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Lead(II) removal from aqueous solution using *Citrus limettioides* peel and its modified form: isotherms, kinetics and thermodynamic studies

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ABSTRACT

The Pb(II) adsorption capacity of carbon derived from *Citrus limettioides* peel (CLPC), which is a novel waste material, was evaluated regarding the contact time, pH and adsorbent dose during batch adsorption processes with raw *C. limettioides* peel (CLP). The optimal contact time for the adsorption of Pb(II) ions onto the peel and peel carbon was 3 h, and the optimal pH ranged from 4.0 to 5.0 for CLP and 4.0–6.0 for CLPC, respectively. The equilibrium data fit well with Langmuir isotherm, indicating that the Pb(II) ions formed a homogenous monolayer on the adsorbent surface. Maximum monolayer adsorption capacity of Pb(II) ions on peel (CLP) and peel carbon (CLPC) was found to be 125.00 and 166.67 mg g^{-1}, respectively. The kinetic studies showed that the adsorption data followed a pseudo-second-order kinetic model. The surface morphology and functionality of the CLP and CLPC were characterized using scanning electron microscopy, energy dispersive X-ray spectroscopy and FT-IR. Various thermodynamic parameters, including the standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°), were evaluated. The CLP and CLPC were tested with Pb(II) plating wastewater through a batch mode process over five cycles; CLPC showed better results than CLP.

Keywords: Adsorption; *Citrus limettioides* peel; Isotherms; Desorption; Kinetics

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1. Introduction

The presence of lead ions in the aquatic environment has been of great concern to scientists due to their increased discharge, non-biodegradable, toxic and other adverse effects on human being as well as the fauna and flora [1]. The major industrial sources of lead released into the environment are battery manufacturing, acid metal plating and finishing, ammunition, tetraethyl lead manufacturing, ceramic and glass industries printing, painting, dying and other industries [2]. The permissible limit of lead in drinking water and surface water intended for drinking, as set by EU, USEPA and WHO are 0.010, 0.015 and 0.010 mg L^{-1}, respectively [3]. The presence of excess lead in drinking water causes diseases such as anaemia, encephalopathy, hepatitis and the nephritic syndrome [4]. Many treatment methods have been applied for the removal of lead from wastewaters, such as precipitation, ion exchange, solvent extraction, coagulation and reverse osmosis [5]. However, most of these methods present several disadvantages like chemical requirements, low efficiency, and usually produce large amounts of sludge that can add other

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environmental problems. One alternate effective process is the adsorption, which relies on the utilization of solid adsorbents with no chemical degradation. It is attractive due to its merits of effectiveness, efficiency and sludge free [6]. Currently, activated carbon is widely used as an adsorbent for removing low lead concentrations and any organic matter in waste streams. Activated carbon derived from various agricultural wastes such as watermelon shell and walnut shell [7], coconut shell [8], muskmelon peel [9], pomegranate peel [10], orange peel [11], date stones [12], apricot stone [13], tamarind nut [14] and gingelly oil cake [15] have shown attracting experimental results for lead(II) removal.

Citrus limettioides is one of the low-cost nutritious fruit variety consumed in rural areas of India and belongs to Rutaceae family. Extracted acid from these fruits is used as flavouring and preservative in food and beverages, especially in soft drinks and the peels are disposed off as waste materials. The *C. limettioides* fruit is mainly composed of d-limonene, myrcene, citronellal and β-citronellol [16]. In this work, it has been reported that the results obtained on the preparation of activated carbon from *Citrus limettioides* peel (CLPC) and compared with raw *Citrus limettioides* peel (CLP) for the removal of Pb(II) from aqueous solution. The influence of several operating parameters, such as contact time, pH, point of zero charge (pHpzc) and adsorbent dose was investigated in batch mode. The kinetic data were fitted to different models and the isotherm equilibrium data were fitted to Freundlich, Langmuir and Dubinin–Radushkevich.

