ADSORPTIVE REMOVAL OF LEAD AND CADMIUM IONS FROM AQUEOUS SOLUTION ON PARTHENIUM-BASED ACTIVATED CARBON

A DISSERTATION

submitted in partial fulfillment of the
requirements for the award of the degree
of

MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING

(with specialization in
Industrial Pollution Abatement)

By

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CANDIDATE’S DECLARATION

I hereby declare that the work being presented by me in this dissertation entitled **“Adsorptive removal of lead and cadmium ions from aqueous solution on parthenium based activated carbon”** in partial fulfillment of the requirements for the award of the degree of Master of Technology in Chemical Engineering with specialization in “Industrial Pollution Abatement” submitted to Department of Chemical Engineering, Indian Institute of Technology, Roorkee; is an authentic record of my original work carried out under the guidance of Dr. Shashi, Associate Professor, Department of Chemical Engineering, IIT Roorkee. The matter embodied in this dissertation has not been submitted for the award of any other degree.

Date: ARTI VERMA

Place: IIT Roorkee

CERTIFICATE

This is to certify that Ms. Arti Verma has completed the dissertation entitled **“Adsorptive removal of lead and cadmium ions from aqueous solution on parthenium based activated carbon”** under my supervision. This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

This compilation is the result of removal of lead and cadmium ions from aqueous solutions by using adsorption process. The adsorbent used for this purpose is activated carbon prepared from *P. hysterophorus* which is a pernicious weed and spread vastly all over. Effect of pH, dose, temperature, contact time and initial concentration of metal ions was assessed and adsorption experiments were conducted in batch wise manner. Optimum pH for lead and cadmium ions were observed to be 5.5 and 6.0 and optimum dose came out to be 0.1 g and 0.2 g respectively. The obtained experimental data were tried to fit various adsorption isotherms Langmuir, Freundlich, Redlich-Peterson, Sips, Temkin and Radke-Prausnitz isotherms using MATLAB. In which, Langmuir, Sips and Radke-Prausnitz showed the best fit for Pb(II) and Sips and Radke-Prausnitz fitted best for Cd(II). From experiments conducted at different time intervals, pseudo first and pseudo second order rate equations were analyzed, among which pseudo second order rate equation model exhibited high correlation coefficient (R^2=0.99) for both the metals.

Keywords: adsorbent, *P. hysterophorus*, batch wise, correlation coefficient

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NOMENCLATURE

b= constant in Lagmuir isotherm (l/mg)

Ce= concentration of adsorbate in solution at equilibrium (mg/L)

Co= initial concentration of adsorbate in solution(mg/L)

Ct= concentration of adsorbate in solution at any time t (mg/L)

K_F= constant in Freundlich isotherm

k_1= adsorption rate constant of pseudo first order kinetics

k_2= adsorption rate constant of pseudo second order kinetics

n= constant in Freundlich isotherm

Qo= constant in Lagmuir isotherm

$q_{e(exp)}$= experimental value of qe

$qe_{(pred)}$= predicted value of qe

qe= amount of adsorbate adsorbed per g of adsorbent at equilibrium

qt= amount of adsorbate adsorbed per g of adsorbent at any time t

R^2= correlation coefficient

V= volume of adsorbate solution

w = mass of adsorbent (g) in chapter

CHAPTER 1

INTRODUCTION

Fast growth of global industrialization and population has resulted into generation of large quantities of wastes that is causing various problems to environment. Heavy metals are necessary in trace amounts for growth of living beings but at higher concentrations, most of them are harmful and toxic. Heavy metals are introduced in the environment through natural phenomena and human activities **(Aballino et al., 2003)** and their concentration is continuosly increasing in wastewater day to day with increase in industrialization.

A large number of treatments methods for heavy metals and dissolved organics are available and some of them include electrochemical reduction, precipitation, ion-exchange, reverse osmosis and evaporation etc. but these methods demand long detention period and large surface area **(Rao et al., 2002)**. Adsorption process for water pollution control is advantageous because of the facility of easy operation, simple design, cost and no effect by toxic harmful substance. Adsorption is a process, which is physico-chemical in nature and has great potency for treating effluents which have undesirable components and furnishes them reusable and safe. Moreover, because sometimes adsorption process is reversible, hence the adsorbents used can be regenerated by desorption process and can be reused.

Much work has been done on the removal of lead and cadmium by clays, minerals such as hydroxyapatite, calcite, goethite and calcite, some industrial by products and waste materials such as slags, sludges, modified asphaltite ashes, bark, fly ash, chitosan, dead biomass, modified wool, moss, peat, seaweed, zeolite, humic acid, carbon aerogel, nanosized metal oxides and others.

1.1 HAZARDOUS HEAVY METALS: LEAD AND CADMIUM

Lead

Lead is a noxious pollutant which badly affects the nervous system. It acts as a accumulative poison. Inorganic Pb^{2+} ion is an enzyme inhibitor. In environment, metallic lead and its salts and oxides come from various industries such as battery industries, paints and pigments, lead smelting industries etc. Through drinking water, food and air it can reach in human body when once transmitted in ionic form.

Lead poisoning can lead to liver damage, kidney problems and reduction in haemoglobin formation, mental retardation, infertility and abnormalities in pregnancy. Chronic lead poisoning may cause three general disease syndromes:

- Gastrointestinal disorders, constipation, abdomen pain, etc.
- Lead lapsy (neuromuscular effects), fatigue, and weakness.
- Nervous system effects that may result to coma and death.

S. Bhattacharjee et al., 2003 studied the removal of lead from contaminated water bodies using sea nodule as an adsorbent and the study told that EU, USEPA and WHO has limited the values of lead in surface water and drinking water upto 10, 50 and 10 mg/l, respectively. Apart from this, the concept of zero lead value in national primary drinking water standard has been given in 2003 by EPA. Limiting value of lead in drinking water is 0.01mg/l, in India. Many research work are being done in this area to remove lead from contaminated water sources and limit its concentration. Several different techniques are also being employed. Much work has been done for adsorption and various adsorbents like low cost activated carbon, sludge, cattle manure, industrial and agricultural waste, clay, red mud, peat have been used and still modifications in adsorbents are being done increase adsorption capacity of these adsorbents.

Cadmium

Heavy metal cadmium is a baneful irritant. It creates irritation to the respiratory tract and chronic exposure to this pollutant can cause anemia and yellow stained teeth also. There are various sources of cadmium and their salts. These are used in paint pigments, smelting, stabilizer, electroplating, plastics, silver cadmium batteries, cadmium-nickel batteries, phosphate fertilizers, mining and alloy industries. Prolonged exposure to very high level of cadmium is likely to cause bone degradation (which is also called itai–itai syndrome), blood damage, kidney disfunction or Fanconi syndrome, cancer and liver damage.

Table 1.1 **Permissible limits of various toxic heavy metals**

Metals	**Permissible limits for industrial effluent discharge (mg/L)**				**Permissible limits for potable water (mg/L)**			
	Indian standard			**WHO**				
	Inland surface water	**Public sewers**	**Marine coastal areas**	**Inland surface water**	**Indian standard IS 10,500**	**WHO**	**USEPA**	**EU Standard**
Nickel	3.0	3.0	5.0		0.02	0.02	0.1	0.02
Zinc	5.0	15.0	15.0	5.0–15.0	5.0	3.0	5.0	
Copper	3.0	3.0	3.0	0.05–1.5	1.5	2.0	1.3	2.0
Cadmium	2.0	1.0	2.0	0.1	0.01	0.003	0.005	0.005
Lead	0.10	1.0	2.0	0.1	0.05	0.01	0.015	0.01
Total chromium	2.0	2.0	2.0		0.05	0.05	0.1	0.05
Arsenic	0.2	0.20	0.2		0.01	0.01	0.01	0.01
Mercury	0.01	0.01	0.01		0.001	0.001	0.002	0.001
Iron	3.0	3.0	3.0	0.1–1.0	0.3	0.2	0.3	0.2
Manganese	2.0	2.0	2.0	0.05–0.5	0.1	0.5	0.05	0.05
Vanadium	0.2	0.2	0.2			1.4		

According to Indian Standard Institution, the discharge of lead into drinking water should be limited to 0.05mg L^{-1} (I.S.I. Specification IA: 2490, 1982) and in surface waters, its tolerance limit is 0.1 mgL^{-1} (I.S.I. Specification IS 10500, 1991).

The principle on which adsorption works is adhesion. The phenomenon of adsorption involves separation of a substance from one phase to another and it involves adhesion of one phase to another which is accompanied by its accumulation at the surface of another. Out of these, one phase which is adsorbing the other phaseis referred to ‘adsorbent’ and the another phase which is concentrated or adsorbed at the surface of adsorbing phase is called ‘adsorbate’. Adsorption process can occur in any of the following systems: liquid-gas, liquid-liquid, solid-liquid and solid-gas.

Adsorption can either result from the universal Vander Waals interactions and electrostatic forces between molecules of adsorbate and the atoms of the adsorbent surface physical adsorption, or it can have the characteristics of a chemical process (chemical adsorption). Chemisorption takes place only as a monolayer, whereas physisorption does not. Physical adsorption can be compared to the condensation process.

Many solid adsorbents possess a complex porous structure. It consist of pores of different sizes and shapes. Total porosity of a adsorbent is can be classified into three groups on the basis of science of adsorption:

Micropores (smaller than 2nm): Size of micropores is approximately same as those of adsorbate molecules. Because of this reason, adsorption in micropores is generally considered as “pore-fillng process”. Thus, the size of the micropores determines the accessibility of adsorbate molecules to the internal adsorption surface.

Mesopores (in the range of 2-50nm): A large number of adsorbent atoms or molecules form the walls of mesopores. The physical meaning of the boundary of interphases (adsorbent surface area) is distinct. The action of adsorption forces occurs very close to mesopore’s walls. Hence, in the surface of mesopores, there is a successive occurrence of monolayer and multilayer adsorption.

Macopores (larger than 50nm): The adsorption on the surface of micropores is generally neglected because microporous solids have very small specific surface area. Also, macropores does not exhibit capillary adsorbate condensation in macropores.

1.2 ADSORBENTS

The most important attributes of an adsorbent for any application are: capacity, selectivity, regenerability, kinetics, compatibility and cost.

- The most salient feature of an adsorbent is adsorption ***capacity*** or "loading". Whatever amount of adsorbate is adsorbed, per unit mass or volume of the adsorbent is called adsorption capacity. Temperature, adsorbate concentration and the conditions like initial condition of the adsorbent affect the capacity.

- ***Selectivity*** can be defined as the proportion of the adsorption capacity of one component to that of another at a particular initial concentration of fluid. As the concentration of fluid tends towards zero, the selectivity approaches a constant value.

- Some sort of chemical and physical attack say attrition or biological contamination can reduce the expected life of the adsorbent. These possible modes can be comprehended by ***Compatibility***. For this, the adsorbent, binder, and surface groups (depending o the type of adsorbent), should be inert to the carrier or solvent, and should not irreversibly react with (or chemisorbed) the adsorbate(s) or contaminants.

- ***Regenerability*** is used in accordance with cyclic application of adsorption. In many cases, adsorption can efficiently operate in sequential cycles with good and uniform performance. Pressure swing, thermal swing, chemical (e.g., by elution or displacement), may accomplish the regeneration. Their combination can also be used for this.

