



ADSORPTIVE REMOVAL OF LEAD (II) USING AN ACTIVATED CARBON PREPARED FROM *PASSIFLORA FOETIDA* SEEDS

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ABSTRACT

The water pollution due to the contamination of heavy metals is drastically increasing. Lead (II) is one of the major heavy metal causing many diseases to human community. In this study, adsorptive removal of lead (II) from aqueous solution was performed using a non-conventional activated carbon (PSC) prepared from the seeds of *Passiflora foetida* plant using HCl as an activating agent. The prepared adsorbent has a surface area of 179 m²/g. The maximum amount of lead (II) removal was observed at a pH of 4.5. The adsorption of lead (II) increases with increasing the initial concentration from 20 to 60 mg/L and it decreases with increases in temperature. The adsorption of lead(II) by PSC follows pseudo-second order kinetics and Langmuir type of isotherm. The negative value of Gibbs free energy indicates the spontaneous nature of adsorption. The adsorption of lead (II) by PSC is favorable and spontaneous in nature. The desorption studies indicates that lead (II) can be desorbed using an eluent with low pH (2.0 to 3.0).

Key words: Adsorption, Surface area, *Passiflora foetida*, Isotherm and kinetics.

INTRODUCTION

Rapid industrialization all over the world creates lot of water pollutants. Among the pollutants discharges into the water bodies, heavy metal pollution seems to be more hazardous as far as the human health is concerned. Lead (Pb) is a typical heavy metals present large quantity in the environment. Many industrial operations like pigment manufacturing, paint manufacturing, manufacture of batteries, disposal of electronic wastes etc creates lot of lead (Pb) related pollution¹. Similarities of lead(II) with calcium(II) makes human body to consumer lead(II) instead of calcium(II). Lead(II) intake can cause brain

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damage in children even at extremely low concentration^{2,3}. The maximum permissible limit of lead(II) in drinking water is 0.05 mg/L⁴.

In the present context, it is highly essential to remove lead(II) present in the water and industrial effluents before discharging them into the fresh water bodies. There are many methods available for the removal of heavy metals from contaminated water. Oxidation, reduction, ion exchange and adsorption⁵. Among these, adsorption using activated materials seems to be the best because of its wide selectivity, simple operation, low separating cost etc. Plenty of materials like were successfully employed for the removal of heavy metal from contaminated waste water⁶⁻⁸. Whereas the high material cost limits the suitability of these adsorbents for the removal of heavy metals⁹. Waste material of biological origin or agro waste materials as a precursor for the manufacture of activated carbon can reduce the cost of synthesis as well as it make a way for the suitable disposal of wastes¹⁰.

Based on the above facts, it is planned to synthesize an activated carbon from *Passiflora foetida* plant seeds. The synthesized activated carbon use for the adsorptive removal of lead(II) from aqueous solutions in batch mode. In the present investigation, the efficiency of low cost adsorbent material prepared from *Passiflora foetida* plant seed for the removal of lead(II) from aqueous solution was tested. The removal amount of lead(II) was measured in different conditions such as adsorbent dosage, initial lead(II) concentration, solution pH, contact time and temperature. Adsorption kinetics, equilibrium isotherm and thermodynamic parameters of the process were also investigated.

EXPERIMENTAL

Preparation of adsorbent

The *Passiflora foetida* plant seeds are collected and dried in sun light to remove the moisture content. The dried seeds were mixed with 4N HCl and boiled for three hours. Then the material soaked in the same acid for 24 h at room temperature. After 24 h, the excess acid was decanted and then the material washed several times with distilled water to remove the free acid. Then the solid mix was dried at outdoor. After drying, the material was heated to 400°C in a muffle furnace. The charred material was washed with double distilled water to remove any soluble impurities present. After washing, the carbon was dried, crushed, and grinded well. Then the material was sieved to obtain average particles of 180 to 300 μ size (ASTM Sieve). The sieved carbon was activated in a muffle furnace at 800°C for 10 min and then stored in an air tight container for further adsorption studies.

Adsorption studies

A stock solution of 1000 mg/L lead(II) is freshly prepared by dissolving 1.600 g of AR $\text{Pb}(\text{NO}_3)_2$ in double distilled water and diluting to one liter. Solutions of desired concentrations are then obtained by successive dilutions. The pH of solution was measured by using digital pH meter (Elico: Model LI-120). The lead(II) adsorption was measured by using visible spectrophotometer (Elico Make: Model SL 207). The conductivity is measured by using Digital Conductivity Meter (Deep vision model M-180). Temperature controlled orbital shaker (Rivotek Model) is used for the equilibrium studies. The effect of pH on lead(II) adsorption was investigated in the initial pH range of 2-7. The initial pH of the solution was adjusted by using 0.1 N HCl or 0.1 N NaOH.

Lead was determined spectrophotometrically using PAR reagent (sodium salt of 4-(2-pyridylazo) resorcinol). 2.5 mL of the sample solution containing lead(II) was transferred to 25 mL standard measuring flask. 10 mL of ammonia and ammonium chloride buffer solution (33.8 g ammonium chloride + 246 mL of ammonia made up to 500 mL with double distilled water) was added to provide a pH of 10.0 followed by 1 mL of 0.01% solution of PAR reagent. The solution was made up to the mark with double distilled water. The concentration of lead(II) was determined at 520 nm.