2. Materials and methods

2.1. Preparation of adsorbent

The CLP was collected from a local juice manufacturing unit in Rasipuram (TK) and dried in the sun. Subsequently, the material was washed with boiling, deionized water five to six times for removing water soluble, extractable organics and acids. The washed material was dried in the sun for 2 d and cut into small pieces using a cutter machine. The dried raw material was subsequently digested with sufficient quantities of perchloric acid at between 300 and 350˚C to break down the fibres and then subsequently treated with concentrated sulphuric acid in a 1:2 ratio by weight and kept at 160 ± 5˚C in an air-oven for 24 h. The carbonized material was washed with distilled water and soaked in 1% sodium bicarbonate for 24 h to remove any free acid. The carbon material was washed, dried and sieved to 20–50 ASTM mesh for use in the experiments (CLPC). The characteristics of the carbon were determined according to ISI-877 [17] and presented in Table 1. Raw peel (CLP) at the same particle size was also evaluated along with carbon, for Pb(II) removal.

2.2. Preparation of the Pb(II) solutions

Stock aqueous solution of Pb(II) having concentration of 1,000 mg L^{-1} was prepared by dissolving 1.59 g of $Pb(NO_3)_2$ in 1,000 mL of distilled water. Lead(II) solutions of desired concentrations were prepared by dilution of the stock solution. The pH of the solution was adjusted to the required value using 0.1 N HCl or 0.1 N NaOH solutions.

2.3. Batch mode adsorption studies

Adsorption experiments were conducted in plastic bottles of 300-mL capacity on a temperature-controlled shaker. About 0.1 g of adsorbents (CLP and CLPC) were added to 100 mL of Pb(II) solutions of 10 mg L^{-1} concentration at a predetermined pH at 300 K and agitated for a definite period of time. For optimization, contact time was varied between 0.5 and 5 h, adsorbent dosage in the range of 0.05–0.5 g and pH between 2 and 12. Adsorption isotherms were conducted with 10–60 mg L^{-1} of Pb(II) solutions by adding 0.1 g of adsorbent/100 mL of solution and equilibrated for 24 h at different temperatures (300–320 K). In kinetic studies, contact time was varied from 0.5 to 6 h by adding 100 mg of adsorbent, for various Pb(II) concentrations over the range 3–10 mg L^{-1} at an optimum pH and at 300 K. The batch experiments were

Table 1
Characteristics of the carbon

Parameter	CLPC
Bulk density (g mL^{-1})	0.51
Moisture (%)	15.70
Ash (%)	7.70
Solubility in water (%)	1.74
Solubility in 0.25 M HCl (%)	14.90
pH	5.50
Decolorizing power (mg g^{-1})	2.70
Phenol number	69.00
Ion-exchange capacity (m equiv g^{-1})	0.47
Surface area (m^2 g^{-1})	89.00
Iron (%)	0.01
Silica (%)	–
Potassium (%)	0.08
Sodium (%)	1.18

repeated for three times and the average results are presented in this work.

At the end of agitation, the solutions were centrifuged and the concentrations of Pb(II) ions were determined by an atomic absorption spectrophotometer (Elico Model-SL 163). Lead(II) removal (%) was calculated using the following equation:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

The adsorption capacity of Pb(II) ions adsorbed per gram of adsorbent (mg g^{-1}) was calculated by:

$$q_e = \frac{C_0 - C_e}{M} \times V \tag{2}$$

where C_0 and C_e are the initial and equilibrium Pb(II) concentrations (mg L^{-1}); V is the volume of the Pb(II) solution (L); and M is the mass of the adsorbent used (g), respectively.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy analysis

Fourier transform infrared spectroscopy (FT-IR) studies were carried out to identify the functional groups on the surface of the adsorbent. The chemical functional groups such as hydroxyl and carboxylic acid groups in CLP, in addition to that sulphonic acid groups in CLPC were identified as potential adsorption sites which are responsible for binding the metal ions to the adsorbent. FT-IR spectrum of CLP and CLPC is shown in Fig. 1(a) and (b). The strong absorption peaks at 3,444, 1,706 and 1,377 cm^{-1} confirm the presence of the hydroxyl, carboxylic and sulphonic acid groups in the CLPC. The peak at 3,422 and 1,741 cm^{-1} is attributed to the stretching vibrations of hydroxyl and carboxylic acid groups in CLP.

