, coagulation), biological (accumulation, microbial degradation) and physical (adsorption, bio adsorption, activated carbon) technologies. The term adsorption implies the presence of excess concentration of any particular component at the surface of liquid or solid phase as compared to that present in the bulk of the material [K.L. Kapoor, 2004].

Table 2: Maximum permissible limits (MPI) of studied metal ions in drinking water

Studied Metal ions	World Health Organization (WHO) std. mg/l	Environmental Protection Agency (EPA) mg/l	Bureau of Indian Standards (BIS) mg/l
As(V)	0.010	0.010	0.050
Pd(II)	0.010	0.050	0.100
Cd(II)	0.003	0.005	0.005
Hg(II)	0.001	0.002	0.002

Commercial activated carbon is the most commonly used adsorbent because of its great capacity for adsorbing diverse compounds such as heavy metals, dyes, pesticides, pharmaceuticals and surfactants. However, taking into account the high cost involves in the preparation and regeneration in carbon adsorption, research has diverted towards non-renewable based potential alternate adsorbents such as agricultural as well as industrial by products.

Chapter 2

Following instrumental techniques have been carried out for the characterization of low cost biosorbents (LCBs) synthesized during my research period are discussed in details in this section-

a) *Scanning Electron Microscopy*: SEM examination yields information about surface features of the biosorbents, shape and size of the constituents making up the LCBs,

b) *Energy Dispersive X-ray spectroscopy*: EDX is used to elemental analysis of synthesized LCBs.

c) *Fourier Transform Infrared (FT-IR) Spectroscopy*: This characterization is used to identify the types of chemical bonds in molecules of synthesized LCBs.

d) *Zeta potential analyzer*: for measuring the surface charge on LCBs at different pH environment.

e) *N_2 Adsorption-Desorption Analysis*: To investigate the surface area and pore size distribution of solid particles of LCBs.

f) *Powder X-ray Diffraction (pXRD)***:** LCBs have been characterized by pXRD for its structural properties.

Adsorption Methodology

Adsorption equilibrium was probed by batch experimental technique. The amount of studied metal ions adsorbed by the LCBs at equilibrium was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{m}$$

Where, C_o and C_e are initial and equilibrium concentrations (mg/l) of studied metal ions in the solution, V the volume (in ml), m the weight (*g*) of the LCBs and q_e is the amount of metal ions adsorbed by the adsorbent at equilibrium (mg/g).

Desorption Methodology

The recovery (% desorption) of studied metal ions from biosorbents were carried out by batch desorption experiments. The amount of studied metal ions desorbed from the LCBs at equilibrium was calculated as follows:

$$\% D = \frac{C_d}{C_o - C_e} \times 100$$

C_d is the concentration of studied metal ions desorbed from biosorbents; C_o and C_e are initial and equilibrium concentrations (mg/l) of metal ions in the solution.

Chapter 3

Effective removal of As(V), Pb(II), Cd(II) and Hg(II) metal ions: major pollutants present in various types of contaminated wastewater was studied onto biosorbent derived from *Terminalia arjuna* fruits. The pore size distribution of the ACTA falls on mesoporous domains with high surface area ($\boldsymbol{S_{BET}}$ **=1226 $\mathbf{m^2g^{-1}}$**). The Langmuir, Freundlich and Temkin models were applied to evaluate the adsorption parameters. The amount of adsorption decreased in the order of As(V)>Pb(II)>Hg(II)>Cd(II). Adsorption kinetics was examined using Lagergren first order and pseudo second order kinetics model. The best results were achieved with the Langmuir isotherm equilibrium model and followed pseudo second order kinetics (R^2=0.99). The possible adsorption interactions were discussed. Adsorption mechanism is verified by fourier transform infrared (FT-IR), powder X-ray diffraction (pXRD), zeta potential (mV), energy dispersive X-ray **(**EDX) techniques. The adsorption mechanism is governed by complex interplay of inter ionic forces, complex formation ability of the metal ions present in aqueous solution at a particular pH value. The highest recovery of metal ions onto adsorbed ACTA were found as 89.73%, 91.24%, 87.31% and 72.19% for As(V), Pb(II), Cd(II) and Hg(II), respectively in 0.05M concentration of HCl solution using 0.2 g ACTA loaded onto 10 mg/l of each metal ions.