For kinetic studies, 100 mL of the lead(II) solution (initial concentrations 20, 30, 40, 50 and 60 mg/L) and 0.3 g activated carbon were agitated until reaching the adsorption equilibrium. After adsorption, the solutions were centrifuged and the concentrations of the solutions were determined by using a visible spectrophotometer. For isotherm studies, 0.3 g of activated carbon samples were mixed with 100 mL solutions of various Pb(II) concentrations between 10 mg/L and 110 mg/L in the isothermal shaker for 90 min at 30, 35, 40 and 45°C constant temperatures. After adsorption, the solutions were centrifuged and the concentrations of the Lead(II) ions remaining un-adsorbed were determined as stated above.

Kinetics of adsorption

Many kinetic models have been proposed to elucidate the mechanism of solute adsorption. The rate and mechanism of adsorption is controlled by various factors like physical and/or chemical properties of adsorbent as well as mass transfer process. These kinetic models are useful for the design and optimization of effluent treatment process. In order to investigate the mechanism of lead(II) adsorption by PSC the following four kinetic models were considered.

Pseudo first-order kinetic model

The pseudo first-order kinetic model was proposed by Lagergren¹¹.

The integrated form of the model is –

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

Hence, a linear trace is expected between the two parameters, $\log(q_e - q_t)$ and t , provided the adsorption follows first order kinetics. The values of k_1 and q_e can be determined from the slope and intercept.

Pseudo second-order kinetics

The adsorption may also be described by pseudo second-order kinetic model¹², if the adsorption does not follow the first order kinetics. The linearized form of the pseudo second-order model is –

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

A plot of t/q_t and t should give a linear relationship if the adsorption follows second order. q_e and k_2 can be calculated from the slope and intercept of the plot.

Elovich model

The Elovich equation is mainly applicable for chemisorption kinetics. The equation is often valid for systems in which the adsorbing surface is heterogeneous¹³. The Elovich model is generally expressed as –

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}$$

Integrating this equation for the boundary conditions, give –

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$$

A plot of $\ln t$ versus q_t gives a linear trace. The constant α , initial adsorption rate and another constant β is related to extent of surface coverage were determined from the slope and intercept.

Intra particle diffusion model

In the batch mode adsorption process, initial adsorption occurs on the surface of the adsorbent. In addition, there is a possibility of the adsorbate to diffuse into the interior pores of the adsorbent. Weber and Morris¹⁴ suggested the following kinetic model to investigate whether the adsorption is intra-particle diffusion or not. According to this theory.

$$q_t = k_d \cdot t^{1/2}$$

A plot of $t^{1/2}$ and q_t should give a linear relationship, if the adsorption follows intra-particle diffusion.

Adsorption isotherm

The equilibrium existence of adsorbate between the liquid and solid phase is well described by adsorption isotherms. Experimental isotherm data collected at different temperatures fit in Langmuir, Freundlich and Dubinin-Raduskevich adsorption isotherm models.

Langmuir model

The Langmuir model¹⁵ was originally developed to describe the adsorption of gas on to solid surface. It suggests the formation of monolayer adsorption and also the surface is energetically homogeneous. The Langmuir isotherm can be expressed as –

$$q_e = \frac{Q_0 \cdot b_L \cdot C_e}{(1 + b_L \cdot C_e)}$$

Linear form of the rearranged Langmuir model is –

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot b_L} + \frac{C_e}{Q_0}$$

The constants Q_0 and b_L can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e .

Freundlich Model

It is a most popular model for a single solute system, based on the distribution of solute between the solid phase and aqueous phase at equilibrium¹⁶. The Freundlich equation is expressed as;

$$q_e = k_f C_e^{1/n}$$

Linear form of Freundlich equation is –

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

When $1/n$ is > 1.0 , the change in adsorbed dye concentration is greater than the change in the solute concentration. The Freundlich parameters k_f and n calculated by the plot of $\log q_e$ versus $\log C_e$.

Tempkin isotherm

Tempkin isotherm takes into account of the effect of indirect adsorbate-adsorbate interaction on adsorption and suggests that the heat of adsorption of all molecules in the adsorbent surface layer would decrease linearly with coverage¹⁷. The linear form of Tempkin isotherm can be expressed as –

$$q_e = \frac{RT}{b_T} \ln a_T + \frac{RT}{b_T} \ln C_e$$

The Tempkin sorption potential (a_T) and the Tempkin constant related to heat of adsorption (b_T) calculated from the slope and intercepts of the plot q_e versus C_e .

Dubinin-Radushkevich isotherm

The isotherm proposed by Dubinin¹⁸ has the following form

$$q_e = q_D \cdot e^{-B\varepsilon^2}$$

Linear form of Dubinin-Radushkevich isotherm is –

$$\ln q_e = \ln q_D - B\varepsilon^2$$

$$\varepsilon = RT \ln(1+1/C_e)$$

A plot of $\ln q_e$ versus ε^2 gives a linear trace and the constants q_D and B calculated from the slope and intercept, respectively. The mean free energy of adsorption E is calculated from B using the following equation

$$E = 1/ (2B)^{1/2}$$

Based on this energy of activation one can predict whether an adsorption is physisorption or chemisorption. If the energy of activation is < 8 kJ/mol, the adsorption is

physisorption and if the energy of activation is 8 to 16 kJ/mol, the adsorption is chemisorption in nature.

