

Adsorption of lead (II) and chromium (VI) onto activated carbon prepared from pineapple peel: Kinetics and thermodynamic study

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The locally available adsorbent pine apple peel (*Ananascosmosus*) has been tested by preparing activated carbon by KOH activation for its effectiveness in removing hexavalent chromium and divalent lead present in the water at low concentrations. Batch adsorption method has been employed to investigate the efficiency of the adsorbent. Adsorption parameters like adsorbent dose, pH, contact time and temperature have been obtained. Adsorption isotherms Freundlich and Langmuir, which states that heterogeneity of the adsorbent surface, were tested and the data obtained best fits to Freundlich model. The adsorption kinetics follow pseudo-second-order kinetic model. Thermodynamic parameters for Pb (II) and Cr (VI) adsorption, enthalpy change, (-0.149 and -0.081kJ/mol), entropy change (0.183 and 0.012kJ/mol), and Gibbs free energy change (-3.138 and -3.554 kJ/mol at 293 K, -3.191 and -3.615 kJ/mol at 298 K, -3.245 and -3.675 kJ/mol at 303 K), respectively have been calculated. The results show that adsorption is feasible, spontaneous in nature, and exothermic.

Keywords: Chromium, Lead, Adsorption, Adsorption isotherms, Kinetic studies, Adsorption thermodynamic

Heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain. The main sources of heavy metal pollution include electroplating, painting and surface treatment industries. The inorganic effluent from the industries contains toxic metals. The heavy metals are of special concern because they are non-degradable and therefore persistent. Commonly encountered metals of concern include Pb^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} etc¹⁻³.

Economically feasible methods are essential for safety assessments of the environment and human health. Adsorption of heavy metals on activated carbon is the most used treatment method to reach water pollution regulations and environmental standards⁴. A great variety of lignocellulosic precursors and activating agents has been used for the preparation of activated carbons for heavy metal removal. Of various adsorbents, activated carbon is particularly useful because of its high adsorption capacities, cost effectiveness and preparation from locally available materials^{5,6}.

Now a days, to mitigate these toxic metals, researchers' devised different conventional and advanced methods such as chemical precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation,

electrochemical treatment and evaporation^{7,8}. However, these methods face drawbacks as cost incompatibility, sludge production, and removal inefficiency. Thus, the searches for low-cost adsorbents that have high metal binding capacities are needed. Activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse kinds of pollutants from aqueous solutions and wastewater⁹⁻¹¹. Thus, the study was aimed to investigate the level of Pb and Cr relative to the maximum permissible limit and also the removal of these metals by adsorption onto activated carbon.

Therefore, this study was carried out to investigate the adsorption capacities of pine apple based activated carbons for the removal of Pb (II) and Cr (VI) from aqueous solution. The activated carbons were synthesized with chemical activation using KOH as the activating agent. The kinetics, isotherms and thermodynamics properties of adsorption of lead and Chromium ions onto the synthesized activated carbons were also investigated.

Experimental Section

Analytical grade reagents and chemicals were used. Potassium hydroxide solution, KOH (25% W/V, sigma Aldrich), hydrochloric acid aqueous solution, HCl (5% V/V, 37%, Riedel-de Haën, Germany), distilled

water, Lead nitrate, $\text{Pb}(\text{NO}_3)_2$ (Riedel-de Haën, Germany), Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$ (99.5%, FINKEM, England), Nitric acid, HNO_3 (Riedel-de Haën, Germany), glacial acetic acid, CH_3COOH ($\geq 99.99\%$, Riedel-de Haën, Germany), sodium acetate, CH_3COONa ($\geq 98\%$ Riedel-de Haën, Germany), ammonia, NH_3 (23-25%, Mumbai, India), and ammonium chloride, NH_4Cl ($\geq 99.5\%$, Riedel-de Haën, Germany). Chemically activated carbon was prepared from pine apple peel (*Ananascosmosus*). The apparatus used for this study were: plastic bottles, volumetric flask, measuring cylinder, crucible, mortar and pestle, and sieve (Model DSCO 1674 JPG, 150 μm , UK). Atomic Absorption spectroscopy (AAS)(Model Analytic JenaNovAA 300, Germany), Electrical furnace (Model Nabertherm^(R), Germany), pH meter (HANNA instruments, pH 211), Electronic balance (Model AFP-110L, ADAM, China), Thermostatic water bath (Model Grant GLS 400, England), Oven (Model GENLAB WIDNES, England), UV-Vis spectrophotometer (Model DR 5000, Hach USA), Scanning Electron Micrograph (SEM) (JSM 6510 LV; Jeol, Japan).