3.2. Scanning electron microscopy–energy dispersive X-ray spectroscopy analysis

The surface structure of CLP and CLPC was analysed using scanning electron microscopy (SEM) and is shown in Fig. 2(a) and (b). This microscope shows an irregular image and porous surface. On the basis of this fact, it can be concluded that the CLP and CLPC adsorbent has an adequate morphology for lead(II) ion adsorption. Energy dispersive X-ray spectroscopy (EDX) pattern was used to confirm the adsorption of Pb(II) ions on the surface of the adsorbent such as CLP and CLPC (Fig. 2(c) and (d)), respectively.

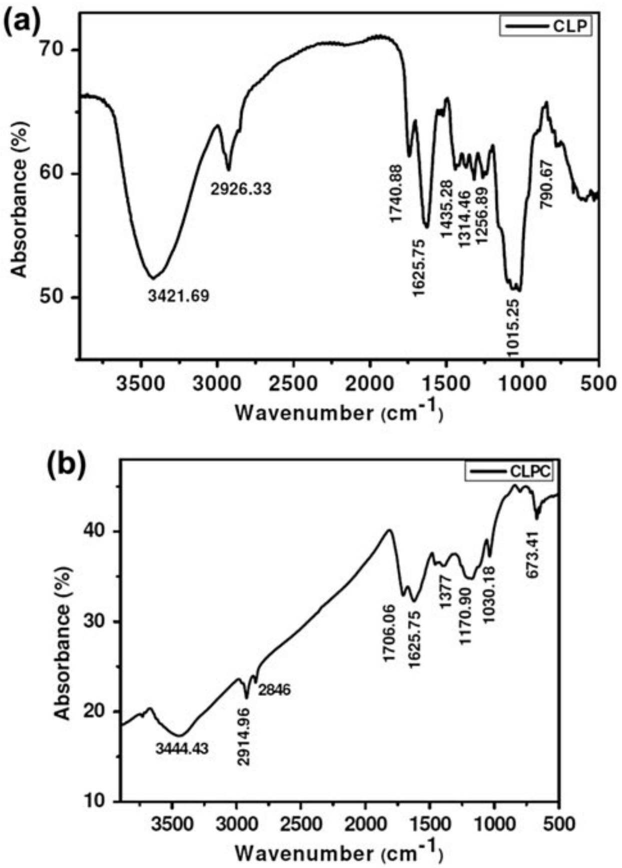

Fig. 1. FT-IR spectrum of (a) CLP and (b) CLPC.

3.3. Effect of contact time

Fig. 3 shows that the removal of Pb(II) ions increased rapidly with time and attains equilibrium in 3 h for CLP and CLPC. The rate of removal is higher in the beginning due to the large number of available adsorption sites on the adsorbent for the removal of Pb(II) ion. Under this condition, the uptake of Pb(II) ion was found to be 85% for CLP and 99% for CLPC, respectively. Hence, the optimum equilibrium was taken as 3 h for subsequent experiments.

3.4. Effect of pH and point of zero charge (pH_{pzc})

The pH of the solution has a significant impact on the uptake of heavy metals, since it determines the surface charge of the adsorbent, the degree of ionization and the speciation of the adsorbate. Fig. 4(a) shows that the metal removal increases with increase in pH and attains a maximum removal of 99 and 85% over a pH range 4.0–6.0 for CLPC and 4.0–5.0 for CLP, respectively. The adsorption of Pb(II) ions is very