Thermodynamics of adsorption

The thermodynamic parameters related to the adsorption of Pb(II) on to PSC was evaluated using the following relationship¹⁹.

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T}$$

Where, K_c is an equilibrium constant, R is the gas constant (8.314×10^{-3} kJ/K/mol) and T is temperature (K). The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the Van't Hoff plots of $\ln K_c$ vs $1/T$. The Gibbs free energy change for the adsorption of Lead(II) by PSC is calculated from the following expression,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

RESULTS AND DISCUSSION

Physicochemical characteristics of the adsorbent

The physical characteristics of the adsorbent prepared from *Passiflora foetida* plant seed (PSC) were given in the Table 1.

Table 1: Physico-chemical characteristics of the adsorbent

S. No.	Parameters	Adsorbent
1	pH	7.54
2	Moisture content (%)	4.66
3	Bulk density (g/mL)	0.71
4	Conductivity (mS/cm)	0.34
5	Specific gravity	1.25
6	Ash content (%)	1.73
7	Iodine value (mg/g)	116
8	pH _{ZPC}	7.85
9	Surface area (S _{BET}) (m ² /g)	179

The activated carbon PSC has a BET surface area of 179 m²/g. The surface area is comparable with the various low cost adsorbents. Presence more moisture will increase the unnecessary weight, thereby reduces the adsorbate removal capacity of adsorbent²⁰. Moisture content of the prepared activated carbon (PSC) was 4.66%, which is good for the large scale applications of PSC. The low ash content of the carbon (1.73%) indicates the lower inorganic content and higher carbon content. The lower bulk density value (0.71 g/mL) shows that the prepared activated carbon is more porous nature. The obtained zero point charge (pH_{ZPC}7.85) implies that the prepared carbon is free from surface charges nearby neutral pH. Hence the carbon is suitable for the treatment of water even at the neutral medium. The high iodine number reveals that the presence of high porosity in the carbon¹⁹. The calculated iodine value and porosity of the prepared activated carbon reveals that it can be used as an adsorbent for the removal of Pb(II) from aqueous solutions.

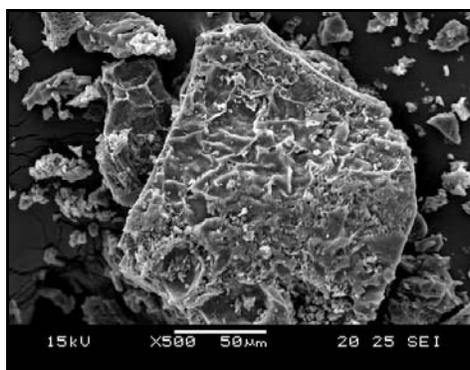


Fig. 1: SEM image of PSC

The SEM image of acid treated activated carbon (PSC) is shown in Fig. 1. The figure represents a higher magnification image of the activated carbon exhibiting pitted surface, heterogeneous, porous morphology. The SEM suggests that activation of the carbon resulted in development of ‘humps and holes’ and porosity on the surface of activated carbon which will ultimately results in increased surface roughness and surface area. This development of void surface favors adsorption on the adsorbent surface. The image shows that the pores are interconnected by the cell walls of the precursor at regular intervals which are meso/micro pores in nature.

Effect of pH

The study on the effect of pH on the adsorption of lead(II) onto PSC was carried over a pH range of 2.0 to 6.0. The variation of Pb(II) adsorption with respect to pH is graphically presented in Fig. 2. At lower pH (pH = 2.0), more H⁺ ions present in the

solution, which will compete with the lead(II) ions for the sorption sites, there by the amount of Pb^{2+} adsorption is very low. On increasing the pH from 2.0 to 4.0 the adsorption slightly increases. At this pH range (2.0 to 4.0) the surface of adsorbent is protonated (the surface of PSC) and hence the repulsive force between the sorbent surface and lead(II) makes poor adsorption. Even at lower pH, with the experimental conditions many species like Pb^{2+} , Cl^- , $PbCl^+$, $PbCl_2$, $PbCl_3^-$ and $PbCl_4^{2-}$ were exists²¹. These anionic species were adsorbed on the positively charged adsorbent surface through ion exchange mechanism. When the pH exceeds 4.5 the adsorption increases sharply and reaches the maximum adsorption of 84% at a pH of 4.5 to 5.5

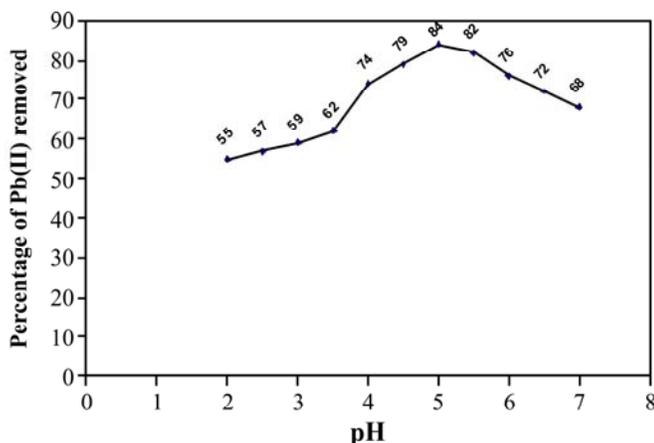


Fig. 2: Effect of pH for the adsorption of lead(II) onto PSC

At these intermediate pH range, the reduction in H^+ ion concentration makes less competition for $Pb(II)$ ion to the sorbent surface. Owing to this, the amount of lead(II) adsorption reached the high level at the pH range of 4.5 to 5.5 similar kind of results were observed for the adsorption of lead(II) on to Ethylenediamine modified yeast biomass coated with magnetic chitosan nano particles²². Beyond the pH of 5.5 $Pb(OH)_2$ formation will takes places, therefore pH 5.5 was fixed for all further adsorption.