Preparation of activated carbon

The collected pine apple peel (*Ananascosmosus*) was washed several times with tap water and then air dried for two weeks in the laboratory. The dried sample was again washed with distilled water and air dried for three days followed by oven dried for 24 h at 65°C for proper drying. The well dried sample was grinded and then sieved. The dried, grinded and sieved biomass was soaked in 25% (w/v) of KOH solution. The mixture was stand for 3 h for agitation. Then, oven dried for 12 h at 105°C. The dried sample was carbonized at a temperature of 800°C for 2 h, and the carbonized sample was cooled. The cooled activated carbon product was treated with 5% HCl solution followed by washing with distilled water until the pH of the washing solution became neutral. Then, the carbonization product which is now called 'activated carbon of the raw sample' was kept in air tight plastic container for further use.

Preparation of stock solution

The stock solution of both Cr (VI) and Pb (II) with a concentration of 1000 mg/L were prepared from $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Pb}(\text{NO}_3)_2$ respectively. This was done by dissolving 2.827 g and 1.599 g of $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Pb}(\text{NO}_3)_2$ in 1000 mL distilled water respectively. From this stock solution, both chromium (VI) and

lead (II) solutions with a concentration of 10 mg/L were prepared by dilution with distilled water.

Adsorption study

The study of the adsorption of heavy metals Pb (II) and Cr (VI) on to activated carbon have been performed by taking contact time, initial metal ion concentration, adsorbent dosage, temperature and pH as parameters influence adsorption.

Results and Discussion

Characterization of Pineapple peel activated carbon (PPAC)

Physiochemical analysis of PPAC

Activated carbons are widely used as adsorbent due to its high adsorption capacity, high surface area, and microporous structure. Some important proximate analysis of PPAC product is given in Table 1. Moisture content of the carbon has no effect on its adsorptive power; it dilutes the carbon and necessitates the use of additional weight carbon during treatment process. Any porous material will have the tendency to absorb moisture. The moisture content of PPAC obtained is normal and comparable with the values reported elsewhere¹². PPAC sample was determined using standard test method for moisture in AC¹³. The lower ash content is attributed to lower inorganic content and higher fixed carbon content. Higher value of fixed carbon content shows that the adsorbent is having more efficiency and stability. The sample was determined using standard test method for ash content of AC¹⁴. Fixed carbon is a calculated value and it is the resultant of summation of percentage moisture, ash, and volatile matter subtracted from 100.

SEM and EDX analysis of PPAC

Scanning electron micrograph (SEM) and energy dispersive spectrum of X-ray (EDAX) were carried out for the adsorbents before and after equilibration using Scanning Electron Microscope. The SEM enables the direct observation of the surface microstructures of different adsorbents¹⁵. From SEM micrographs (Fig. 1), a well-developed porous surface was observed at higher magnification. The pores observed from SEM images are considered as channels to the micro porous

Table 1 — Physio-chemical properties of pineapple peel activated carbon PPAC

Parameter	% Yield
Moisture content (%)	10.8
Ash content (%)	21.8
Volatile matter (%)	3.9
Fixed carbon (%)	63.5
pH	7.44