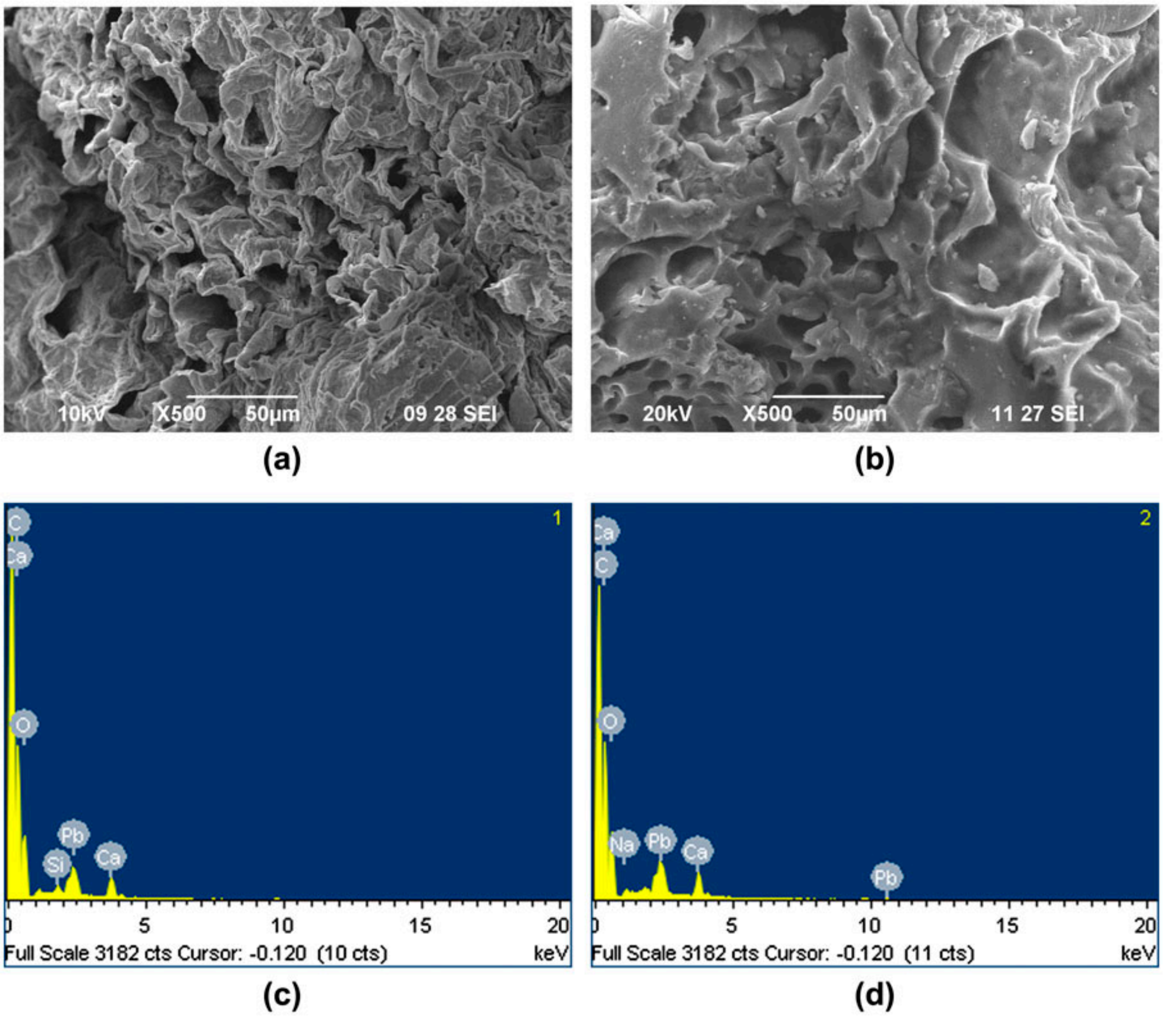

Fig. 2. (a) SEM image of CLP and (b) CLPC; (c) EDX patterns of CLP and (d) CLPC after Pb(II) adsorption.