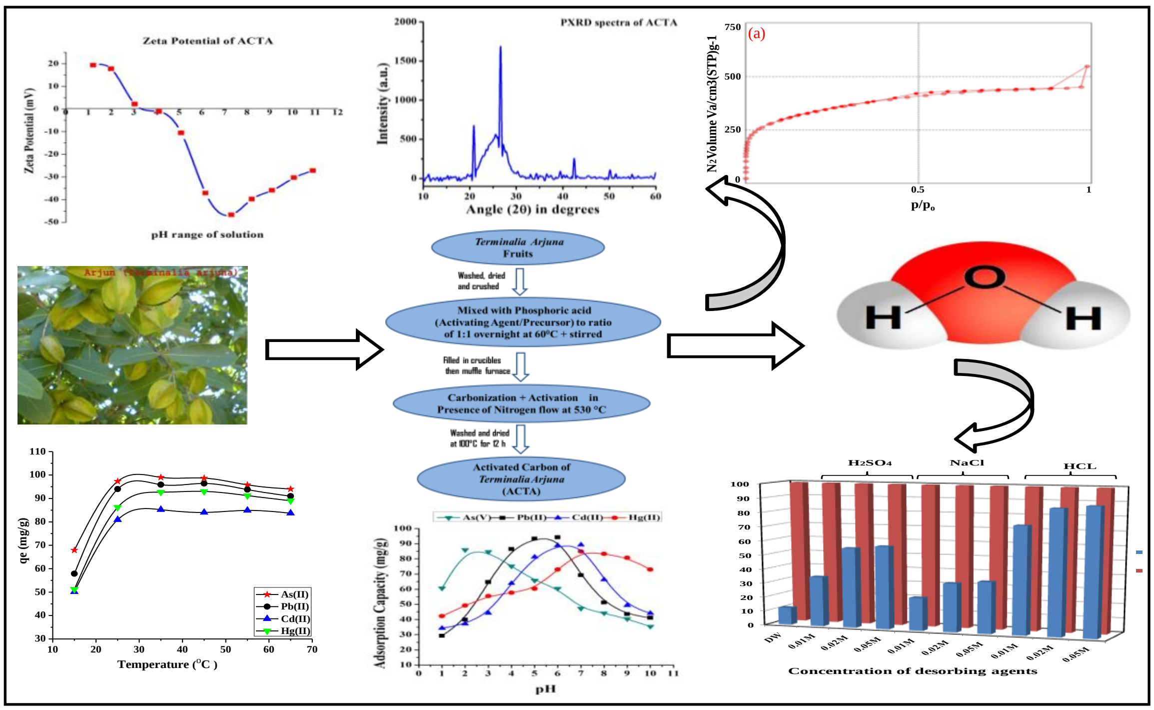

Fig.1: Graphical abstract of synthesis of ACTA and its application for removal of As(V), Pb(II), Cd(II) and Hg(II) metal ions from their aqueous solutions

Chapter 4

This study aimed to develop an inexpensive adsorbent from de-oiled mustard cake for the effective removal of As(V), Pb(II), Cd(II) and Hg(II) metal ions from their aqueous solutions. The chemical composition of the powdered activated mustered cake was Si (28.53%), Ca (31.23%), Mg (8.71%), K (6.41%), P (6.44%) and Al (0.62%). The scanning electron microscopy (SEM), powder X-ray diffraction (pXRD), fourier transform infrared (FTIR) and N_2 adsorption/ desorption (BET) techniques were used to characterize the derived biosorbent. The adsorption processes of all titled metal ions follow pseudo-second order kinetics. The best isotherm fits follow the sequence: Langmuir > Temkin > Freundlich. The impact of temperature, pH and adsorbent dose onto the adsorption were also studied. The adsorption characteristics of the Si-PAMC was primarily attributed to the presence of mesoporous silica or mixed oxides of elements present in it and not by the carbon as has been previously reported. The adsorption mechanism is governed by complex interplay of inter ionic forces, complex formation ability of the metal ions present in aqueous solution at a particular pH value. The desorption study revealed that the peak desorption was found to be 53.73% for As(V),62.42% for Pb(II), 69.11 for Cd(II) and 50.99 for Hg(II) in 0.1M concentration of HCl solutions, respectively.