- Mass transfer ***kinetics*** term is related to intraparticle mass transfer resistance. This is a vital attribute because it controls the cycle time of a fixed bed adsorption process. Slow kinetics give in an extended breakthrough curve while fast kinetics yields a sharp breakthrough curve.

- ***Cost*** may vary greatly depending upon the adsorbent used, hence its an important aspect of adsorption process.

Activated carbon adsorbents

Many researchers are researching for the usage of activated carbon for the removal heavy metals**.** These adsorbents are efficient and very useful because of their large micropore and mesopore volumes and consequently, high surface area.

Usage of coal-based commercial activated carbon has been reduced, nowadays. This has increased the cost of commercial activated carbon. In the view of this point, putting the decline in the pollutants adsorption at stake, various low cost activated carbon composite can be a good choice. For heavy metal removal, many carbonaceous materials are being converted into activated carbon. reviewed the waste materials for Preparation of activated carbon from waste materials is surveyed by **Dias et al., 2007**. **Guo et al**., **2010** explored about poultry litter-based activated carbon and found that it possess very high adsorption capacity for heavy metals. It was even higher than commercial activated carbon.

From the economical point of view, *P.hysterophorus* utilization for pollutant removal is a very good choice. *P.hysterophorus*, which is commonly known as carrot weed or congress weed is **(Sharma et al., 2008)** is a highly toxic weed. It is vastly spread in India and some parts of Africa and it was originated in America. **I**t can cause respiratory malfunction, allergy, asthma and dermatitis. It is found mostly in uncultured lands, drainage etc. It is highly adapted in warm weather of India and its germination rate is high, hence, it is spread vastly. Fig 1.1 shows the photograph of this weed.

Fig 1.1 *Parthenium hysterophorus*

1.3 OBJECTIVES

- Development of *Parthenium Hysterophorous* weed based activated carbon
- Determine the adsorption efficiency of the activated carbon for the toxic and hazardous metal ions: lead and cadmium
- Examine the study of the effect of various parameters on the adsorption of lead and cadmium ions over activated carbon i.e., effect of contact time, effect of pH, effect of adsorbent doses, effect of initial concentrations
- Fitting of various rate equation models to search for the appropriate kinetics for the process of adsorption

CHAPTER 2

LITERATURE REVIEW

Almost all carbonaceous materials may be used as a precursor for the preparation of activated carbon. However, the selection of raw material is based mainly on the following parameters:

(i) Low inorganic matter content
(ii) Ease of activation
(iii) Availability at low cost
(iv) Low degradation on storing

In practice, wood, charcoal, nutshells, soft coal, lignite, bituminous coal, petroleum coke etc. are found to be adequate for the production of activated carbon. These activated carbons possess several advantages and disadvantages. Therefore, in most of the adsorption studies, activated carbon has been prepared by low cost, easily available carbonaceous materials. In this respect, various types of precursor have been used and adsorption capacity of prepared activated carbon has been investigated to get rid of different heavy metal ions. The adsorption capacity has been evaluated in terms of equilibrium isotherm and kinetic models. Therefore, in literature, various studies on raw material, preparation technique of activated carbon and on adsorption equilibrium isotherm and kinetic models have been made.

The adsorption of mercury, cadmium and lead from aqueous solutions on heat-treated and sulphurized activated carbon has been studied comparatively by **V. Gomez-Serrano, 1998.** Various metal ions were adsorbed at 25°C using adsorptive solutions at different pH values and then at this condition, behavior of different adsorption isotherms was studied. For mercury, the removal by adsorption was observed to be higher than for cadmium and lead ions. Sulphurized carbon was responsible to increase the adsorption of mercury drastically. Only for few adsorbents, pH change affected the adsorption of cadmium and lead. This did not happen for mercury.

Nadeem M. et al. (2006) used an agricultural waste, husk and pods of *Moringaoleifera* (*M. oleifera*) activated it with steam and prepared chemically modified activated carbon from it. Lead removal was aqueous solution was studied using this adsorbent Intra-particle diffusion, pseudo first order and pseudo second order equations were used to check the consistency of adsorption kinetics data. Chemically modified adsorbents highly enhanced the adsorption rate for mercury rather than unmodified. Langmuir and Freundlich models were studied to see the compatibility and authenticity of adsorption data. correlation coefficient (R^2) was used to show the goodness of fit. R^2 values for Langmuir model found to be in the range 0.994 to 0.998 and thus, proved to be better than Freundlich. . Maximum adsorption capacities were found to be 96.58, 91.8, 88.63, 79.43% for phosphoric, sulfuric, hydrochloric acid treated and untreated carbon adsorbents, respectively.

Issabayeva G. et al., 2006 studied the removal of Pb(II) ions from aqueous solutions and for this purpose, they used activated carbon prepared from palm shell. pH 3.0 and 5.0 were chosen to conduct the adsorption experiments. Malonic and boric acid were used to see the modifications in the adsorption of Pb(II). At pH 5, maximum removal took place with adsorption capacity of 95.2 mg/g. This uptake value was quite high making palm shell activated carbon an ideal for lead removal. The observation was that the malonic acid decreased lead uptake, while boric acid did not affect it much. The extent of adsorption was predicted using diffuse layer surface complexation model. The data was fitted well.

In order to remove heavy metals cadmium and lead from synthetic aqueous solutions, **Jusoh A. et al. (2007)** carried out a study and examined the adsorption capability of granular activated carbon (GAC). Continuous filtration process was used and the actual condition of adsorption was simulated by employing fixed bed column test. They used different flow rates. To obtain the adsorption capacity and to predict the breakthrough curve, Adam-Bohart breakthrough curve equation was used and this equation was in conformity with the experimental data and removal was good.

There is another study by **Aroua M.K. et al. (2008).** They, also used palm shell-based activated carbon and tried to remove lead from aqueous solution and ion selective electrode was employed to find the kinetics o adsorption of lead. Using ion selective electrode, adsorption data can be recorded at very less time intervals. Agitation speed and initial Pb(II) concentration parameters were studied. Various models which were implemented to find the adsorption process were: Pseudo first-order, pseudo second- order, intraparticle diffusion and liquid film diffusion and Elovich models.

Ahn C.K. et al (2009) tried to impregnate the activated carbons to increase their capacity to adsorb heavy metals. They used *anionic surfactants* to impregnate and change the properties of activated carbons and removal of Cd(II) was studied. *Dioctylsulfosuccinate sodium (DSS), sodium dodecyl benzene sulfonate (SDBS),* sodium *dodecyl sulfate (SDS)* were used. The effects of adsorbent dosage, solution pH and contact time on the adsorption were analysed. Upto 0.198 $mmolg^{-1}$ of removal took place. This was quite higher than one without surfactant as without surfactant, uptake was 0.016 $mmolg^{-1}$. Impregnation with surfactant was done in different proportions and this influenced the adsorption capacity of activated carbon. Like other studies, in order to find kinetics of the adsorption, they fitted Langmuir and Freundlich model, among which Freundlich was observed to be better. Surface charge also plays an important role in the adsorption process because it determines the attraction or repulsion of adsorbate molecules depending on their charge. Activated carbon exhibited the negative pH from 2 to 6. As it was obvious, anionic adsorbents increased the adsorption and hence removal of cations.

Dong L. et al. (2010) simultaneously removed lead and cadmium ions by using MnO_2-loaded D301 weak basic anion exchange resin as adsorbent. Along with dose and pH, effect of coexistent ions was also studied. Experiments told that optimum dose was 0.6 g/L and optimum pH ranged between 5-6 to remove Pb^{2+} and Cd^{2+} simultaneously. Presence of Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-} and HCO_3^- did not greatly affect the removal efficiency of metal ions, while HPO_4^{2-} did. howed no important effect on of both Pb^{2+} and Cd^{2+} under the experimental checks. Pb^{2+} removal did not undergo any change with presence of Mg^{2+} and Ca^{2+} ions, while it increased the removal of Cd^{2+}. 80.64 mg/g and 21.45 mg/g were the maximum adsorption capacity for Pb^{2+} and for Cd^{2+} respectively. The adsorption equilibrium for Pb^{2+} and Cd^{2+} could be magnificently described by the Langmuir isotherm model with R^2> 0.99. Pseudo first-order kinetics model was fitted perfectly the adsorption data. R^2> 0.99 was obtained for Langmuir that was fitted better than Freundlich adsorption isotherm.

In an study of **Ye H. et al. (2010)**, the natural and modified rice husk were examined to remove Cd(II) ions from water and alkali treatment was done for its preparation. For the two adsorbents, Cd(II) adsorption increased with the increase of pH. 6.5 was the optimum pH at which highest removal took place. As per expectation, the modified rice husk showed higher adsorption capacities and faster kinetics than the natural rice husk. Structural changes of surface of the material could be responsible by it as report by the author. Adsorption equilibrium could be magnificently described by the Langmuir isotherm rather than Freundlich. Equilibrium adsorption data are more consistent with the Langmuir isotherm equation than with the Freundlich equation. Maximum adsorption capacity in case of natural and modified rice husk were 73.96, 125.94 mg/g respectively. Pseudo second order and pseudo first order both were in accordance with adsorption data. Both pseudo-first-order and pseudo-second-order equations were able to explain properly the kinetics of Cd(II) adsorption.

Ozdes D. et al. (**2011)** studied the removal of lead and cadmium ions from Turkish illitic clay (TIC) from aqueous solutions. Experiments were conducted in batch mode. Effects of various factors on which adsorption process can depend were checked and adsorbent characterization was also done to find the properties. Optimum dose of Turkish illitic clay for removal of both the ions was 1.0 g L^{-1} and optimum pH was 4. Similarly, optimum initial concentration was obtained to be 50 mg L^{-1} and 250 mg L^{-1} for Cd(II) and Pb(II) respectively. The maximum adsorption capacity of the adsorbent was 11.25 mg g^{-1} for Cd(II) and 238.98 mg g^{-1} for Pb(II) at optimum contact time of 240 min. Adsorption took place at room temperature. *Freundlich, Langmuir, Dubinin Radushkevich* (D-R) and *Temkin* isotherm models were used for examining experimental data. Pseudo-second-order model was in conformity with adsorbent information rather than Elovich, intra-particle diffusion or pseudo first order model for both the metal ions. Adsorption process was endothermic in the temperature range of 5-40 °C and it was feasible and spontaneous as indicated by thermodynamic parameters including the Gibbs free energy (DG), enthalpy (DH), and entropy (DS) changes.

Rivera-Utrilla J. et al (2011) re-examined the activated carbon modifications to increase its water treatment applications. They focused on modifying the activated carbon surface and finding the pros and cons of the different methodologies used for this purpose. They also tested for their capabilities in waste water treatment. Acidic surface functional groups were emphasized to increase in this modification process using H_2O_2, O_3 and HNO_3. As these acidic groups may increase the removal of heavy metal ion, which are basic in nature, albeit, this treatment can reduce the AC surface area. Hence, researchers tried for different methodologies without the undesirable effect of pore blockage.

These methodologies have been categorized into four broad groups: oxidation, sulfuration, ammonification, and coordinated ligand anchorage.