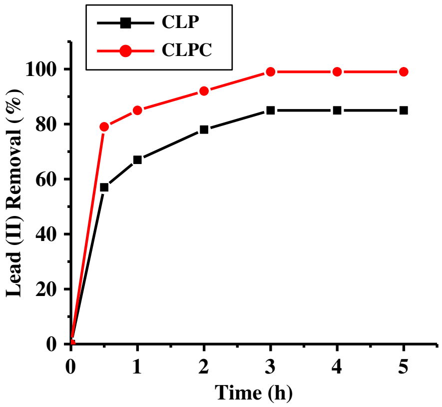

Fig. 3. Effect of contact time on Pb(II) adsorption (C_0: 10 mg L^{-1}, pH: 5.0, adsorbent dose: 0.1 g/100 mL and Temp: 300 K).

low at acidic pH values. This can be explained by the fact that at low pH values, electrostatic repulsion forces act between H_3O^+ and Pb^{2+} ions. As pH increases, adsorption of Pb(II) ions takes place on the surface of the adsorbent replacing H_3O^+. Above optimum pH, Pb(II) starts precipitating as $Pb(OH)_2$ and hence causing a decrease in the adsorption yield. The point of zero charge (pH_{pzc}) was determined by the solid addition method [18]. The pH_{pzc} of CLP and CLPC in distilled water is found to be 5.5 and 6 (Fig. 4(b)) showing that surface is positively charged below pH 6 and at high pH value (above 6) Pb(II) species mainly present as $Pb(OH)_2$.

The mechanism of Pb(II) removal may also be explained based on ion-exchange model. A pure carbon surface is considered to be non-polar, but in actual practice, some carbon–oxygen complexes

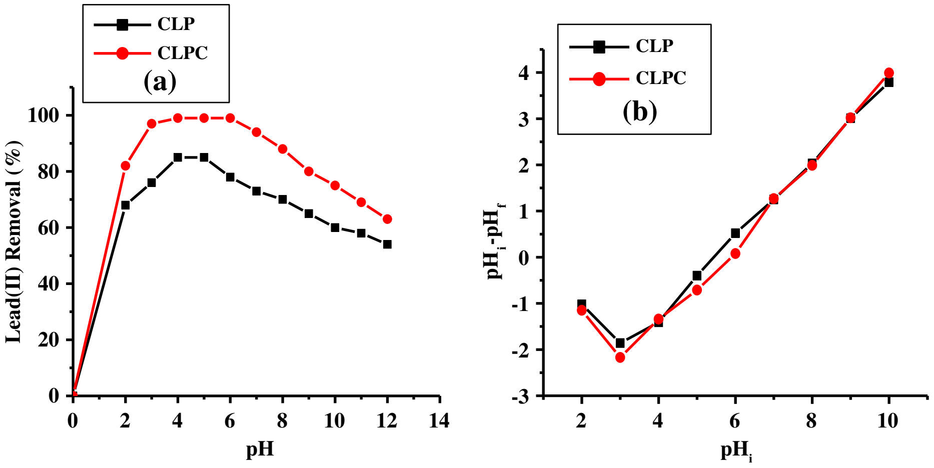

Fig. 4. (a) Effect of pH on the adsorption of Pb(II) by CLP and CLPC and (b) effect of point of zero charge (pH_{pzc}) on the adsorption of Pb(II) by CLP and CLPC.

(C_XO, CO_X and C_XO_2) are usually present, which render the surface slightly polar. The surface oxygen complexes hydrolyse water molecules as shown below.

$$C_XO + 2H_2O \rightarrow C_XOH_2^{2+} + 2OH^-$$

$$CO_X + xH_2O \rightarrow C(OH)_X^+ + xOH^-$$

$$C_XO_2 + H_2O \rightarrow C_XO^{2+} + 2OH^-$$

Since the CLPC is prepared upon treatment with H_2SO_4 followed by treatment with $NaHCO_3$, groups such as C_XONa^+, $C_XONa_2^{2+}$, C_XSO_3H and C_XSO_3Na are also assumed to be present. Hence, it is expected that Na^+ may be exchanged with Pb(II) and soluble complexes of Pb(II) as follows:

$$2C_XOH^+ + Pb^{2+} \rightarrow (C_XO)_2Pb^{2+} + 2H^+$$

$$C_XOH_2^{2+} + Pb^{2+} \rightarrow C_XOPb^{2+} + 2H^+$$

$$2C_XONa^+ + Pb^{2+} \rightarrow (C_XO)_2Pb^{2+} + 2Na^+$$

$$C_XONa_2^{2+} + Pb^{2+} \rightarrow C_XOPb^{2+} + 2Na^+$$

$$2C_XSO_3H + Pb^{2+} \rightarrow (C_XSO_3)_2Pb + 2H^+$$

$$2C_XSO_3Na + Pb^{2+} \rightarrow (C_XSO_3)_2Pb + 2Na^+$$

3.5. Effect of adsorbent dose

As depicted in Fig. 5, it was observed that the percentage of lead removal increased as the adsorbent dose is increased but after a certain value (0.1 g/100 mL for CLPC and 0.3 g/100 mL for CLP), the removal was found to be almost constant. It is evident that 100 mL of Pb(II) solution containing 10 mg L^{-1} of Pb(II) ions, a minimum adsorbent dose of 0.1 g CLPC is required for the maximum removal of 99% and in the case of CLP, 0.3 g is required for the removal of 94% only. The data clearly indicate that CLPC is nearly three times more effective than CLP and this may be due to moderate ion-exchange capacity exhibited by CLPC as compared to CLP.

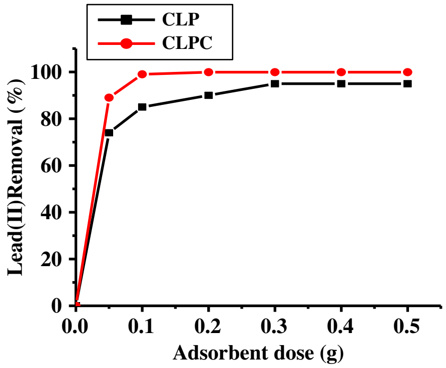

Fig. 5. Effect of adsorbent dose on sorption of Pb(II) by CLP and CLPC (C_0: 10 mg L^{-1}, pH: 5.0 and contact time: 3 h).

3.6. Adsorption isotherms

Adsorption isotherm is an important to describe how solutes interact with adsorbent. In this study, equilibrium data were analyzed using Freundlich, Langmuir and Dubinin–Radushkevich isotherms expression at different temperatures (300–320 K).

The Freundlich [19] isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of the heat of sorption. It can linearly be expressed as follows:

$$\log q_e = \log K_F + (1/n)\log C_e \tag{3}$$

where K_F (mg g^{-1}) and $1/n$ are the Freundlich constants related to sorption capacity and intensity, respectively. The values of $1/n$ less than 1 represent a favourable adsorption. The Freundlich constants can be obtained from the plot of log q_e vs. log C_e.

The Langmuir [20] isotherm assumes that adsorption occurs at specific homogenous sites within the adsorbent. The equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \tag{4}$$

where C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate; q_e (mg g^{-1}) is the amount of adsorbate per unit mass of adsorbent; b (L mg^{-1}) is the Langmuir adsorption constant; and Q_0 (mg g^{-1}) is the amount of maximum adsorption. The Langmuir constants can be obtained from the plot of C_e/q_e vs. C_e. To determine whether the adsorption is favourable, a dimensionless constant separation factor or equilibrium parameter R_L is defined based on the following equation [21]:

$$R_L = \frac{1}{1 + bc_0} \tag{5}$$

Dubinin–Radushkevich [22] isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has often successfully fitted high solute activities and intermediate range of concentrations data well.

$$q_e = (q_s)\exp(-K_{ad}\varepsilon^2) \tag{6}$$

$$\ln q_e = \ln q_s - (K_{ad}\varepsilon^2) \tag{7}$$

where q_e is the amount of adsorbate in the at equilibrium (mg g^{-1}), q_s is the theoretical isotherm saturation capacity (mg g^{-1}), K_{ad} is the Dubinin–Radushkevich isotherm constant (mol^2 kJ^{-2}) related to sorption energy and ε is the Dubinin–Radushkevich isotherm constant. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy, E per molecule of adsorbate can be computed by the relationship [22]:

$$E = \left[\frac{1}{\sqrt{2K_{ad}}}\right] \tag{8}$$

The Dubinin–Radushkevich isotherm constants, theoretical isotherm capacity (q_s) and sorption energy (K_{ad}) are calculated from the plot of ln q_e vs. ε. The magnitude of E is used to determine the type of adsorption mechanism. When one mole of ions is transferred to the adsorbent surface, its value is less than 8 kJ mol^{-1} which indicates the physical adsorption. If the value of E is between 8 and 16 kJ mol^{-1}, it indicates the adsorption process follows ion exchange and when its value is in the range of 20–40 kJ mol^{-1}, it indicates chemisorptions [23].