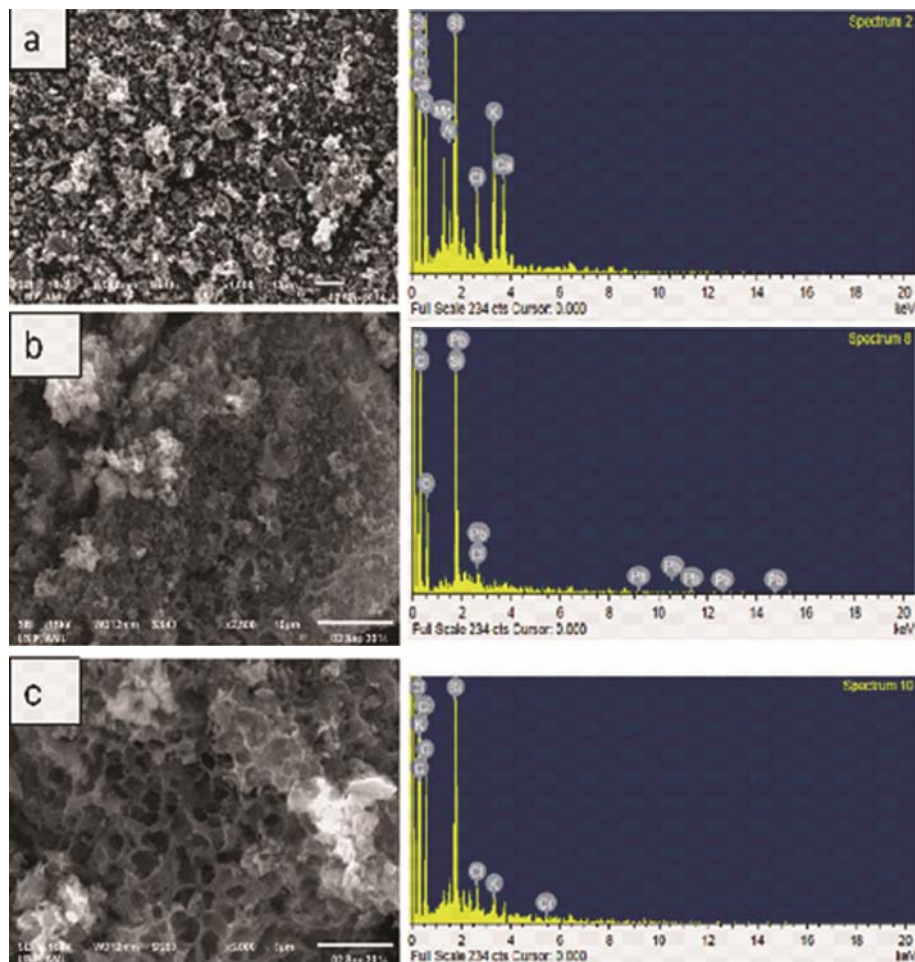


Fig. 1 — SEM of PPAC (a), lead loaded adsorbent (b), and chromium loaded adsorbent (c) along with their respective EDX spectra

Table 2 — FT-IR results from metal laden activated carbon

S.No	Absorption bands (cm^{-1})					
	Before adsorption cm^{-1}	Cr(VI) laden AC cm^{-1}	Difference	Pb(II) laden AC cm^{-1}	Difference	Assignment
1	3411	3428	17	3427	16	Bonded -OH groups
2	2920	2921	1	2922	2	Aliphatic C-H group
3	1568	1590	22	1592	24	Secondary amine group
4	1038	1095	57	1085	47	Carboxylic group, alcoholic C-O stretching

network. So it can be observed that the adsorbent has rough texture with heterogeneous surface and a variety of randomly distributed pore size.

It can also be observed from SEM micrographs that the progressive changes occurred in the surface of native adsorbent (Fig. 1a) after its surface was loaded by lead and chromium ions (Figs 1b and 1c). The SEM of exhausted adsorbents clearly indicates the presence of layer over the surface of metal – loaded adsorbents which are absent in the native adsorbent¹⁶. The lead and chromium ions cover the surrounding adsorbent particles and fill the voids (Figs 1b and 1c).