In early **2012,** work done by **Sheela T. and Nayaka Y.A.** demonstrates the capability of NiO nanoparticles for the adsorptive removal of Cd(II) and Pb(II) ions. As earlier reviews, again they used batch process to run adsorption experiments at different concentrations, time and temperature of the suspension. The effect of initial pH and other factors were observed with the help of experiments. Equilibrium experiments showed that the Pb(II) ions were more easily absorbable on NiO nanoparticles than Cd(II) ions. First hydrolysis equilibrium constant and hydrated ionic radius are responsible for such behavior. The experimental data were well suited by the pseudo-second-order model as film diffusion controlled the adsorption as explained by kinetic data. Langmuir adsorption isotherm exhibited high correlation coefficients than other models and fitted well. The spontaneity of the process was suggested by the negative value of free energy (ΔG°) and the endothermic nature of the process was indicated by the heat of adsorption (ΔH°).

Wang et al., (2009) prepared the activated carbon from Phaseolus aureus hulls and studied the removal of Pb(II), Cu(II), Zn(II) and Cd(II) ions from aqueous solutions with the help of this low cost adsorbent. Phaseolus aureus (In India, commonly known as moong beans) and its hulls is an agricultural waste. Batch method was applied to conduct adsorption experiments. 500 mg and 325 mg amount of adsorbent were optimally enough for the appropriate removal of lead and cadmium respectively. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models were studied. From experiments pseudo second order kinetic model came to be best-fitted. The maximum adsorption capacity values of the adsorbent were 21.8 mg g^{-1} for Pb(II) and 15.7 mg g^{-1} for Cd(II). Desorption experiments were also performed using HCl solutions.

There was a reduction in adsorption capacity with increase in the adsorbent dose after a limit, it was mainly because of the increase of unsaturation of adsorption sites through the adsorption reaction. Another reason which they have provided was the particle interactions, such as aggregation, resulting from high sorbent concentration. Such aggregation leads to decrease in total active surface area of the adsorbent.

Author	**Adsorbent**	**Ion removed**	**Monolayer adsorption capacity (mg/g adsorbent)**	**Best fitted model**	**Remarks**
Kadirvelu et al. (2001)	Activated carbon prepared from coirpith	Hg(II) Pb(II) Cd(II) Ni(II) Cu(II)	100% 100% 100% 92% 73%	-	The percent adsorption increased with increase in pH from 2 to 6 and remained constant up to 10
Dastgheib and Rockstraw (2002)	activated carbon produced from pecan Shells (PS400)	Hg(II) (II)	-	Sips and Freundlich	BET surface area of PS400 is 417 m^2/g. Phosphoric acid activation
Aroua et al. (2006)	palm shell activated carbon (PSAC)	Pb(II)	95.2 (at pH 5.0)	diffuse layer surface complexation model	BET specific surface area (m^2 g^{-1}) 957.04 Effect of presence of complexing agents (malonic and boric acids) on the adsorption of lead were also evaluated. The presence of boric acid resulted in higher uptake of lead compared to single lead at pH 5.0
Kula et al. (2008)	AC prepared from olive stones by $ZnCl_2$ activation	Cd(II)	Cd(II) adsorption increases from 0.68 mg/g to 1.654 mg/g at 303.15 K	Langmuir and Freundlich isotherms	specific surface area 790.25 m^2 g^{-1} kinetic data supports pseudo-second order model and intra-particle model
Wang et al. (2009)	activated carbon prepared from *Phaseolus aureus hulls (ACPAH)*	Pb(II) Zn(II) Cd(II) Cu(II)	21.8 21.2 15.7 19.5	Freundlich and Temkin model	Specific surface area of ACPAH 325 m^2/g effect of pH, contact time, adsorbent dose, and initial concentration of metal ions on the removal was evaluated by batch method, pseudo-second-order kinetics

Zaini et al. (2009)	cattle-manure-compost based activated carbon (CMC AC)	Pb(II) Cu(II)	-	Langmuir equation.	The influence of $ZnCl_2$ activation ratios and solution pH on the removal of Cu(II) and Pb(II) were studied, preferable removal of Cu(II) over Pb(II) could be due to the rich nitrogen content as well as the higher mesoporous surface area in the CMC AC
Li et al. (2010)	AC prepared from Enteromorpha prolifera by zinc chloride activation (EPAC)	Pb(II)	146.85	Freundlich adsorption isotherm	EPAC has a high surface area of 1688m^2/g
Anirudhan and Sreekumari (2011)	activated carbon derived from waste coconut buttons	Pb(II) Hg(II) Cu(II)	92.72 78.84 73.60	Freundlich model	Steam activation method used for AC, The maximum removal of the metal ions is observed at the pH 6.0 for Pb(II), pseudo second order kinetics for adsorption
Sheela and Nayaka (2012)	NiO nanoparticles	Pb(II) Cd(II)	151 90.3	Langmuir adsorption isotherm	Selectivity of NiO nanoparticles towards Pb(II) ions is more than that of Cd(II) ions

Table 2.1 Studies on heavy metal ion removal by adsorption

CHAPTER 3

PREPARATION AND CHARACTERIZATION OF PARTHENIUM BASED ACTIVATED CARBON

3.1 ACTIVATION PROCESSES

The activation process is employed to raw carbonaceous material to increase the surface area and to improve the surface properties and pore structure. In the course of this process, space which exists between elementary crystallites is vacated by removal of carbonaceous materials which are less organized and loosely bound. A large internal surface area is offered with the help of resulting channels through graphite regions, the space which exists between the basic crystallites, fissures and parallel porous structure.

There are two types of activation processes for preparation of activated carbon:

(i) Physical activation
(ii) Chemical activation

3.1.1 Physical activation

Physical activation is also known as thermal activation. It is carried out generally by burning off some of raw carbon in an oxidizing environment to create micropores. Physical activation can be done by one or combining the two processes: (i) Carbonization of carbonaceous material (ii) Activation/oxidation of the resulting char in the presence of activating agents.

In carbonization, the carbonaceous material is pyrolysed at high temperature ranging from 600-900°C in an inert atmosphere in the presence of gases like nitrogen and argon. This leads to the elimination of bulk of volatile matter. The carbonization of carbonaceous material is exposed to oxidizing atmosphere in the presence of activating agents like carbon dioxide, steam, and air and fuel gas at temperature range of 600-1200°C. Here, the activation step can be called as gasification of carbonized material using mild oxidizing agent and the reactive carbon atoms of the structure are selectively eliminated by this gasification process which are responsible for generating the porosity and in turn they make active surface area of material.

3.1.2 Chemical activation

The chemical activation is also known as a single step method of preparation of activated carbon and it is done in the presence of chemical agents. Raw carbonaceous material is impregnated with dehydrating chemical agents in the chemical activation process, carbonization at temperature ranging from 450-900°C follows the impregnation. In carbonization step, the precursor is pyrolysed. Various impregnating agents include acids like H_3PO_4, H_2SO_4 and bases such as KOH, NaOH and salts for example $ZnCl_2$ etc. Porosity is developed after heat treatment and eliminating the chemical agent.

3.2 PREPARATION OF PARTHENIUM BASED ACTIVATED CARBON

Micropore formation and pore widening are the two mechanisms in chemical activation. When the chemicals are added to the raw material, then micropore formation starts and inside these formed pores, the chemical changes are the consequence of pore widening.

Thus, the H_2SO_4 to parthenium ratio along with micropores volume also affects the micropore size distribution **(Lozano- Castello et al., 2001).** Time of pyrolysis, temperature and the heating rate are the variables which directly affect the final pore texture of the activated carbon. In the carbonization process, some gases are evolved, which are needed to be removed. Faster the gases are removed, better and efficient is the creation of micropores **(Kyotani (2000).**

The last step is the washing stage which finally prepares the chemically activated carbon. The activating agent used in the process is needed to wash off finally leaving the pores behind. For washing or leaching the pyrolyzed mixture water or acid/ hydroxide solutions are used. The washing also eliminates some of the ash from the material. For higher impregnation ratio, washing is of much importance.

Small plants of parthenium weed having approximately same stem thickness were brought which were highly spread in the proximity of the Institute premises. To remove dust and filth from it, twigs were washed carefully and repeatedly. Pieces of size 5–6mm were cut and the moisture was removed by drying it in sunlight. Chemical activation process was selected to prepare the activated carbon. The next step was impregnation with activating agent, for this concentrated H_2SO_4 was chosen. The dried mass was impregnated with concentrated H_2SO_4 in the ratio of 1:2 by weight (weight of parthenium: weight of acid) and was kept at 131±5℃ for 6 h for carbonization, which was done in a horizontal furnace by creating inert atmosphere in the furnace. After carbonization, obtained material was washed several times with distilled water to remove free acid. For the complete removal of acid, carbonized material was further soaked into 1% sodium bicarbonate solution overnight. Again it was washed many times so that no leachable matter was present in it and it was oven-dried at 100℃. Crushing and sieving were the last steps which finally yielded the particles of activated carbon slightly granular having size less than 0.5mm.

3.3 CHARACTERIZATION OF ACTIVATED CARBON

As adsorption capacity of activated carbon depends not only on its surface area, but on its internal pore structure, presence of functional group on pore structure and surface characteristics. These characteristics, in turn depend on the carbonaceous source i.e. precursor and method of preparation, therefore, the characterization of the adsorbent is crucial to the adsorption phenomena.

Table 3.1 Characteristics of activated carbon

S.No.	**Properties**	**PAC**
1	BET surface area m^2/g	220
2	Ash content (%)	9.6
3	Moisture content (%)	1.7

3.3.1 FTIR

Fig 3.1 shows the FTIR spectra of parthenium activated carbon. Fourier Transform Infrared spectroscopy gives the idea about functional groups present in the sample. The range taken for FTIR spectroscopy was from 4000 cm^{-1} to 500 cm^{-1}. A band was observed at 3432 cm^{-1} which purports to the presence of ν(O-H) vibrations in hydroxyl groups or surface-bonded water. For alcohols and phenols, the location of hydrogen-bonded OH groups is generally observed in the range of 3200- 3650 cm^{-1}. The presence of band around 1414 cm^{-1} could be assigned recommended the presence of -COOH group (carboxylate groups). There was a sharp peak around 2923 and 2855 cm^{-1}, this suggests the occurance of ν(C-H) vibrations in methyl and methylene groups. Slight peak around may correspond to $R\text{-}OSO_2\text{-}OR_2$ group, which falls in the range 1415-1380 cm^{-1}, because of H_2SO_4 activation. The bands between 1300 and 900 cm^{-1} recommended the C-O stretching vibrations.

3.3.2 XRD

For phase identification, X-ray diffraction analysis was carried out for parthenium based activated carbon using CuKα radiation (at 40 kV, 30 mA) in thin samples. Fig 3.2 shows the X-ray diffraction patterns for parthenium based activated carbon. XRD data is analyzed with the help of Xpert High Score software. The absence of sharp peaks in XRD pattern of the sample suggests that most of the material is amorphous in nature. Carbon (major) present may be in graphite form.

3.3.3 DTA-TG ANALYSIS

Thermal analysis techniques are those in which a physical property of a substance or its reaction products is measured as a function of temperature while the substance is subjected to a controlled temperature programme.