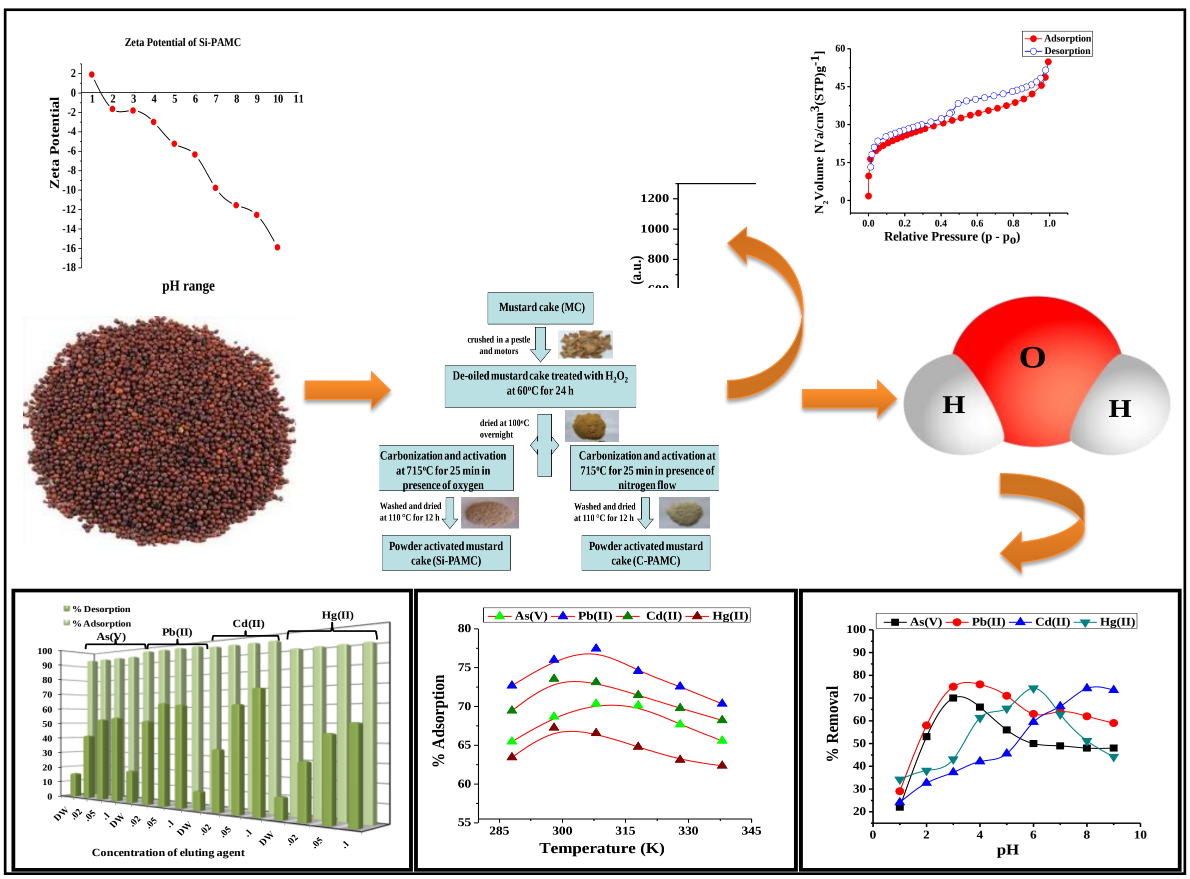

Fig.2: Graphical abstract of synthesis of Si-PAMC and its application for removal of As(V), Pb(II), Cd(II) and Hg(II) metal ions from their aqueous solutions

Chapter 5

The peels of an aquatic plant *Trapa bispinosa* was used as precursor to derive a low cost biosorbent and was characterized for the effective removal of As(V), Pb(II), Cd(II) and Hg(II) metal ions from their aqueous solutions. The BET and BJH plots were used to evaluate the surface area, pore diameter and pore distribution of *Trapa bispinosa* activated carbon (TBC). The fourier transform infrared (FT-IR) and scanning electron microscopy (SEM) analysis were used to characterize the surface functionality and surface texture of the TBC. It had micro porous and meso porous pore size distribution with high surface area (**S_{BET} =642.53 m^2g^{-1}**) and high carbon content (84.20%). The carboxylate, hydroxyl, keto, oxo and lactones functional group was established on the surface of derived adsorbent. The Langmuir, Freundlich and Tempkin models were applied to evaluate the adsorption parameters. Adsorption kinetics was examined using Lagergeren first order and pseudo second order kinetics models. The best results were achieved with the Langmuir isotherm equilibrium model and followed pseudo second order kinetics (R^2=0.99). The adsorption mechanism is governed by complex interplay of inter ionic forces, complex formation ability of the metal ions present in aqueous solution at a particular pH value. Different eluting agents (HCl, H_2SO_4 and NaCl) were used to recover the metal ions by batch experiments. The highest recovery achieved was 67.21%, 75.90%, 80.52%, 70.27% for As(V), Pb(II), Cd(II) and Hg(II) ions, respectively from 0.05M of HCl concentration.