The EDX spectra of the native adsorbent and lead and chromium ions loaded adsorbent are illustrated in Figs 1a, 1b and 1c below. It shows lead and chromium ions were sorbed onto the adsorbent and provided direct evidence for the adsorption of lead and chromium onto the adsorbent¹⁶.

Infrared spectroscopic studies

The FT-IR spectroscopic characteristics spectra of the pineapple peel activated carbon (PPAC) and metal laden activated carbon are shown in Table 2. This demonstrates that after the adsorption the shifting

occurs both to higher and lower wave numbers. This shifting indicated that there were binding processes, taking place on the surface of activated carbon.

The peak at 3411 cm^{-1} is associated to O-H stretching vibration mode. The peak at 2920 cm^{-1} may be aliphatic methyl asymmetric C-H stretching. The peak observed around 1568 cm^{-1} is because of C=C stretching band. The peak at 1038 cm^{-1} is associated to carboxylic group, and alcoholic C-O stretching. FT-IR transmission spectra in the range of $500\text{--}4000\text{ cm}^{-1}$ for the PPAC, the PPAC laden with Cr (VI), and Pb (II) were obtained respectively.

Effect of pH on adsorption of Pb (II) and Cr (VI) on AC adsorbent

The adsorption experiment was carried out showing the effect of pH ranging from 1.0 - 11.0 by contacting 0.25 g of PPAC with 25 mL of 10 ppm Pb (NO_3)₂ and $\text{K}_2\text{Cr}_2\text{O}_7$ solution. The mixture was shaken in thermostatic water bath shaker at 200 rpm at 25°C for 180 min. In the case of Pb (II) the maximum adsorption was obtained at pH 5.0.

At $\text{pH} < 2.5$, H^+ ions compete with Pb (II) ions for the surface of the adsorbent which would hinder Pb (II) ions from reaching the binding sites of the sorbet caused by the repulsive forces. At $\text{pH} > 6.0$, the Pb (II) gets precipitated due to hydroxide anions forming a lead hydroxide precipitate.

The highest efficiency (96.46%) was observed at pH of 5.0. For Cr (VI) the observed result suggest that at pH 3, percentage adsorption was higher (96.22%) and after equilibrium was reached the adsorption decreases and remains the same with increasing pH up to 11. This is because of the fact that Cr (VI) removal by activated carbon is enhanced in the acidic range of pH. Similar results have been reported^{17,18}. The favourable effect of low pH can be attributed to the neutralization of negative charges on the surface of the adsorption by excess hydrogen ions, thereby facilitating the diffusion of hydrogen chromate ions (HCrO_4^-) or CrO_4^{2-} ions and their subsequent adsorption. HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are the predominant species and ionic form of Cr (VI) at low pH^{19,20}. This ionic form was found to be preferentially adsorbed on the surface of carbon.

Effect of contact time

Figures 2 (a) and (b), showing the equilibrium time dependent on the adsorbate concentration. At 10 - 100 and 10 - 70 min for Pb (II) and Cr (VI) respectively, percent adsorption was found slightly increased. At lower adsorbate concentration (0.02 mg/L) percentage of adsorption was found to be high at 98.36% and