Effect of initial lead(II) concentration

The variation of lead(II) adsorption onto PSC at various initial lead(II) concentration are shown in Fig. 3. The maximum percentage of adsorption decreases from 89.9% to 67.2% on increasing the initial metal ion concentration from 20 to 60 mg/L. Through the percentage of adsorption decreases, the amount of lead(II) adsorbed per gram of adsorbent increases from 4.49 mg/g to 10.08 mg/g on increasing the initial metal ion concentration from 20 to 60 mg/L. As the concentration increased, the number of lead(II) ions competing for the

sorbent surface increases leads to high uptake at higher concentrations. The study on the effect if adsorption of lead(II) by PSC is depends lead(II) ion concentration.

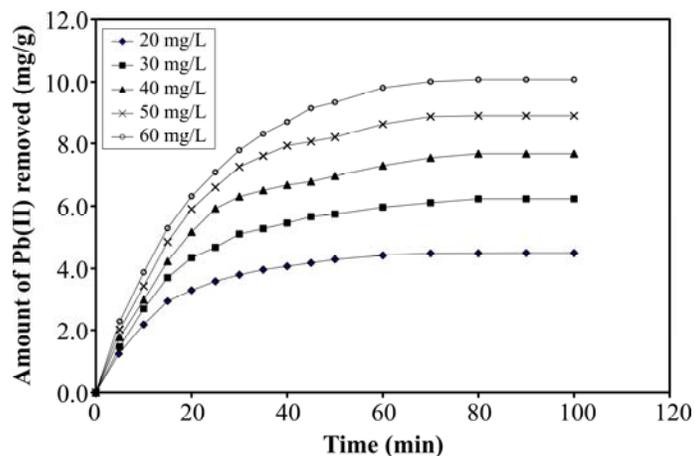


Fig. 3: Effect of initial concentration for the adsorption of lead(II) onto PSC

Effect of temperature

In-order to analyze the effect of temperature on the adsorption of lead(II) by PSC adsorption experiments were carried out by varying the solution temperature from 30 to 45°C by fixing the initial lead(II) concentration at 40 mg/L as shown in Fig. 4. On increasing the temperature from 30 to 45°C the adsorption lead(II) by PSC decreased from 7.67 mg/g to 6.30 mg/g.

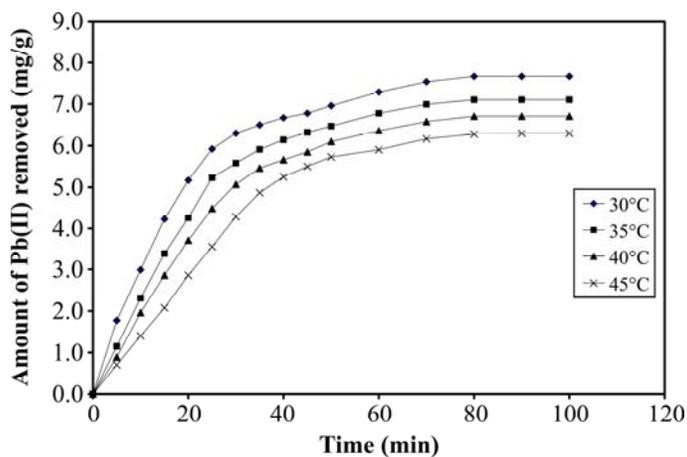


Fig. 4: Effect of temperature for the adsorption of lead(II) onto PSC

The decrease of adsorption on increasing the temperature indicates the exothermic nature of adsorption. At high temperature the rate of adsorption increased due to high kinetic energy of lead(II) ions, Which ultimately leads to lower adsorption at lower temperature²³.

Adsorption kinetics

The adsorption of lead(II) by PSC is analyzed kinetics for the using pseudo-first order, pseudo-second order, Elovich kinetics models and the adsorption mechanism was analyzed using intra-particle diffusion model. The kinetic studies are essential to investigate the mechanism of adsorption and the potential rate controlling step²³.

Pseudo-first order, pseudo-second order plots for the adsorption of lead(II) on to PSC is shown in Fig. 5a and 5b. (Elovich plot not shown) and the results of the kinetic models are given in Table 2. On increasing the lead(II) concentration from 20 to 60 mg/L, the pseudo-first order rate constant varies from 4.882×10^{-3} to 5.044×10^{-2} min on increasing the temperature from 30 to 45°C. The q_e calculated using pseudo-first order kinetic model shows good similarities with the experimental values at low concentrations and low temperature. It deviates from the experimental q_e at higher concentrations as well as higher temperatures. The pseudo-second order rate constant show a steady decrease on increasing the initial concentration as well as temperature of the solution. Among the three kinetic models analyzed in this study, pseudo-second order kinetic model shows a good fit with the experimental data. The good fitness of the data for the adsorption of lead(II) onto PSC with the second order kinetic model indicates that the adsorption follows second order kinetics. The rate limiting step for this adsorption might be chemisorption involving through sharing or exchange of electrons between the adsorption sites and lead(II) ions²⁵.