The isotherm constants and correlation coefficients (R^2) are summarized in Table 2. From Table 2, the CLP and CLPC at different temperatures fit well into Langmuir model based on the R^2 value. This fact is further supported by low chi-square values of Langmuir isotherm model. The R_L values lying between 0 and 1 indicated that the conditions are favourable for adsorption. It could be concluded that the homogeneous distribution of active sites on the adsorbent system is predominant. The monolayer adsorption capacity (Q_0) is decreased with increasing temperature, indicating an exothermic process. According to Langmuir isotherm, the adsorption capacity (Q_0) of Pb (II) ion was found to be 166.67 mg g^{-1} for CLPC, which was about 1.3 times greater than that of CLP (125.00 mg g^{-1}) at 300 K, respectively. Based on Dubinin–Radushkevich model, the calculated E values (Table 2) obtained in the present study are below 8 kJ mol^{-1}, which suggests that the adsorption of lead(II) onto the CLP and CLPC surface is physical adsorption type. The higher adsorption capacity of lead(II) on CLPC than CLP may be related to the physical and chemical characterization of the adsorbents. Based on carbon characteristics, an ion-exchange mechanism may also be predominantly operating in CLPC for the lead(II) removal process.

The maximum adsorption capacity (Q_0) of CLPC is compared with those of other adsorbents reported in the literature in Table 3. The high adsorption capacity

Table 2
Isotherm and thermodynamic parameters for Pb(II) removal from aqueous solutions

Isotherm models and thermodynamics	Parameters	Temperature (K) CLP 300 K	 310 K	 320 K	 CLPC 300 K	 310 K	 320 K
Freundlich	K_F (mg g^{-1})	10.470	10.140	9.570	23.820	21.730	20.610
	$1/n$	0.794	0.759	0.715	0.826	0.753	0.707
	R^2	0.993	0.990	0.985	0.997	0.993	0.989
	χ^2	1.76E-4	7.93E-5	1.14E-4	1.37E-5	2.24E-5	1.02E-5
Langmuir	Q_0 (mg g^{-1})	125.00	111.11	90.91	166.67	125.00	100.00
	b (L mg^{-1})	0.090	0.091	0.100	0.034	0.034	0.035
	R^2	0.995	0.998	0.991	0.998	0.998	0.997
	χ^2	1.67E-7	4.77E-6	1.73E-6	8.43E-8	1.87E-7	2.10E-7
	R_L	0.526–0.156	0.524–0.155	0.500–0.167	0.746–0.329	0.746–0.329	0.741–0.323
Dubinin–Radushkevich	q_s (mg g^{-1})	41.060	40.130	38.780	48.470	46.110	44.790
	k_{id} (mol^2 kJ^{-2})	4.6×10^{-7}	4.7×10^{-7}	4.8×10^{-7}	7.0×10^{-8}	1.0×10^{-7}	1.0×10^{-7}
	E (kJ mol^{-1})	1.038	1.037	1.019	2.674	2.236	2.236
	R^2	0.888	0.887	0.890	0.920	0.916	0.905
	χ^2	9.80E-3	1.11E-2	1.20E-2	5.70E-3	8.20E-3	8.01E-3
Thermodynamic	ΔG° (kJ mol^{-1})	−6.037	−5.963	−5.872	−4.326	−3.729	−3.333
	ΔH° (kJ mol^{-1})	−8.510			−19.188		
	ΔS° (kJ mol^{-1} K^{-1})	−0.008			−0.050		

of CLPC reveals that it should be a promising adsorbent for removing Pb(II) from aqueous system.