DTA-TG (Differential thermal analysis) shows the difference in temperature (ΔT) between a standard and specimen vs. temperature of the specimen. The presence of peak (crest) in DTA curve shows that the compound will exhibit *exothermic reaction*.

TG (Thermogravimetry) curve is plotted is plotted between weight percent loss or gain with temperature or time, which shows the moisture removal or weight loss along with increase in temperature and thermal stability of the compound.

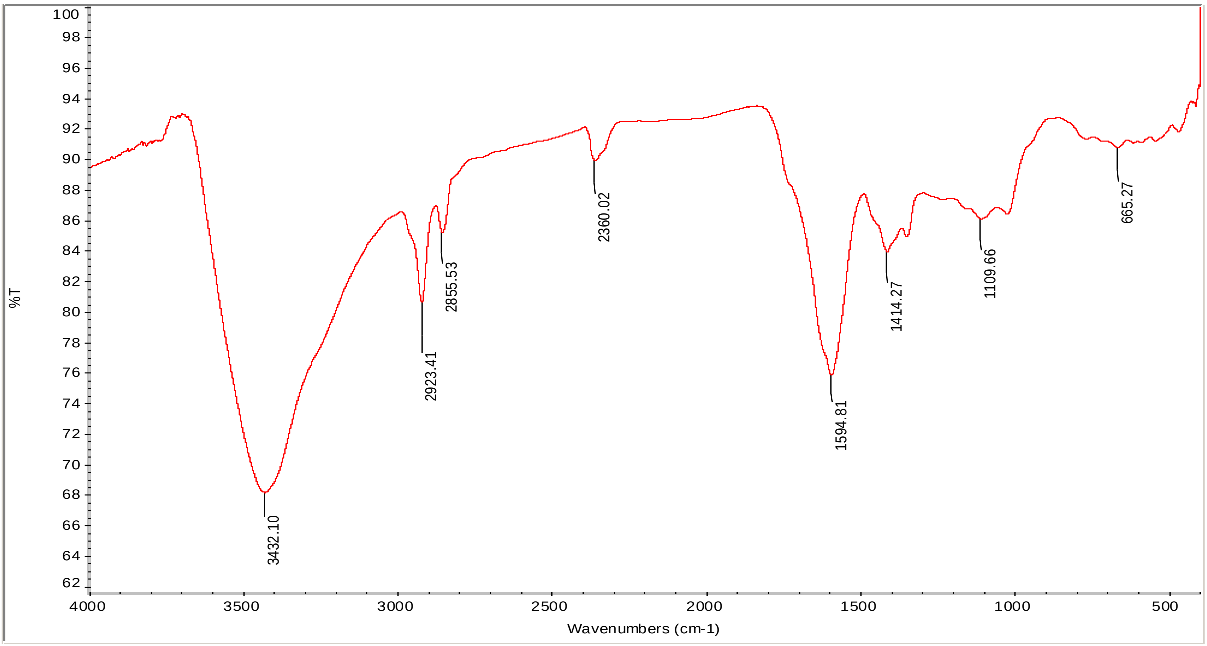


Fig 3.1 FTIR spectrum of parthenium based activated carbon

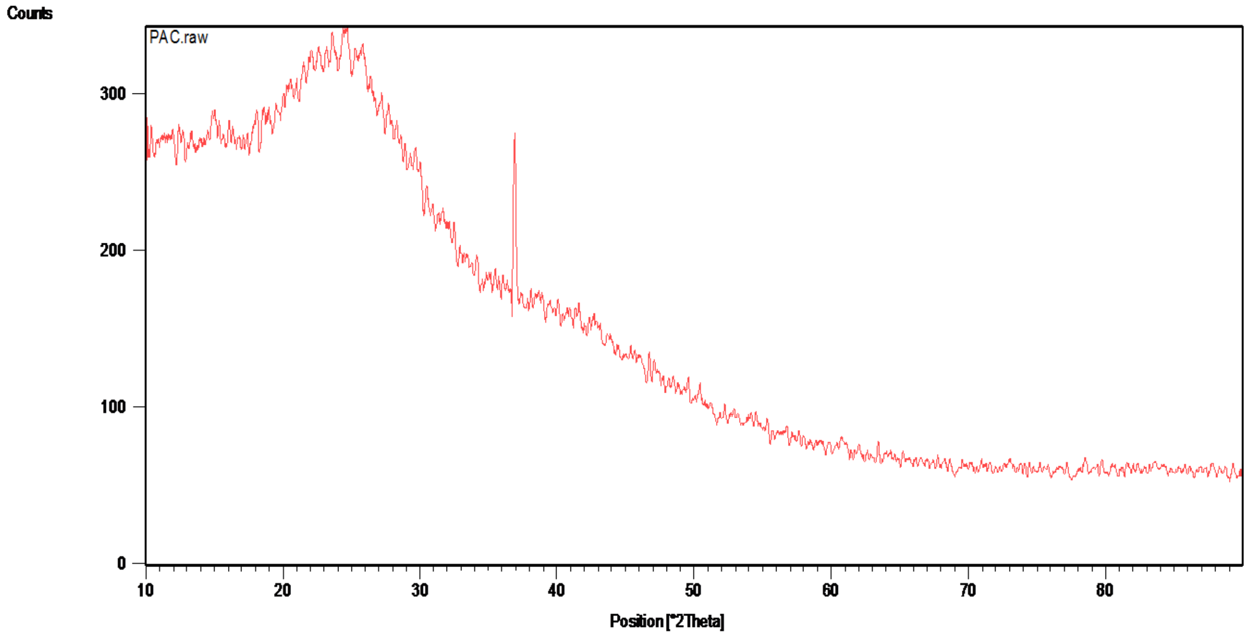


Fig 3.2 XRD pattern for parthenium based activated carbon

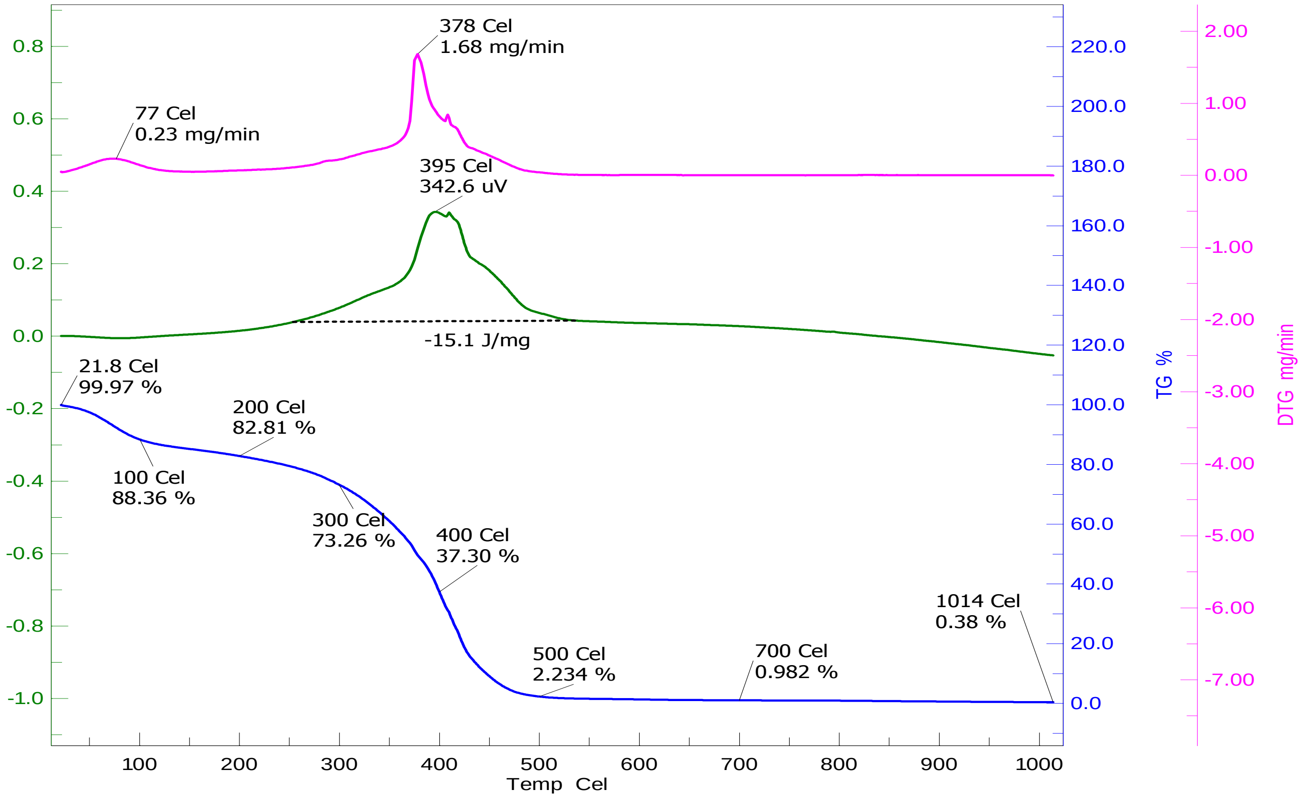


Fig 3.3 DTA-TG curve for parthenium based activated carbon

CHAPTER 4

ADSORPTION OF LEAD AND CADMIUM IONS ON ACTIVATED CARBON

4.1 ADSORPTION

4.1.1 Mechanism of liquid adsorption

Adsorption can be classified into two types from the criteria of types of forces between the liquid molecules and the molecules of solid:

(i) Physical adsorption
(ii) Chemical adsorption (Chemisorption)

Physical adsorption is a readily reversible phenomena which occurs when the inter molecular forces of attraction between molecules of adsorbate are greater than the force between molecules of adsorbent (liquid in this case). This is also known as *van der Waals adsorption* because attraction forces which work here are van der Waals. The adsorbed substance remains only upon surface, it does not penetrate within the crystal lattice of adsorbent. But, if the adsorbent is highly porous, the adsorbate will penetrate the adsorbent if it wets the adsorbent. The physical adsorption may occur in monomolecular layer, or may be two, three or more layers.

Chemisorption (activate adsorption) which is the result of chemical interaction between the adsorbate and the adsorbent, involves the formation of chemical bonds between these two in a monolayer. Adhesive forces are generally much greater than those in physical adsorption. Heat of chemisorption is of the order of heat of chemical reaction and is larger than heat of vaporization. The process is mostly irreversible.

4.1.2 Equilibrium and kinetics

The feasibility of adsorption is determined by the adsorbent and its performance in equilibria and kinetics. An adsorbent with slow kinetics, inspite of good capacity is not an attractive and economical option. Consequently, the output rate is slow. On the other hand, an adsorbent with fast kinetics and low capacity is not suitable because a large amount of adsorbent is required to get desired output rate. This concludes that an adsorbent to be the most suitable, it should exhibit effective adsorption capacity along with fast kinetics.

The activated carbon has high capacity and it has proved to provide fast adsorption rate for various organic compounds present in waste water. Thus, equilibrium and kinetic data are needed to provide an engineering design for adsorption processes. Both the rate and extent of adsorption are influenced by the properties of adsorbate (molecular structure, concentration etc.), adsorbent and the system operating conditions (temperature, pH). The properties of adsorbent include surface area, pore size and their distribution, size of adsorbent functional groups etc.