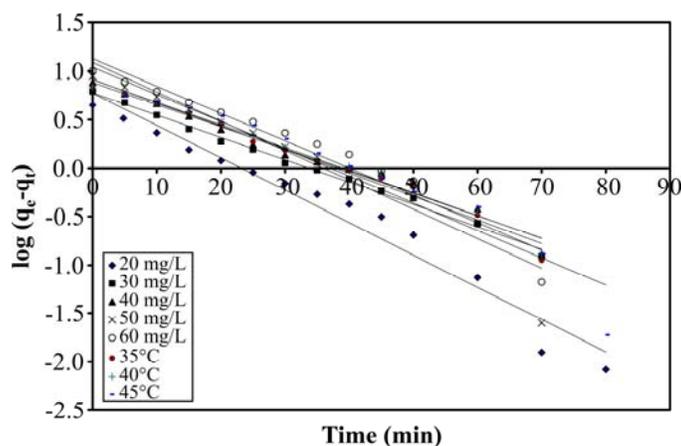


Fig. 5a: Pseudo-first order plot for the adsorption of lead(II) onto PSC

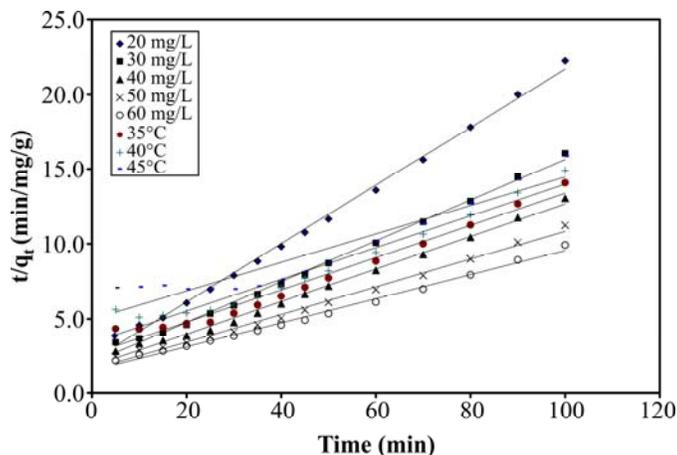


Fig. 5b: Pseudo-second order plot for the adsorption of lead(II) onto PSC

Table 2: Calculated kinetic parameters for the adsorption of lead(II) onto PSC

Parameters	Initial lead(II) concentration, mg/L					Temperature (°C)			
	20	30	40	50	60	30	35	40	45
$q_{e,exp}$ (mg/g)	4.49	6.23	7.67	8.90	10.08	7.67	7.11	6.71	6.30
<i>Pseudo first order kinetics</i>									
$k_1 \times 10^{-2}$ (min ⁻¹)	7.715	5.320	5.297	6.978	6.494	5.297	5.044	4.905	4.951
$q_{e,cal}$ (mg/g)	5.97	6.00	7.67	12.27	13.42	7.67	7.43	7.46	7.89
r^2	0.9614	0.9946	0.9781	0.9065	0.9539	0.9781	0.9935	0.9948	0.9748
<i>Pseudo second order kinetics</i>									
$k_2 \times 10^{-2}$ (g/mg/min)	1.703	0.895	0.648	0.535	0.420	0.648	4.363	3.266	1.811
h	0.4488	0.49	0.55	0.63	0.6536	0.55	0.378	0.293	0.201
$q_{e,cal}$ (mg/g)	5.13	7.36	9.22	10.82	12.47	9.22	9.31	9.47	10.54
r^2	0.9968	0.9955	0.9938	0.9922	0.9936	0.9938	0.9752	0.9547	0.8926
<i>Elovich model</i>									
α (mg/g/min)	0.921	0.615	0.483	0.406	0.352	0.483	0.465	0.466	0.455
β (g/mg)	0.985	1.018	1.135	1.267	1.325	1.135	0.79	0.64	0.49
r^2	0.9466	0.9639	0.9608	0.9608	0.9731	0.9608	0.9636	0.9708	0.96

Cont...

Parameters	Initial lead(II) concentration, mg/L					Temperature (°C)			
	20	30	40	50	60	30	35	40	45
<i>Intra particle diffusion model</i>									
k_{id} (mg/g/min ^{1/2})	3.918	2.678	2.335	1.886	1.220	2.335	2.256	2.151	2.003
r^2	0.9912	0.9828	0.9916	0.9824	0.9819	0.9916	0.9955	0.9894	0.9493

The intra-particle diffusion model plot of $\ln t$ versus $t^{1/2}$ at different initial lead(II) concentrations as well as different temperatures are shown in Fig. 6 and results calculated from this plot are given in Table 2. The plot shows multi-linearity with three stages of adsorption. The initial portion of the plot show a sharp increase, which is due to the external surface adsorption or instantaneous adsorption stage. The second linear portion is due to the intra-particle diffusion of solutes on to PSC. The second portion is the slowest one, which is the rate determining step. The third portion is linear was due to the attainment of equilibrium. The second linear portion does not pass through the origin, indicating that intra-particle diffusion is not the sole rate limiting step. Along with pore diffusion film diffusion also plays a significant role for the adsorption of lead(II) onto PSC²⁶.