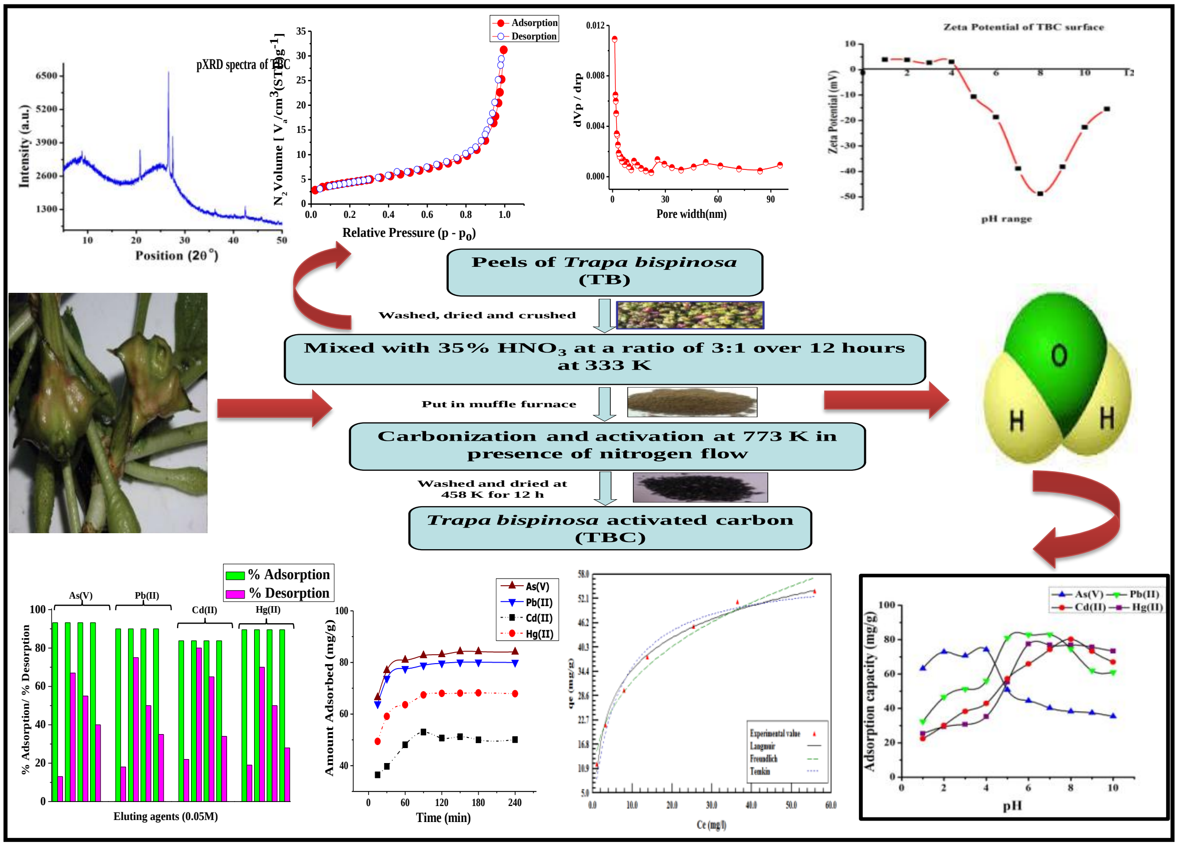

Fig.3: Graphical abstract of synthesis of TBC and its application for removal of As(V), Pb(II), Cd(II) and Hg(II) metal ions from their aqueous solutions