The adsorbent loading is expressed as mass of adsorbent per unit mass of adsorbent. In case of vapour-liquid and liquid-liquid equilibrium, phase distribution may be estimated by using K-values. For a given adsorbate- adsorbent system the adsorption equilibrium data may be expressed as follows:

$$q_t = f(C,T) \tag{4.1}$$

where q_t is adsorbate loading i.e. mass of adsorbate per unit mass of adsorbent, T is temperature and C is concentration of the adsorbate in the liquid solution. At constant temperature, the adsorbate loading can be expressed as

$$q_t = f(C) \tag{4.2}$$

The equation (4.2) is an adsorption isotherm. Thus, the variation of adsorbate loading on an adsorbent with concentration of adsorbate in the liquid at constant temperature over a range of liquid concentrations is known as adsorption isotherm.

For liquid phase adsorption, single component adsorption refers to the adsorption of a single adsorbate from solutions of inert solvents. This is the consequence of the assumption that change in composition of the bulk liquid in contact with the porous solid is entirely due to adsorption of the solute. This assumption gives no serious error in the results for dilute liquid mixture. But consequences are serious when concentration is high.

An adsorbate material balance, assuming that there is no adsorption of solvent on adsorbent and no change in the total moles of liquid mixture, gives

$$q_t = (C_o - C_t)V / m \tag{4.3}$$

Where C_o is initial concentration of adsorbate,

C_t is concentration of adsorbate at any time t,

V is the volume of adsorbate solution and

m is the mass of adsorbent dose (g).

The experimental data are obtained at constant temperature over an entire concentration range, processed with equation (4.3), and plotted as adsorption isotherms.

Among various isotherms, to describe the adsorption characteristics of the activated carbon for wastewater treatment, Freundlich isotherm is most commonly. In order to select best model for the given system, first a model system is selected, the experimental data are fitted to the model and parameters are estimated. If the predicted values by the model agree with the experimental ones, model may reasonably describe what is occurring physically in the real system.

The rate of adsorption of adsorbate is also an important consideration. The most widely used kinetics models for adsorption of heavy metals on activated carbon are “pseudo first order” type or “pseudo second order” type as given below. Pseudo first order kinetics model is represented by following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4.4}$$

and pseudo second order kinetics model is represented by

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4.5}$$

where q_e and q_t are the amounts of lead and cadmium ions adsorbed per unit mass of adsorbent at equilibrium and at any time t respectively. k_1 and k_2 are adsorption rate constants and units are (min^{-1}) and ($\text{g.mg}^{-1}.\text{min}^{-1}$) respectively. Integrated forms of equations (4.4) and (4.5) with the initial condition, $q_t\,(t=0) = 0$, are given below,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4.6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4.7}$$

If the first order kinetic equation is applicable, the plot of $\ln(q_e - q_t)$ against t should give a linear relationship. q_e and k_1 can be determined from intercept and slope respectively. On the other hand, if the second order kinetic equation is applicable, the plot of t/q_t against t should give a linear relationship. The value of q_e and k_2 can be evaluated from slope and intercept.

4.2 MATERIALS AND METHODS

4.2.1 Preparation of activated carbon

The adsorbent used in the present study *'Parthenium based activated carbon'* was prepared in the laboratory. For this purpose, parthenium weed was collected from nearby places and its preparation methods have been dicussed in chapter 3.

4.2.2 Preparation of adsorbate solution

Lead nitrate and cadmium nitrate of analytical reagent grade were procured from s.d.fine chemicals limited, Mumbai (India)"and with the help of these salts, synthetic aqueous solutions of various concentrations were prepared as needed in the study. The stock solution of 1000 mg L^{-1} were prepared, for this 1.598 g of $Pb(NO_3)_2$ and 2.744 g of $Cd(NO_3)_2.4H_2O$ were dissolved in a small amount of distilled water, separately, shaken well so that they were dissolved in water completely and then 1L measuring flask is filled upto the mark. For the experiments, fresh solutions of various desired concentrations were prepared by successive dilution of stock solutions.

4.2.3 Determination of concentration of Pb^{++} and Cd^{++} in solution

The concentration of lead and cadmium in the solutions was determined by estimating the absorbance of the sample solutions (7, 10, 15, 18, 10 mg/L for Pb(II) and 0.2, 0.3, 1, 1.2 and 1.5 mg/L for Cd(II)) at maximum wavelength 217 nm and 229 nm respectively, using atomic adsorption spectrometer (GBC Avanta). The calibration plot of absorbance versus concentration for Pb(II) and Cd(II) showed a linear variation in the given range (Fig A1 and A2 in Appendix). Therefore, the samples with concentration higher than the given range were diluted with distilled water, whenever necessary, to bring the samples' concentration in given range so that the sample point may lie on the straight line portion of the calibration curve. This value of concentration was multiplied by a multiplier as per dilution made, to calculate true concentration.

4.2.4 Adsorption experiments

The adsorption experiments of lead and cadmium ions from aqueous solution were conducted batch wise. All chemicals used in the experiment were of analytical grade (AR) and were obtained from SD fine chemicals. All glasswares and sample bottles were properly rinsed and cleaned with distilled water many times. Stock solutions of Pb(II) and Cd(II) ions of concentration 1000 mg L^{-1} were prepared separately by dissolving $Pb(NO_3)_2$ and $Cd(NO_3)_2.4H_2O$ respectively in distilled water. Dilutions of the stock solutions were done to get the required concentrations of metal ion solutions. The effect of various factors was studied. The required initial pH of solution were adjusted by adding 0.1 M HCl or NaOH. Then, the flasks were shaken continuously at 150 rpm by mechanical shaker for prescribed length of time attain to equilibrium. After the completion of run, solutions were filtered using Whatman filter paper (No.292). Determination of concentration of lead and cadmium ions after filtration was executed by atomic adsorption spectrometer (GBC Avanta).

Selected pH range for taking adsorption runs was below 6 for Pb(II) and below 8 for Cd(II) as above this limit metal hydroxide formation starts.

The percentage removal (% adsorption) and adsorption capacity (q_e) can be calculated using (4.8) and (4.9):

$$\%Adsorption = (C_o - C_e)/C_e \times 100 \tag{4.8}$$

$$q_e = (C_o - C_e)V/1000\,w \tag{4.9}$$

Where C_o is the initial concentration (mg.L^{-1})

C_e is metal concentration at various time intervals (mg.L^{-1})

V is the volume of heavy metal solution (mL)

w is the mass of adsorbent (g)

4.3 Results and discussions

4.3.1 Effect of initial pH

Adsorption on the solid surface is a phenomenon which depends upon the charge present on the surface of adsorbent. The pH of the solution influences the surface charge which in turn influences the adsorption. Hence in the most of studies pH is considered as an important controlling parameter to be studied. The effect of hydrogen ion concentration was studied for the pH range 3.0-8.0. Fig 4.1 shows the removal of Pb(II) and Cd(II) as a function of pH. The optimum pH was observed to be 5.5 for Pb(II) and 6.0 for Cd(II). Below optimum pH values, metal ion removal was observed to be lower, which can be understood in terms of competition of H^+ ion and metal ions which are present in the form of M^{2+} and $M(OH)^+$ at surface sites. When the pH was higher than the optimum pH values for the metal ions, the metal ions may get converted to their hydroxides and this may lead to decrease in removal of metal ion by the adsorbent.

4.3.2 Effect of adsorbent dosage

Determination of optimum adsorbent dose is an important task in adsorption studies because it determines the minimum quantity of adsorbent to meet required and feasible amount of adsorption. Fig 4.2 shows the effect of adsorbent dose on the percent adsorption of lead and cadmium at initial metal ion concentration of 50 mg L^{-1}. Figure is evident of the fact that increment in the adsorbent dose increases the percent adsorption of Pb(II) and Cd(II) ions upto 98.284% and 98.908% with optimum dose of 0.05 g/50 mL and 0.1 g/50 mL respectively. Hence, more adsorbent is needed to remove Cd(II) as compared to Pb(II). As for a fixed initial adsorbate concentration, increasing adsorbent dose provides greater surface area or more adsorption sites, hence the removal efficiency increased with increasing adsorbent dosage.

Runs were taken for adsorbent doses 0.01, 0.05, 0.1, 0.2, 0.3, 0.5 and 1 g for the initial concentration of 50 mg L^{-1}. It is observed that after 0.05 g and 0.1 g, percentage adsorption is almost constant for Pb(II) and Cd(II), respectively.

4.3.3 Effect of contact time

For an economical wastewater treatment system, equilibrium time is very important parameter. The experimental results showing the effect of contact time on removal of Pb(II), and Cd(II) are shown in Fig. 4.3. It is clear that removal is fast and the majority of metal ion removal was attained within first 30min. Minimum time to attain satisfactory removal is 150 min for Pb(II) and 100 min for Cd(II).

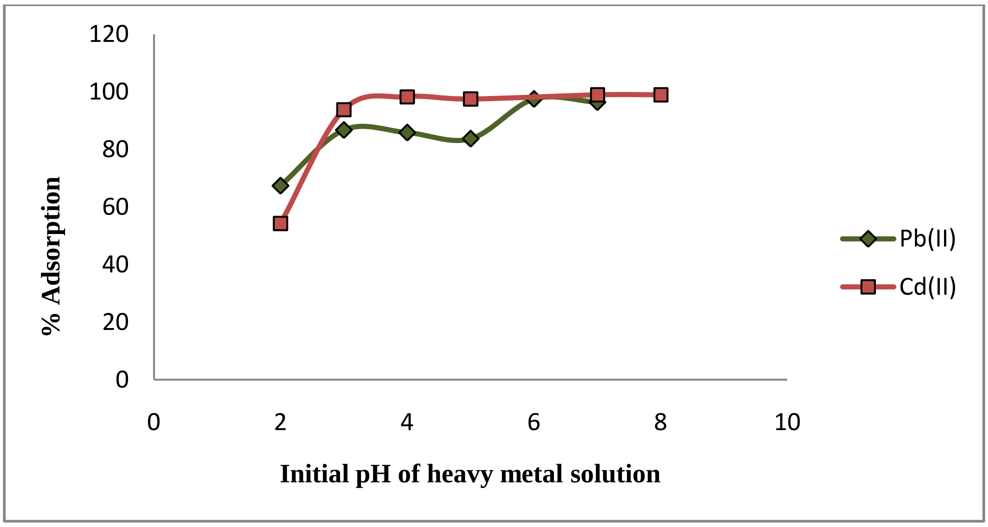


Fig 4.1 Effect of initial pH on adsorption of Pb(II) solution (Initial concentration 10 mg/L, contact time 90 min, adsorbent dose 0.1g/50 mL solution, temperature 30℃, 150 rpm) and Cd(II) solution (Initial concentration 10 mg/L, contact time 150 min, adsorbent dose 0.1g/50 mL solution, temperature 30℃, 150 rpm)