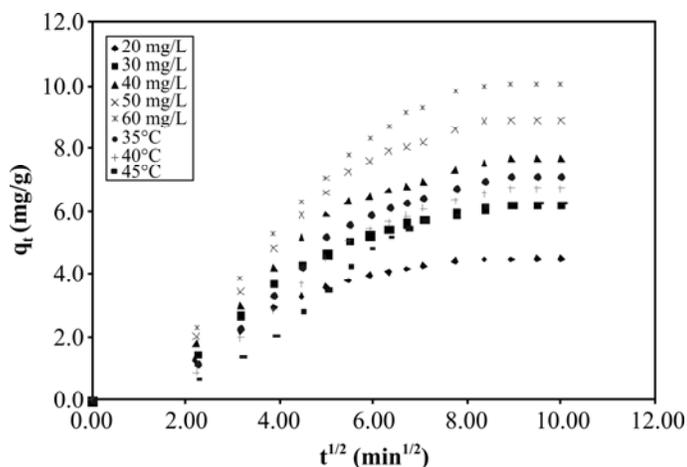


Fig. 6: Intra-particle diffusion plot for the adsorption of lead(II) onto PSC

Isotherm studies

In-order to evaluate the adsorption capacity and the surface properties of adsorbent related to adsorption, it is essential to analyze the adsorption isotherms. In this study, Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich isotherm models were employed for the isotherm studies.

Langmuir isotherm initially derived for gas adsorption based on the assumption of a) monolayer adsorption of solute on the adsorbent surface b) all adsorption sites are energetically equivalent and identical c) one atom or molecule will be accommodated for each between adsorbents²⁷.

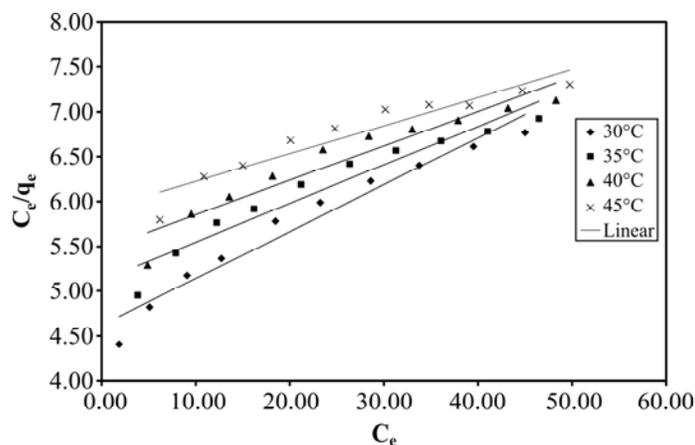


Fig. 7a: Langmuir plot for the adsorption of lead(II) onto PSC

The Langmuir and Freundlich (Tempkin and D-R plots are not shown) plots are shown in Fig. 7a and 7b respectively, the results calculated from the isotherm plots are given in Table 3. The Langmuir constant b_L decreases from 11.33×10^{-3} to 5.28×10^{-3} (L/mg) on increasing the temperature from 30 to 45°C. The Langmuir monolayer adsorption capacity for the adsorption of lead(II) onto PSC increases from 19.02 to 32.05 mg/g on increasing the temperature from 30 to 45°C.

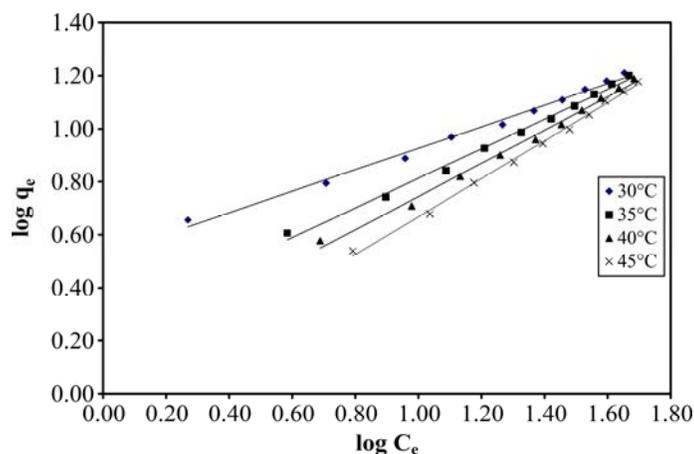


Fig. 7b: Freundlich plot for the adsorption of lead(II) onto PSC

Freundlich isotherm is derived based on the assumption of heterogeneous surface. The value of n varies from 2.47 to 1.39 for the range of temperatures under investigation. The value of n (between 1 to 10) indicates the favorable adsorption of lead(II) onto PSC surface on comparing the correlation coefficients of Langmuir and Freundlich isotherm models, Freundlich model is more appropriate to explain the adsorption of lead(II) onto PSC. As the r^2 value of Freundlich model is more (0.9921 to 0.9969) indicating more surface heterogeneity in PSC during the adsorption of lead(II).