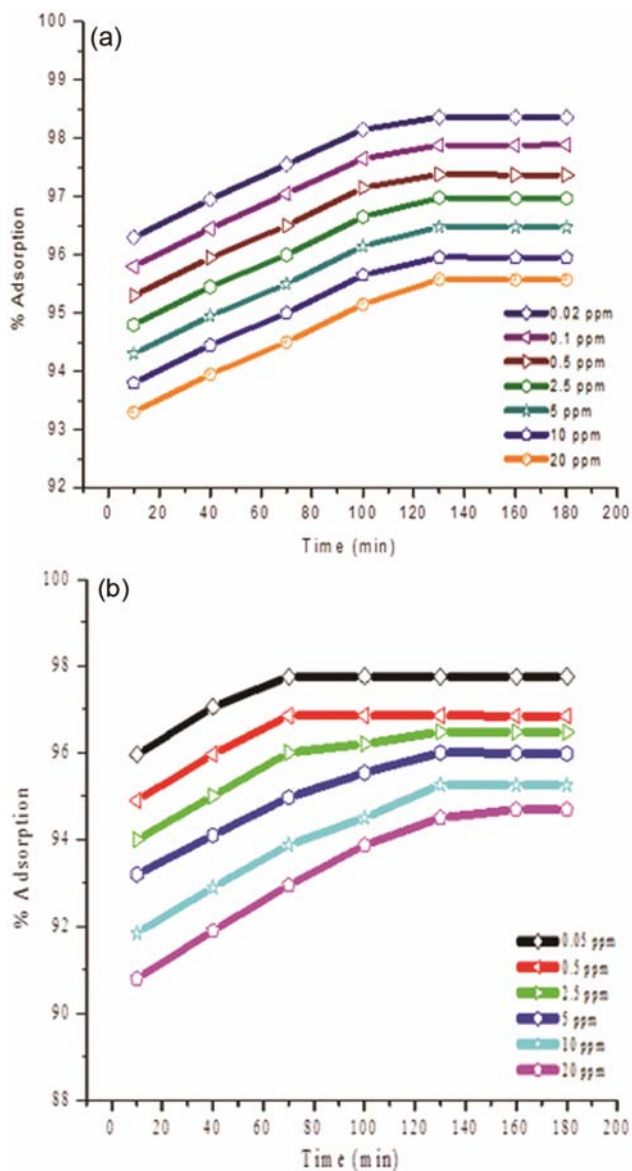


Fig. 2 — (a) Effect of contact time on Pb(II) and (b) Cr(VI) adsorption at different time interval from 10-180 min

gradually becomes constant. From above observation in the early stages it was exposed that the rate of uptake was fast but progressively decreased and become constant when equilibrium reached, similar results has also been reported²¹.

This fast uptake rate could be due to the large number of vacant spaces available on the adsorbent surface at the early stage. Above 100 and 70 min a relatively slower adsorption was observed until it appeared to reach constant state. Further increase in contact time did not show any increase in adsorption. The relatively slower adsorption above 100 and 70 min until equilibrium can be explained in such a way that at

about 100 and 70 min of shaking time, most of the adsorption sites on the surface of the adsorbent are occupied by adsorbate ions and repulsion between adsorbed ions and those approaching to occupy the remaining vacant surface sites from the bulk solution increases. As a result, the rate at which both Pb (II) and Cr (VI) ions get adsorbed will decrease²².

Effect of adsorbent dosage

The effect of adsorbent dosage on adsorption of Pb (II) and Cr (VI) was studied show the results that percentage adsorption increases from 97.34% to 98.375% and 97.44% to 98.26% with increasing dosage from 0.1 to 0.25 g for both Pb (II) and Cr (VI), respectively. Beyond 0.25 g, the percentage was not increased significantly and reached the maximum of 98.375% and 98.26% for both Pb (II) and Cr (VI) at dosage of 0.25 g respectively. This phenomenon can be due to the greater availability of active sites or surface area making easier penetration of the Pb (II) and Cr (VI) ions to the adsorption sites of activated carbon, and increasing dosage beyond 0.25 g had no much effect once equilibrium achieved²³.

Effect of temperature

Adsorption of Pb (II) and Cr (VI) ions on the adsorbent witnessed the increase in adsorption percentage from 20 to 25°C and no significant change with further increase of temperature. It was observed, that the percentage adsorption increases from 97.8 to 98.54% for Pb (II), and 97.37 to 98.364% for Cr (VI) ion with the rise in temperature from 20 to 45°C. This observed increment may be due to the fact that increase in temperature is known to increase the diffusion rate of the adsorbate molecules across the external boundary layer and within the pores. The percentage adsorption of Cr (VI) and Pb (II) increases as the rate of diffusion of these ions in the external mass transport process increases with temperature²⁴. It would be expected that an increase solution temperature would result in the enlargement of pore size due to ‘activated diffusion’ causing the micro-pores to widen and deepen and create more surface for adsorption²⁵.