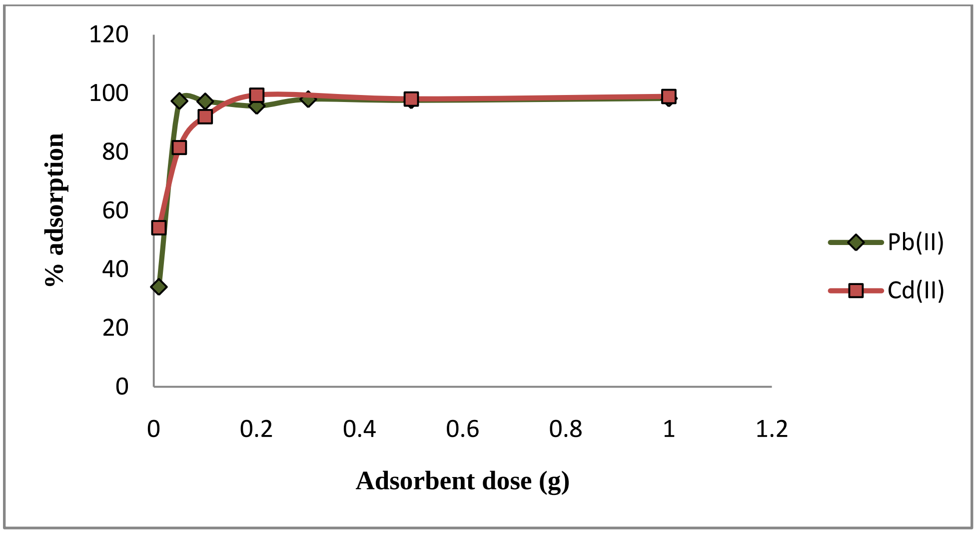
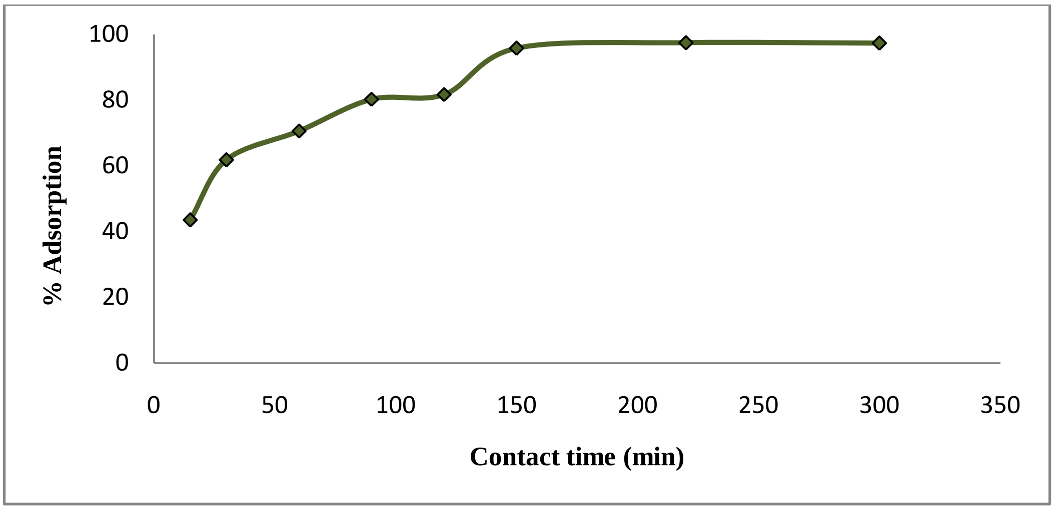
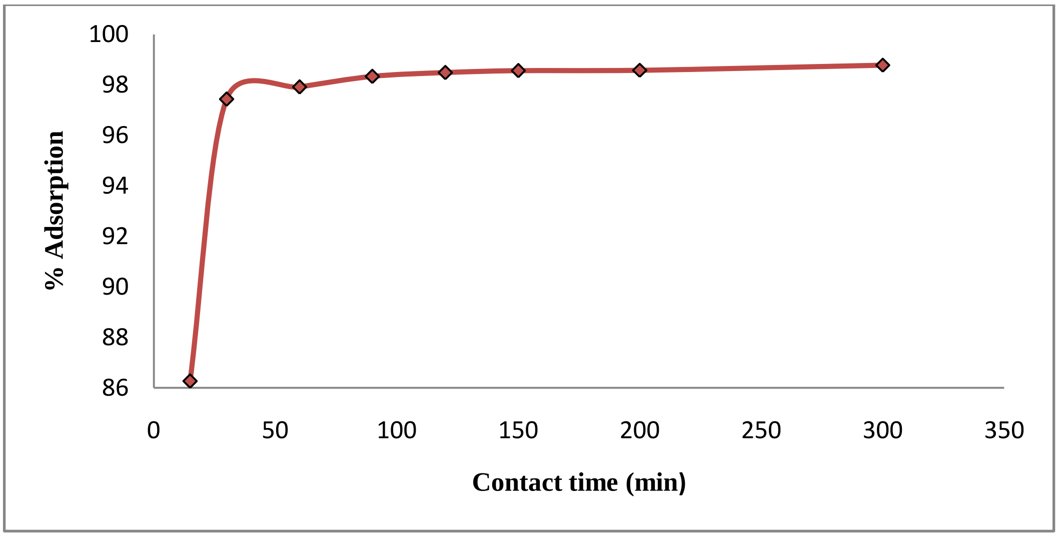


Fig. 4.2 Effect of adsorbent dose on adsorption of Cd(II) solution (Initial concentration 50 mg/L, pH 6, contact time 200 min, adsorbent dose 0.1g/50 mL solution, temperature 30℃, 150 rpm), Effect of adsorbent dose on adsorption of Cd(II) solution (Initial concentration 10 mg/L, contact time 90 min, adsorbent dose 0.1g/50 mL solution, temperature 30℃, 150 rpm)



(a)



(b)

Fig 4.3(a) Effect of contact time on adsorption of (a) Pb(II) solution (Initial concentration 10 mg/L, pH 5.5, adsorbent dose 0.05g/50 mL soln, temperature 30℃, 150 rpm)

(b) Cd(II) solution (Initial concentration 10 mg/L, pH 6.0, adsorbent dose 0.1g/50 mL soln, temperature 30℃, 150 rpm)

The curve suggests that at the initial stage, adsorption takes place rapidly on the external surface of the adsorbent. From the figure it is clear that the removal of metal ions increased with increase in agitation time and attained equilibrium by 60 min for Pb(II) and Cd(II) with initial concentration of 10 mgL^{-1} onto the PAC.

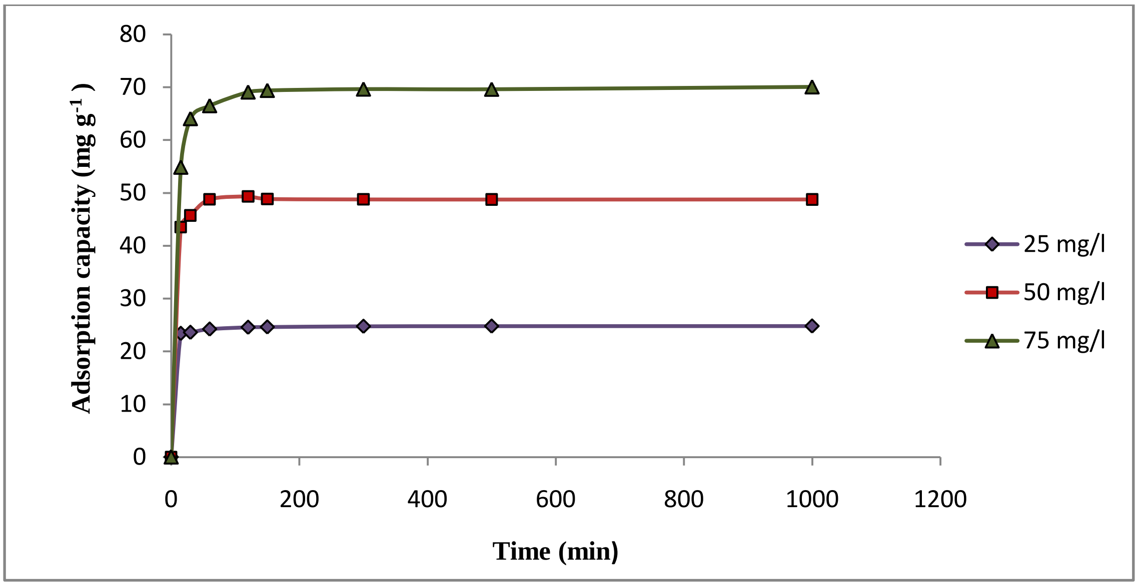


Fig 4.3 (c) Effect of contact time on Pb(II) removal at different concentrations

4.3.4 Effect of initial concentration

In order to study the effect of initial heavy metal ion concentration some experiments were conducted. To investigate effect of Pb(II) ions, experiments were conducted for different initial concentrations 25 mg/L, 50 mg/L and 75 mg/L keeping pH of solution, adsorbent dose and temperature constant at 6, 0.1 g/L and 30°C respectively. Fig 4.4 shows the uptake of Pb(II) and Cd(II) with time at different initial concentrations.

4.3.5 Effect of temperature

It is expected that adsorption processes (either from gas or liquid phase) are exothermic due to the heat released after bond formation between solute and adsorbent.

The general behaviour of an adsorption process is that uptake of adsorbate decreases with increase in temperature for a given temperature range. As observed from the Fig 4.5, removal slightly increases as temperature increases from 25°C to 35°C and then it decreases when temperature is increased upto 45°C.