Table 3: Results of isotherm studies for the adsorption of lead(II) onto PSC

Parameters	Temperature °C			
	30	35	40	45
Langmuir isotherm				
Q_0 (mg/g)	19.12	23.31	26.04	32.05
$b_L \times 10^{-3}$ (L/mg)	11.33	8.38	7.02	5.28
r^2	0.9589	0.9339	0.9123	0.9013
Freundlich isotherm				
n	2.47	1.79	1.60	1.39
k_f (mg ^{1-1/n} L ^{1/n} g ⁻¹)	3.32	1.80	1.31	0.89
r^2	0.9921	0.9945	0.9939	0.9969
Tempkin isotherm				
b_T (mg/g)	680.50	532.23	414.51	393.91
a_T (L/mg)	1.197	0.430	0.208	0.165
r^2	0.9326	0.9342	0.9662	0.9653
Dubinini-Raduskevich isotherm				
q_D (mg/g)	13.03	13.06	12.97	12.88
$B \times 10^{-6}$ (mol ² /J ²)	4.0	10.0	20.0	20.0
$E \times 10^{-3}$ (kJ/mol)	2.0	2.0	1.41	1.41
r^2	0.7324	0.7936	0.8334	0.8491

The Tempkin sorption potential (a_T) and the Tempkin constant related to heat of adsorption (b_T) calculated from the slope and intercepts of the plot “ q_e ” versus “ C_e ” (figure

not shown) are given in Table 3. The sorption potential (a_T) decreases from 1.197 to 0.165 L/mg and constant related to heat of adsorption (b_T) varies from 680.5 to 393.91 (mg/g) for the range of temperatures investigated. However, the applicability of this model to describe the adsorption of lead(II) onto PSC is not much appropriate owing to its less degree of fitness.

The values of q_D and B (for D-R model) were calculated from the intercept and slope of the plot " $\ln q_e$ " versus ε^2 (figure not shown). The energy of adsorption E gives information about the mechanism of adsorption (whether physisorption or chemisorption with ion exchange mechanism). The range of mean adsorption energy at 2-20 kJ/mol could be considered physisorption in nature. The magnitude of E ranged between 2.0×10^{-3} to 1.41×10^{-3} kJ/mol indicating the physical nature of bonding between adsorbent and adsorbate. The energy changes involved during the adsorption needs to be confirmed by the thermodynamic studies as the fitness of the isotherm data for the adsorption of lead(II) by PSC is very poor ($r^2 = 0.7324$ to 0.8491) for D-R isotherm model.

Thermodynamics of adsorption

In-order to evaluate the heat changes involved, spontaneity as well as the degree of randomness, it is essential to study the thermodynamics of adsorption.

The Van't Hoff's plot for the adsorption of lead(II) on to PSC is shown in Fig 8. The results of thermodynamic studies are given in Table 4. The Gibbs free energy change (ΔG) is negative for all the range of temperatures under investigation, indicating the favorable and spontaneous nature of adsorption²³. More negative ΔG values at lower temperatures indicating that the adsorption is favored by decrease of temperature.

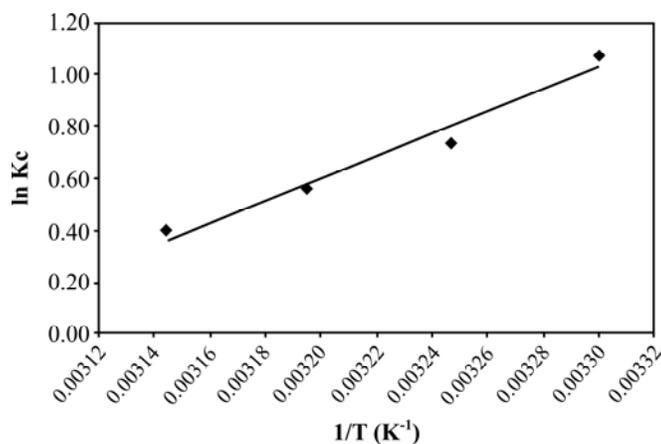


Fig. 8: Van't Hoff's plot for the adsorption of lead(II) onto PSC

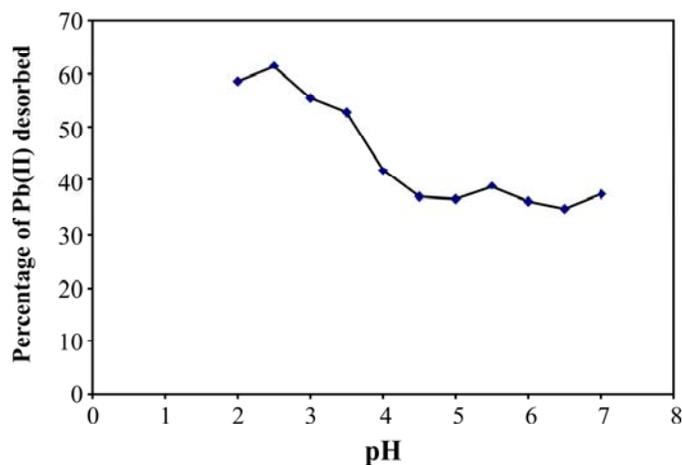
Table 4: Thermodynamic parameters

Temp. (°C)	ΔG° , kJ/mol	ΔH° , kJ/mol	ΔS° , J/K/mol
30	-10.58		
35	-10.76		
40	-10.93	-1.66	34.92
45	-11.11		

The negative ΔH may be due to as the de-protonation process is easy at high temperatures²². The negative value of ΔS indicates that the randomness decreases at the solid-liquid interface when the adsorption progresses. As more and more solute concentrate on the surface of solid, the randomness decreases.