Adsorption isotherm study

The linear form of the Langmuir isotherm, Fig. 3, is given as the following Equation:

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m b_L} \quad \dots (1)$$

where; q_e (mg/g) is the equilibrium concentration of Pb (II) or Cr (VI) ion in the adsorbed phase and

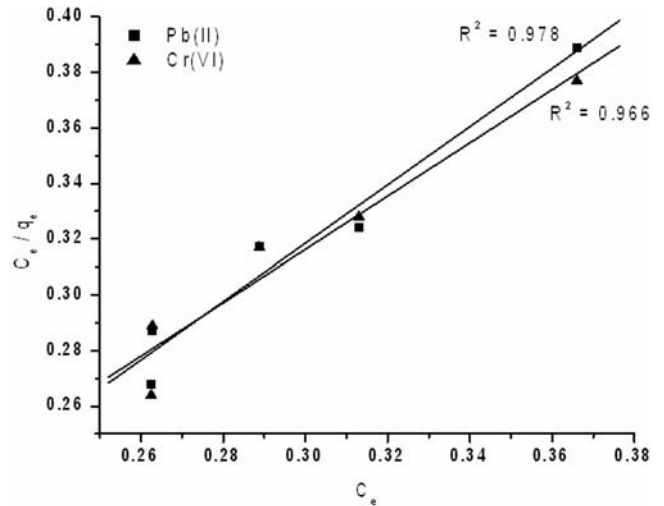


Fig. 3 — Langmuir plot of adsorption of Pb(II) (square) and Cr(VI) (triangle) onto PPAC

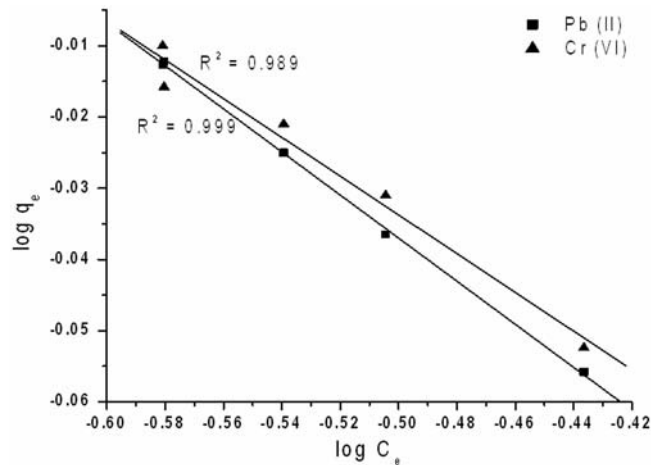


Fig. 4 — Freundlich plot of Pb(II) (square) and Cr(VI) (triangle) adsorption onto PPAC

C_e (mg/L) is the equilibrium concentration of Pb (II) or Cr (VI) ion in the liquid phase. Langmuir constants, which are related to the maximum adsorption capacity (q_m) and energy of adsorption (b_L) can be calculated from the slope of the linear plot of C_e/q_e vs C_e . The essential characteristics of the Langmuir Equation can be expressed in terms of a dimensionless factor, R_L which is given

$$R_L = \frac{1}{1 + b_L C_0} \quad \dots (2)$$

where, C_0 is the highest initial Pb (II) and Cr (VI) ion concentration (mg/L).

The linear form of the Freundlich isotherm, Fig. 4, is given as the following Equation:

Table 3 — Results of isotherm models for the adsorption of Pb (II) and Cr (VI) onto PPAC at 25°C.