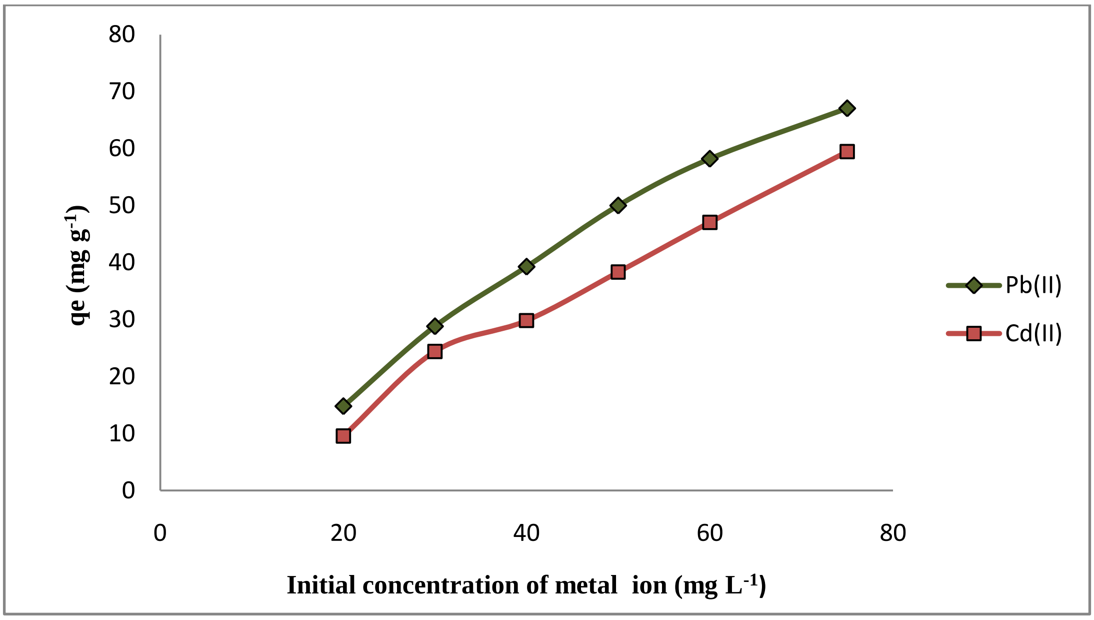


Fig 4.4 Effect of initial concentration of metal ions on their removal by PAC

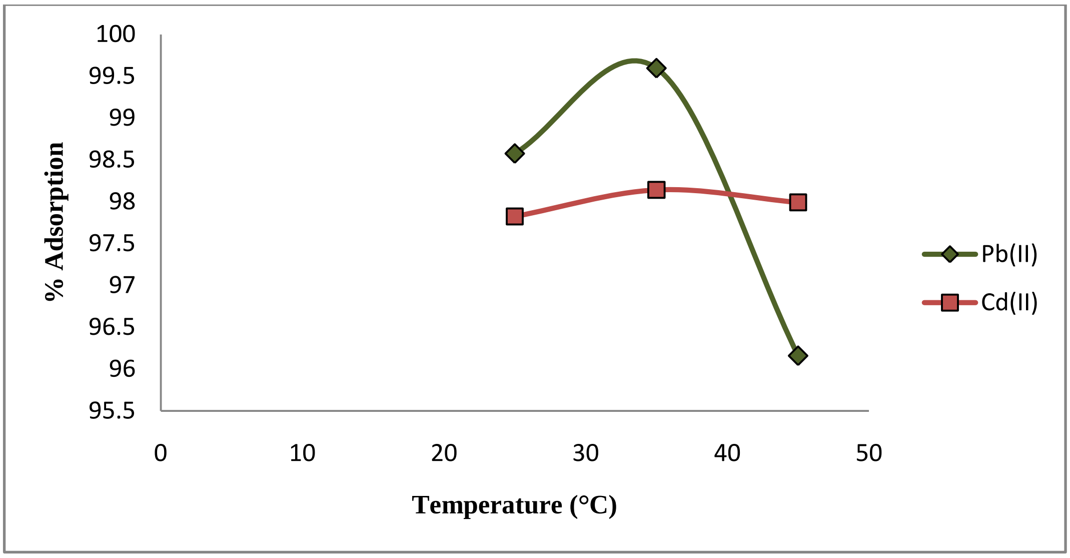


Fig 4.5 Effect of temperature on removal of metal ions

4.3.6 Adsorption Isotherms

Langmuir equation and Freundlich equation were applied for adsorption equilibrium for parthenium based activated carbon. Adsorption isotherm data for Pb^{++} and Cd^{++} adsorption were plotted and presented in Fig. 4.6 and 4.7. Equilibrium data obtained for the two adsorbents were fitted to the Langmuir and Freundlich isotherms. The following expressions of a straight line were used, found by means of mathematical transformation of isotherms.
Langmuir isotherm equation $q_e = Q_o b C_e / (1 + bC_e)$ can be linearized to:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o}$$

where C_e is the liquid phase concentration of adsorbate at equilibrium (mg.L^{-1}), q_e is the amount of adsorbate absorbed at equilibrium (mg. g^{-1}), Q_o is the monolayer adsorption capacity of the adsorbent (mg. g^{-1}) and b is Langmuir adsorption constant (L. mg), related to the free energy of adsorption. Q_o and b can be calculated from the slope and intercept of the linear plot, C_e/q_e versus C_e. Such adsorption is valid when: (i) the adsorbent surface is homogeneous, (ii) both surface and bulk surface exhibit ideal behavior, and (iii) the adsorption film is monolayer **(Mostaedi et al., 2010).**

The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant of separation factor or equilibrium parameter, R_L, which is defined as

$$R_L = \frac{1}{1 + bC_o}$$

where b is the Langmuir constant and C_o is the initial concentration of metal ions. The R_L value indicates the shape of isotherm. R_L values between 0 and 1 indicate favorable adsorption, while $R_L > 1$, $R_L = 1$, and $R_L = 0$ indicate unfavorable, linear, and irreversible adsorption isotherms respectively.

The Freundlich isotherm equation $q_e = k_f C_e^{(1/n)}$ can be written in the linear form as given below

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

where C_e is the equilibrium metal ion concentration (mg.L^{-1}), q_e is the amount of metal ion absorbed at equilibrium (mg. g^{-1}), k_f and n are the Freundlich constants which are related to the sorption capacity and intensity, respectively. The Freundlich constants k_f and n can be calculated from the intercept and slope of the linear plot with log q_e versus log C_e.

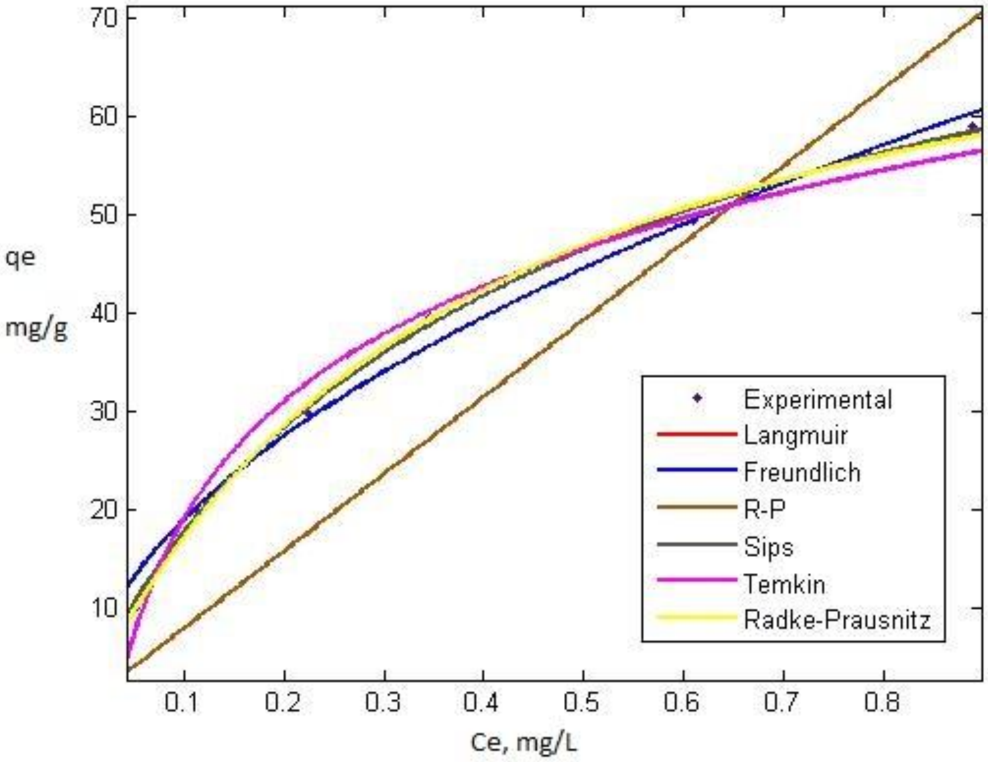


Fig 4.6 Adsorption isotherms for Pb(II)

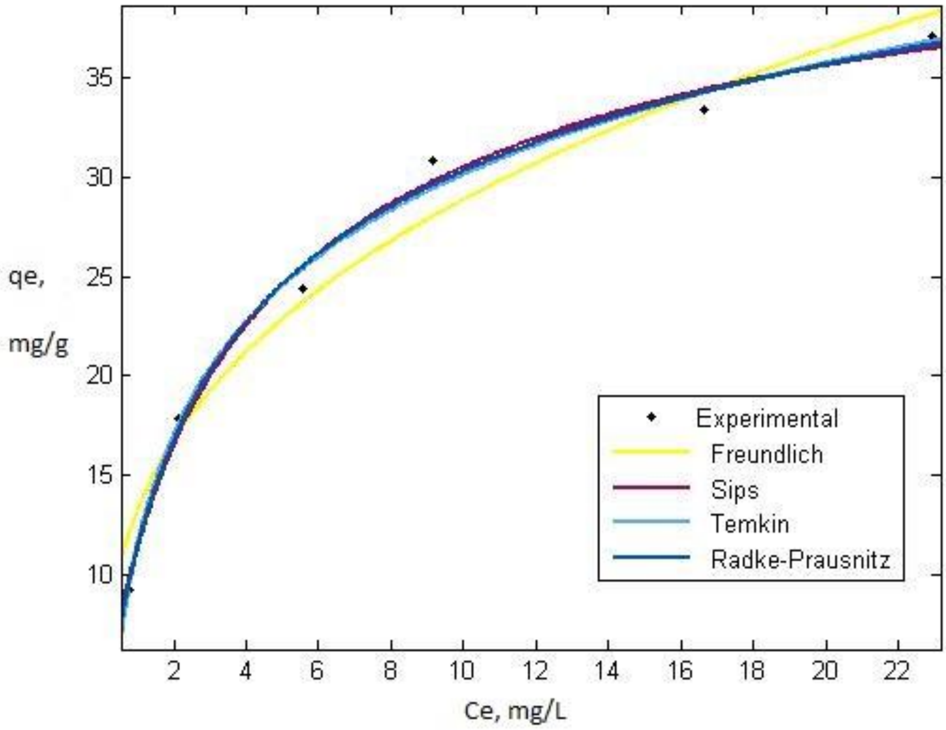


Fig 4.7 Adsorption isotherms for Cd(II)

Metal ion	**Langmuir** $q_e = \frac{Q_o b C_e}{1 + b C_e}$			**Freundlich** $q_e = K_F C_e^{1/n}$			**R-P** $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$			
	Q_o	b (mg/g)	R^2	K_F (L/mg)	n	R^2	a_R (L/mg)	K_R (L/mg)	g	R^2
Pb(II)	82.8	2.622	0.9966	64.29	1.889	0.9837	78.47	19.05	215.5	0.6537
Cd(II)	47.6	0.584	0.8427	13.27	2.965	0.9643	1.056	1.131	0.313	0.4114

Metal ion	**Sips** $q_e = \frac{K_s C_e^{\beta_S}}{1 + a_s C_e^{\beta_S}}$				**Temkin** $q_e = \frac{RT}{b_T} \ln A_T C_e$			**Radke-Prausnitz** $\frac{1}{q_e} = \frac{1}{K C_e} + \frac{1}{k C_e^{1/n}}$			
	Ks	a_s(mg/g)	β_S	R^2	A_T (L/mg)	b_T	R^2	K	k	n	R^2
Pb(II)	164.9	1.71	0.8792	0.9977	30.84	145.6	0.9849	217.1	82.81	-1.27e+4	0.9943
Cd(II)	15.06	0.3217	0.7646	0.9914	4.166	306.9	0.9425	20.04	26.36	7.593	0.9922

Table 4.1 Equilibrium isotherm constants for Pb(II) and Cd(II) adsorption on parthenium based activated carbon at 35°C

4.3.7 Adsorption kinetics

In order to determine the kinetic parameters, experiments were conducted at different initial concentrations. For Pb(II), three initial concentrations 25, 50, 75 mg/L taken, keeping pH constant at 6.0, temperature 30°C and adsorbent dose at 0.05 g/50mL. At each initial concentration, the concentration, the concentrations were estimated at various time intervals and qt values were calculated using equation (4.3). The equilibrium value qe was calculated after 300min.