Desorption studies

The desorption studies are helpful to assess the stability and reusability of adsorbent for the adsorptive removal of pollutants present in water. The repeated usage of adsorbent can serve economical benefits for large scale industrial operations. The lead(II) available on the surface of PSC is more desorbed at lower pH. At lower pH the bonding between metal ion and the adsorbent surface is destroyed²⁸, which give more desorption. The desorption studies indicates that the PSC can be effectively used for many cycles for the adsorptive removal of lead(II) from aqueous solutions.

**Fig. 9: Desorption studies of lead(II) onto PSC**

CONCLUSION

Adsorptive removal of lead (II) ion was successfully demonstrated using an activated carbon synthesized from the *Passiflora foetida* plant seed using HCl as an activating agent. The adsorption studies of PSC with lead(II) indicates that, the removal capacity of PSC increases with increasing the concentration of the solute and decreases with increasing the solution temperature. The adsorption of lead(II) by PSC follows pseudo-second order mechanism with good correlation coefficient. The intra particle diffusion studies indicates that pore diffusion also plays a significant role along with intra particle diffusion mechanism. The results of Langmuir isotherm indicates that the surface of PSC favors the monolayer adsorption of lead(II) and the Freundlich isotherm indicates that the surface of PSC is less heterogeneous during the lead(II) adsorption. The correlation coefficient of Freundlich isotherm (0.9921 to 0.9969) is more than the Langmuir isotherm (0.9013 to 0.9589).

REFERENCES

1. M. Momcilovic, M. Purenovic, A. Bojic, A. Zarubica and M. Ranpelovic, *Desalination*, **276**, 53 (2011).
2. Z. H. Li, X. J. Chang, X. J. Zou, X. B. Zhu, R. Nie, Z. Hu and R. J. Li, *Analytica Chimica Acta*, **632**, 272 (2009).
3. L. Zhang, X. J. Chang, Z. H. Li and Q. He, *J. Molecular Str.*, **964**, 58 (2010).
4. M. C. Basso, E. G. Cerrella and A. L. Cukierman, *Ind. Eng. Chem. Res.*, **41**, 180 (2002).
5. World Health Organisation, *Guidelines for Drinking Water Quality, Recommendations*, WHO, Geneva (1984).
6. M. Santhi and P. E. Kumar, *Int. J. Sci. Res.*, **4(5)**, 1968 (2010).
7. P. E. Kumar, *Studies on Characteristics and Fluoride Removal Capacity of Jambonut Carbon*. M.Phil., Disseration: Bharathiar University, Coimbatore, Tamilnadu, India (1991).
8. P. E. Kumar and V. Perumal, *Nat. Environ. Pollut.*, **9(3)**, 513 (2010).
9. K. Velumani, P. E. Kumar and V. Sivakumar, *Ras. J. Chem.*, **9(2)**, 149 (2016).
10. Q. He, Z. Hu, Y. Jiang, X. J. Chang, Z. F. Tu and L. N. Zhang, *J. Haz. Mat.*, **175**, 710 (2010).

11. S. K. Lagergren, *Handingarl*, **24**, 1 (1898).
12. Y. S. Ho and G. McKay, *Pro. Biochem.*, **34**, 451 (1999).
13. A. B. Perez-Marin, V. Meseguer Zapata, J. F. Ortuno, M. Aguilar, J. Saez and M. Llorens, *J. Haz. Mat.*, **B139**, 122 (2007).
14. W. J. Weber and J. C. Morris, *Proc. Int. Conf. Advances in Water Poll. Res.*, **2**, 231 (1963).
15. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
16. H. Freundlich, *Z. Phys. Chem.*, **57**, 385 (1906).
17. M. J. Tempkin and V. Pyzhev, *Acta Physiochim. URSS*, **12**, 217 (1940).
18. M. M. Dubinin, *Chem. Rev.*, **60**, 235 (1960).
19. V. Sivakumar, M. Asaithambi and P. Sivakumar, *Adv. App. Sci. Res.*, **3(1)**, 219 (2012).
20. S. Karthikeyan, P. Sivakumar and P. N. Palanisamy, *E. J. Chem.*, **5**, 409 (2008).
21. J. Zhu, J. Yang and B. Deng, *Environ. Chem. Lett.*, **8**, 277 (2010).
22. T. Li, Y. Liu, Q. Peng, X. Hua, T. Liao, H. Wanga and M. Lu, *Chem. Engg. J.*, **214**, 189 (2013).
23. Y. Tian, C. Jin, M. Zhao, M. Xu and Y. S. Zhang, *Chem. Eng. J.*, **165**, 474(2010).
24. G. Jin, X. Zhu, C. Li, Y. Fua, J. Guan and X. Wu, *J. Environ. Chem. Engg.*, **1**, 736 (2013).
25. C. Septhum, S. Rattanaphani, J. B. Bremner and V. Rattanaphani, *J. Hazard. Mater.*, **148**, 185 (2007).
26. A. Ozcan and A. S. Ozcan, *J. Hazard. Mater.*, **125**, 252 (2005).
27. A. H. Chen, C. Y. Yang, C. Y. Chen, C. Y. Chen and C. W. Chen, *J. Hazard. Mater.*, **163**, 1068 (2009).
28. Y. Ren, N. Li, J. Feng and T. Luan, *J. Colloid Interface Sci.*, **367**, 415 (2011).

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