Adsorption isotherms	Values	
	Pb(II)	Cr(VI)
Langmuir		
q_m (mg/g)	0.952	0.935
b_L (L/mg)	2.850	2.822
R^2	0.978	0.966
R_L at 20 mg/L	0.017	0.017
Freundlich		
k_f	1.030	1.029
$1/n$	0.200	0.280
R^2	0.999	0.989

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad \dots (3)$$

The constant k_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process and the smaller $1/n$, the greater the expected heterogeneity²⁶. If n lies between one and ten, this indicates a favourable sorption process²⁷. From the data in Table 3, that value of $1/n = 0.2$ and 0.28 while $n=5$ and $n= 3.57$ indicating that the sorption of Pb^{2+} and Cr (VI) onto PPAC is favourable and the R^2 value is 0.999 and 0.989 for both Pb (II) and Cr (VI) respectively. The value of R_L found (0.0172 and 0.0174) is between 0 and 1, which indicates favourable adsorption²⁸. Using the Freundlich isotherm, the value of n found 5 and 3.57 denotes spontaneous adsorption. Values of n in the range $1 < n < 10$ indicate favourable bio sorption²⁹.

Adsorption kinetic studies

In order to evaluate the kinetic parameters, Pseudo first order and Pseudo second order models were implemented to analyze the experimental data. The pseudo first order Equation can be expressed as³⁰:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \dots (4)$$

where, q_e and q_t represent the amount of adsorbed (mg/g) at equilibrium and at any time t , k_1 is the first order rate constant (min^{-1}). From the plots of $\log(q_e - q_t)$ versus t in Fig. 5, k_1 can be calculated from the slope and theoretical q_e can be obtained from intercepts.

Pseudo second order Equation can be given by³¹.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \dots (5)$$

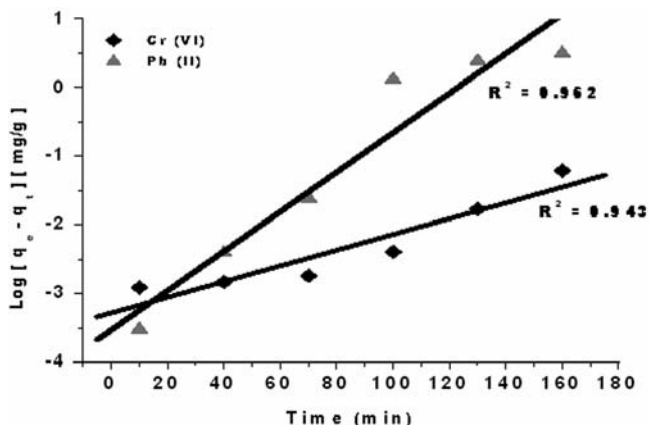


Fig. 5 — Pseudo-first-order kinetics plot for the adsorption of Pb(II) (triangle) and Cr(VI) (square) onto PPAC

Table 4 — Kinetics parameters for the adsorption of Pb (II) and Cr (VI) onto PPAC at 298 K

Kinetic parameters	Values	
Pseudo-first order/constants	Pb(II)	Cr(VI)
q_e (mg/g)	0.004	0.024
k_1 (min^{-1})	0.007	0.146
R^2	0.962	0.943
Pseudo-second order/constants		
q_e (mg/g)	1.1510	0.987
k_2 (g/mg.min)	0.017	0.025
R^2	0.999	0.999

where, k_2 is the rate constant of second order adsorption. The linear plots of t/q_t versus t determine $1/q_e$ as slope and $1/k_2 q_e^2$ as intercepts. The linear plots of pseudo second order model were obtained and the parameter values are tabulated in Table 4.