For Cd(II), three initial concentrations 25, 50, 75 mg/L were taken, keeping pH constant at 6.0, temperature 35°C and adsorbent dose at 0.1 g/50mL. The equilibrium value qe was calculated after 150min.

The goodness of fit of a correlation with experimental data is generally measured in terms of correlation coefficient, normalized deviations.

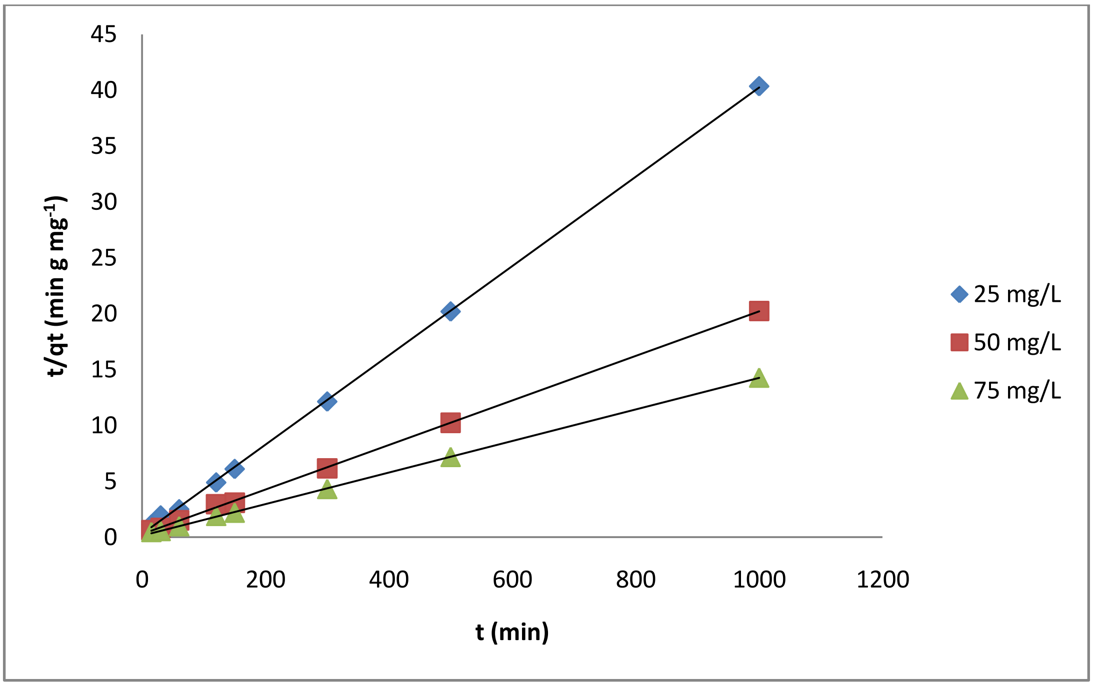


Fig 4.8 Pseudo-second-order kinetics plots for the removal of Pb(II)

Table 4.2 Pseudo-first order kinetic constant for adsorption of Pb(II) on parthenium based activated carbon

S.No.	Concentration of Pb(II) (mg/L)	Pseudo-first order kinetics			
		k_1 (min^{-1})	q_e predicted(mg g^{-1})	q_e experimental (mg g^{-1})	R^2
1	25	0.027	4.124	24.736	0.7524
2	50	0.0749	18.239	48.761	0.858
3	75	0.0341	30.087	69.582	0.9428

Table 4.3 Pseudo-second order kinetic constant for adsorption of Pb(II) on parthenium based activated carbon

S.No.	Concentration of Pb(II) (mg/L)	Pseudo-second order kinetics			
		k_2 (g mg^{-1} min^{-1})	q_e predicted(mg g^{-1})	q_e experimental (mg g^{-1})	R^2
1	25	5.424×10^{-3}	25.06	24.736	0.9997
2	50	1.36×10^{-3}	50.25	48.761	0.9996
3	75	1.359×10^{-3}	70.92	69.582	0.9998

Taking into account the value of correlation coefficient, we can say Pseudo-second order is the best-fitting.

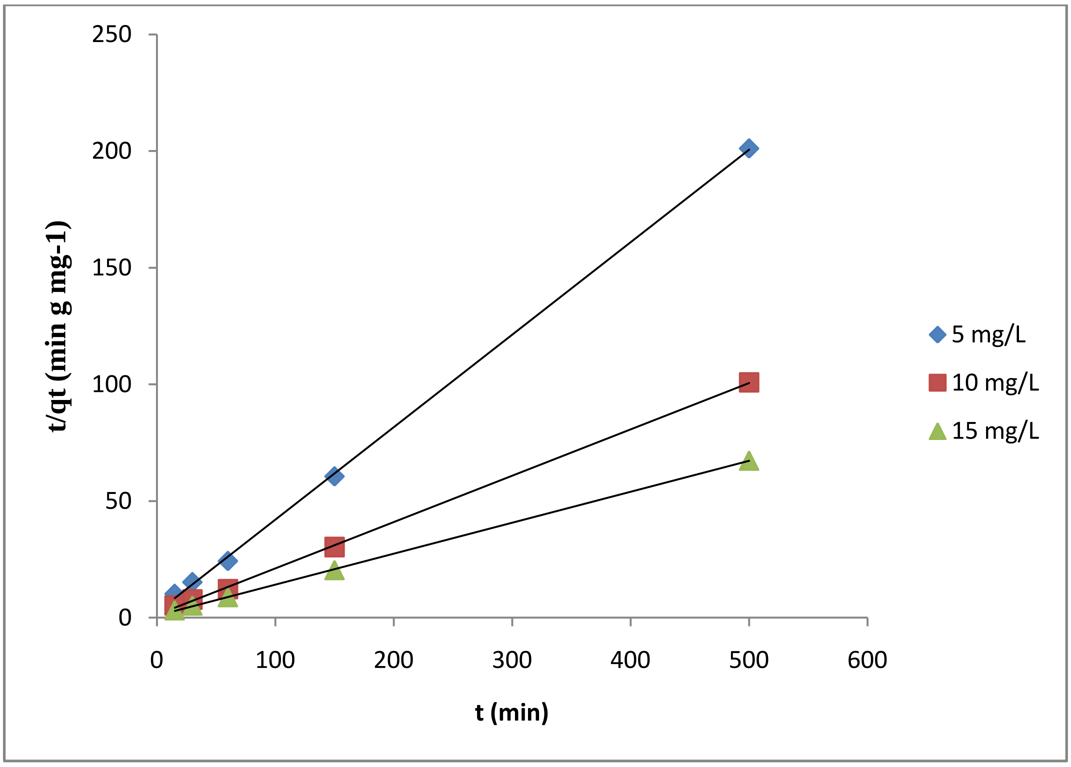


Fig 4.9 Pseudo-second-order kinetics plots for the removal of Cd(II)

Table 4.4 Pseudo-first order kinetic constant for adsorption of Cd(II) on parthenium based activated carbon

S.No.	Concentration of Cd(II) (mg/L)	Pseudo-first order kinetics			
		k_1 (min^{-1})	q_e predicted(mg g^{-1})	q_e experimental (mg g^{-1})	R^2
1	5	0.1135	8.328	24.736	0.9589
2	10	0.0863	9.96	48.761	0.9708
3	15	0.0351	4.3776	69.582	0.9999

Table 4.5 Pseudo-second order kinetic constant for adsorption of Cd(II) on parthenium based activated carbon

S.No.	Concentration of Cd(II) (mg/L)	Pseudo-second order kinetics			
		k_2 (g mg^{-1} min^{-1})	q_e predicted(mg g^{-1})	q_e experimental (mg g^{-1})	R^2
1	5	0.0638	2.525	24.736	0.9997
2	10	0.0297	5.04	48.761	0.9995
3	15	0.0184	7.547	69.582	0.9998

4.4 CONCLUSIONS

P. hysterophorus which is a pernicious weed and spread vastly all over is proved to be a very efficient adsorbent for very toxic metal ions lead and cadmium. Effect of pH, dose, temperature, contact time and initial concentration of metal ions was assessed and adsorption experiments were conducted in batch wise manner. Optimum pH for lead and cadmium ions was observed to be 5.5 and 6.0 and optimum dose came out to be 0.1 g and 0.2 g respectively. The obtained experimental data were tried to fit various adsorption isotherms Langmuir, Freundlich, Redlich-Peterson, Sips, Temkin and Radke-Prausnitz isotherms using MATLAB. In which, Langmuir, Sips and Radke-Prausnitz showed the best fit for Pb(II) and Sips and Radke-Prausnitz fitted best for Cd(II), with R^2 >0.99. From experiments conducted at different time intervals, pseudo first and pseudo second order rate equations were analyzed, among which pseudo second order rate equation model exhibited high correlation coefficient (R^2=0.99) for both the metals.

From the result of percentage removal, we can say for future use, *P. hysterophorus* can be very useful in wastewater treatment.

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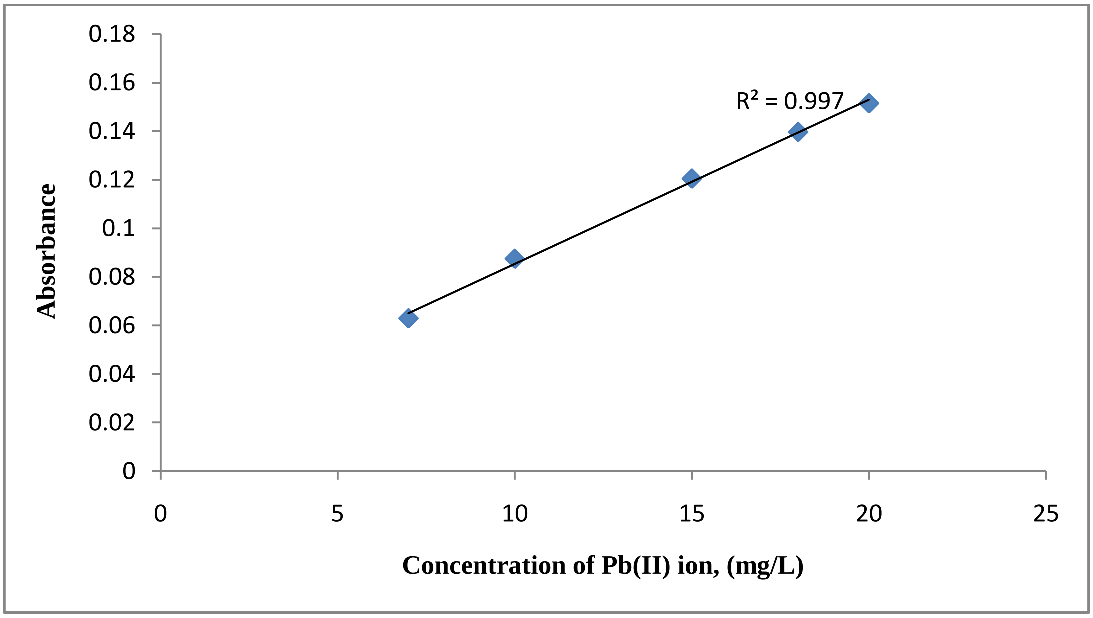
APPENDIX

Calibration curve for lead ions



Calibration curve for cadmium ions