Chapter 6

A low cost activated carbon derived from the fruits of *Kigelia africana* (KA) was characterized for effective removal of titled metal ions from their aqueous solutions. The pore size of derived carbon from *Kigelia africana* (CKA) falls on micro porous and meso porous domain with high surface area (**S_{BET} = 799.91 m^2g^{-1}**) and high carbon content (79.42 %). The batch experiments are carried out to investigate the effect of various process parameters such as solution concentration, pH, temperature, contact time, adsorbent dose on adsorption. The maximum adsorption was found at pH 2.0 for As(V), 5.0 for Pb(II), 6.0 for Cd(II) and 4.0 for Hg(II) ions. Various isotherm models were modeled to evaluate the equilibrium adsorption data. The adsorption isotherm data was best fitted by Langmuir model with adsorption capacity 77.51, 71.42, 84.74 and 87.71 mg/g for aforesaid metal ions, respectively at 35 ºC. Thermodynamic study demonstrates spontaneous and endothermic nature of the adsorption. Kinetic studies were examined using different kinetic models and pseudo second order kinetics was found well fitted for adsorption process. Recoveries of studied metal ions from CKA surface has been analyzed using different concentrations of eluting agent and found best desorption at 0.1M HCl concentration for studied metal ions.

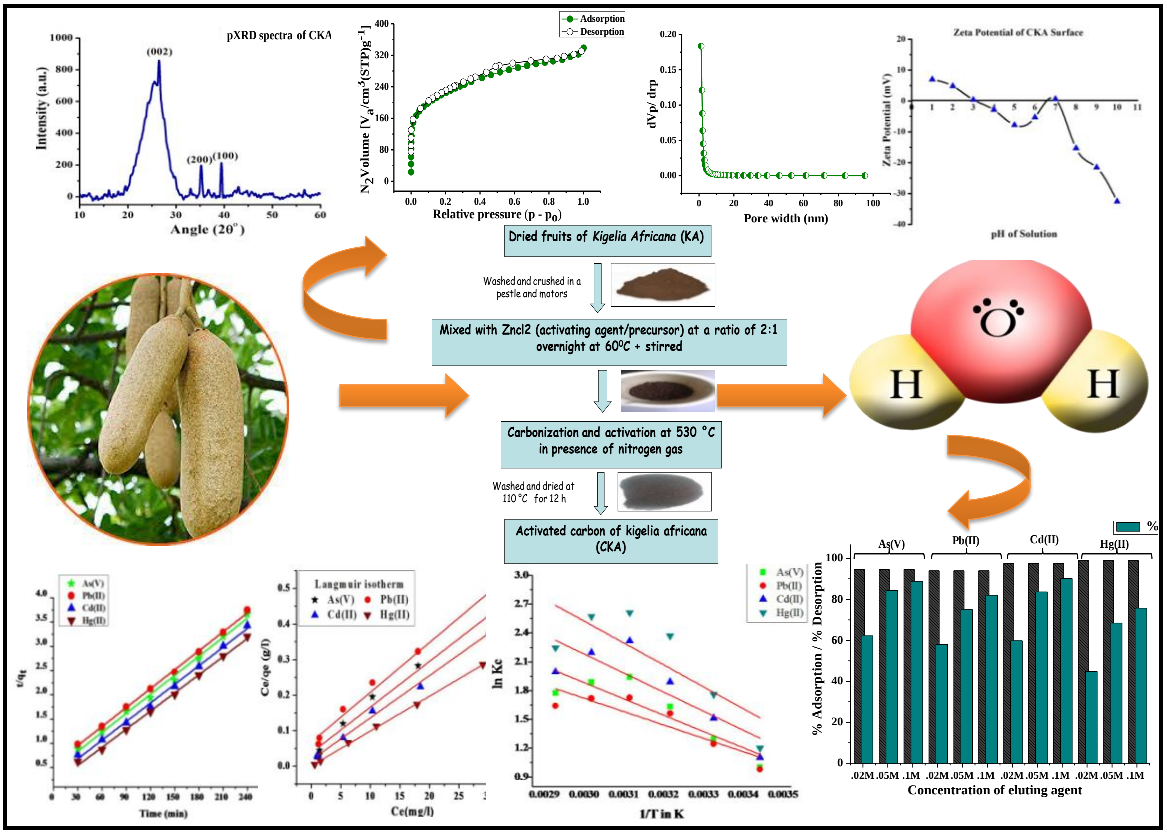

Fig.4: Graphical abstract of synthesis of CKA and its application for removal of studied metal ions from wastewater

Chapter 7

This chapter deals the comparisons of adsorptive removal of As(V), Pb(II), Cd(II) and Hg(II) metal ions from aqueous solution onto different synthesized adsorbents such as Activated carbon of *Terminalia arjuna (ACTA)* , *Kigelia africana* activated carbon (CKA), *Trapa bispinosa* activated carbon (TBC) and Powdered activated mustard cake (Si-PAMC).