Adsorption thermodynamic study

The adsorption thermodynamic parameters, the change in Gibbs free energy (ΔG), could be calculated using:

$$\Delta G = -RT \ln K_c \quad \dots (6)$$

where R is the gas constant (8.314 J/ mol.K), T is the absolute temperature in Kelvin, and K_c (L/g) is the standard thermodynamic equilibrium constant defined by $\frac{q_e}{C_e}$.

$$\text{Similarly } \ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \dots (7)$$

ΔH° (kJ.mol^{-1}) and ΔS° ($\text{kJ.mol}^{-1}.\text{K}^{-1}$) were calculated from the slope and intercept of the linear

Table 5 — Thermodynamic parameters for the adsorption of Pb (II) and Cr (VI) ions onto PPAC at different temperatures

Heavy metals	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)	ΔG° (kJ/mol)		
			293 K	298 K	303 K
Pb (II)	-0.149	0.183	-3.138	-3.191	-3.245
Cr (VI)	-0.081	0.012	-3.554	-3.615	-3.675

Table 6 — Table showing results of percent removal of Pb and Cr from contaminated water by the applied method

Contaminated water Samples	Concentration in (ppm)		Amount removed (ppm)		% Removal	
	Pb	Cr	Pb	Cr	Pb	Cr
1	0.0196	-	0.0193	-	98.35	-
2	-	0.055	-	0.054	-	97.75
3	0.0195	-	0.0192	-	98.35	-

plot of $\ln K_c$ versus $1/T$. These thermodynamic parameters of the adsorption process were calculated using Equations (6) and (7) above and the calculated values of these parameters are given in Table 5.

The negative value of enthalpy change confirms the exothermic nature of the adsorption process and a given amount of heat is evolved during the binding of Pb (II) and Cr (VI) ions on the surface of adsorbent. The positive values of the standard entropy change, ΔS represent the increased randomness at solid-liquid interfaces during the adsorption of metal ions onto adsorbent. Furthermore, the positive value of ΔS also reflects that some structural changes occur in the adsorbate and adsorbent during the adsorption process^{32,33}.

Negative values of ΔG confirm the adsorption process is spontaneous, which becomes more negative with an increase in temperature. This indicates that a higher adsorption is actually occurred at higher temperatures³⁴. At higher temperature, ions are readily desolvated and thereby their adsorption becomes more favourable³⁵.

Application of the developed method for real sample

Water samples were collected from three different points of distribution and digested before using it for the calibration applying AAS and UV-Vis spectrophotometer. Batch adsorption experiment was applied on these samples at the optimum conditions obtained for the method. Obtained results were tabulated in Table 6.

Conclusion

In this study, locally available adsorbent pine apple peel (*Ananascosmosus*) has been tested for its

effectiveness in removing hexavalent chromium and divalent lead present in the water at low concentrations. Activated carbon have been prepared from pineapple peel by chemical activation method. The batch study parameters: pH, adsorbent dose, initial concentration, contact time and temperature have been investigated. The optimum value (pH = 5 and 3 for Pb and Cr, adsorbent dose = 0.25 g, initial concentration = 0.02 ppm and 0.05 ppm for Pb and Cr, contact time = 100 min and 70 min for Pb and Cr, temperature = 25°C) are obtained. The adsorption was found to be strongly influenced by pH, contact time and initial metal ion concentration. The adsorption kinetic data are modeled using the pseudo-first order and pseudo-second order kinetic equations. It is inferred that the Pseudo second order model gave better R^2 values confirming suitability of the model for describing the adsorption system. Both Freundlich and Langmuir models are used to fit the data and estimate model parameters, but the overall data is slightly better fitted by Freundlich isotherm reflecting surface heterogeneity of PPAC. Different thermodynamic parameters ($\Delta H = -0.149$ and -0.081 kJ/mol for Pb and Cr, $\Delta S = 0.183$ and 0.012 kJ/mol for Pb and Cr, and $\Delta G = -3.138$ and -3.554 kJ/mol at 293 k, -3.191 and -3.615 kJ/mol at 298 k, -3.245 and -3.675 kJ/mol at 303 k for Pb and Cr, respectively) have also been calculated and it is been found that the adsorption is favourable, spontaneous and exothermic in nature. The positive values of the entropy change suggest that the increased randomness at solid-liquid interfaces during the adsorption of metal ions onto adsorbent.

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