Table 7.3: Comparative assessment of adsorption properties of derived adsorbents for As(V) ion removal from its aqueous solution

Parameters	**ACTA**	**Si-PAMC**	**TBC**	**CKA**
Isotherm model	Langmuir	Langmuir	Langmuir	Langmuir
Adsorption capacity (q_m)	221.11	109.05	64.74	77.51
Kinetic model	Pseudo second	Pseudo Second	Pseudo second	Pseudo second
Δ G^o	Spontaneous (-ve)	Spontaneous (-ve)	Spontaneous (-ve)	Spontaneous (-ve)
Δ H^o	Endothermic (+ve)	Exothermic (−ve)	Endothermic (+ve)	Endothermic (+ve)
Δ S^o	(+ve)	(+ve)	(+ve)	(+ve)
pH	2.0-3.0	3.0	4.0	2.0
% Recovery of As(V)	89.73	53.73	67.21	88.60

Table 7.4: Comparative assessment of adsorption properties of derived adsorbents for Pb(II) ion removal from its aqueous solution

Parameters	**ACTA**	**Si-PAMC**	**TBC**	**CKA**
Isotherm model	Langmuir	Langmuir	Langmuir	Langmuir
Adsorption capacity (q_m)	212.99	114.94	58.85	71.42
Kinetic model	Pseudo second	Pseudo second	Pseudo Second	Pseudo second
Δ G^o	Spontaneous (-ve)	Spontaneous (-ve)	Spontaneous (-ve)	Spontaneous (-ve)
Δ H^o	Endothermic (+ve)	Exothermic (−)	Endothermic (+ve)	Endothermic (+ve)
Δ S^o	(+ve)	(+ve)	(+ve)	(+ve)
pH	6.0	4.0	6.0	5.0
% Recovery of Pb(II)	91.24	62.24	75.90	82.10

Table 7.5: Comparative assessment of adsorption properties of derived adsorbents for Cd(II) ion removal from its aqueous solution

Parameters	**ACTA**	**Si-PAMC**	**TBC**	**CKA**
Isotherm model	Langmuir	Langmuir	Langmuir	Langmuir
Adsorption capacity (q_m)	196.15	95.5	48.20	84.74
Kinetic model	Pseudo second	Pseudo second	Pseudo Second	Pseudo second
Δ G°	Spontaneous (-ve)	Spontaneous (-ve)	Spontaneous (-ve)	Spontaneous (-ve)
Δ H°	Endothermic (+ve)	Exothermic (−ve)	Endothermic (+ve)	Endothermic (+ve)
Δ S°	(+ve)	(+ve)	(+ve)	(+ve)
pH	7.0	6.0	8.0	6.0
% Recovery of Cd(II)	87.31	69.11	80.52	90.16

Table 7.6: Comparative assessment of adsorption properties of derived adsorbents for Hg(II)

Parameters	**ACTA**	**Si-PAMC**	**TBC**	**CKA**
Isotherm model	Langmuir	Langmuir	Langmuir	Langmuir
Adsorption capacity (q_m)	208.24	90.6	52.03	87.71
Kinetic model	Pseudo second	Pseudo second	Pseudo Second	Pseudo second
Δ G°	Spontaneous (-ve)	Spontaneous (-ve)	Spontaneous (-ve)	Spontaneous (-ve)
Δ H°	Endothermic (+ve)	Exothermic (-ve)	Endothermic (+ve)	Endothermic (+ve)
Δ S°	(+ve)	(+ve)	(+ve)	(+ve)
pH	7.0	8.0	6.0	4.0
% Recovery of Hg(II)	72.19	50.99	70.27	75.70

India is an agricultural country and these agro waste materials are abundantly available, thus, the work studied in this thesis will definitely has impact on socio-economic development of the country, particulary for the walfare of the marginal farmers below poverty line (BPL). Thus, the present study revealed that the synthesized low cost adsorbents could be successfully employed as adsorbents for the removal of contaninants from water/wastewaters.

The studied alternative adsorbents are found to be highly efficient for the removal of As(V), Pb(II), Cd(II) and Hg(II) metal ions. They will not only be beneficial for the industries but the living organisms and the surrounding environment from the potential toxicity caused by heavy metal ions. Thus, the use of studied low-cost adsorbents may contribute to the sustainability of the environment. Undoubtedly, tested low-cost adsorbents seem to offer a lot of probable benefits for commercial purpose in the future.

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