3.7. Adsorption thermodynamics

The Gibbs free energy change of the adsorption process is related to the equilibrium constant by the classic Van't Hoff equation:

$$\Delta G^\circ = -RT \ln K \tag{9}$$

$\Delta G^\circ = -RT \ln K$ where K (L g^{-1}) is an equilibrium constant obtained by multiplying the Langmuir constants Q_0 and b [29]. T is the absolute temperature (K) and R is the gas constant (8.314 J mol^{-1} K^{-1}). The relationship between the changes in the Gibbs free energy, entropy (ΔS°) and enthalpy (ΔH°) can be expressed as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{10}$$

ΔS° and ΔH° can be calculated from the plot of ΔG° vs. T. The calculated thermodynamic parameters are presented in Table 2. The negative value of ΔG° and ΔH° indicates the spontaneous and exothermic nature of the adsorption. The negative value of ΔS° suggests that the process is enthalpy driven.

Table 3
Monolayer adsorption capacities in the literature for Pb(II) adsorption

Adsorbents	Q_0 (mg g^{-1})	References
Muskmelon peel	167.80	[9]
Date stone	38.46	[12]
Apricot stone	21.38	[13]
Tamarind nut	21.88	[14]
Gingelly oil cake	114.94	[15]
Palm shell	95.2	[24]
Coconut shell	40.12	[25]
Palm shell	82.46	[26]
Hazelnut husks	13.05	[27]
Tamarind wood	134.22	[28]
CLP	125.00	Present study
CLPC	166.67	Present study

3.8. Kinetics of adsorption

In order to investigate the controlling mechanism of adsorption processes, the pseudo-first-order and pseudo-second- order rate equations were applied to analyze the kinetic adsorption data obtained at four different initial Pb(II) ion concentrations.

A pseudo-first-order equation of Lagergren [30] is generally expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (11)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption amount at equilibrium and at time t (min), respectively. k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption process. The constants were determined experimentally by plotting of $\log(q_e - q_t)$ vs. t.

Pseudo-second-order model was also generally applied to fit the experimental data. The linear form of pseudo-second-order model [31] can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of adsorption. By plotting a curve of t/q_t against t, q_e and k_2 can be evaluated. The initial adsorption rate, h_0 (mg g^{-1} min^{-1}), is defined as [32]:

$$h_0 = k_2 q_e^2 \quad (13)$$

In order to compare quantitatively the applicability of kinetic models in fitting to data, the percentage relative deviation (P %) was calculated by the following equation:

$$P(\%) = 100/N \sum \left[\frac{q_{e(\mathrm{exp})} - q_{e(\mathrm{theo})}}{q_{e(\mathrm{exp})}}\right] \quad (14)$$

where $q_{e(\mathrm{exp})}$ and $q_{e(\mathrm{cal})}$ are the experimental and calculated value of Pb(II) adsorbed on the adsorbents, N is the number of measurements made. It is found that the lower value of percentage deviation (P %), better is the fit. It is generally accepted that when P (%) value is less than 5, the fit is considered to be excellent [33].

All kinetic parameters, correlation coefficients and P (%) are listed in Table 4. The correlation coefficient (R^2) for the pseudo-second-order model is much closer to unity. The calculated q_e value is found to be much closer to the experimental q_e value. Furthermore, the per cent relative deviation (P %) is also found to be less than 5% in the case of pseudo-second-order. These results confirm that the adsorption kinetics of Pb(II) ions onto the CLP and CLPC is mainly governed by pseudo-second-order equation. This means that the overall rate of Pb(II) ion adsorption process seems to be controlled by the chemical process

Table 4
Pseudo-first-order and pseudo-second-order constants for Pb(II) adsorption onto CLP and CLPC at different initial concentrations

			Pseudo-first-order				Pseudo-second-order				
Adsorbent	C_0 (mg L^{-1})	q_e (exp) (mg g^{-1})	k_1 (min^{-1})	q_e (cal) (mg g^{-1})	R^2	P (%)	k_2 (g mg^{-1} min^{-1})	q_e (cal) (mg g^{-1})	h_0 (mg g^{-1} min^{-1})	R^2	P (%)
CLP	3	2.81	0.018	2.25	0.924	19.93	0.015	2.92	0.13	0.995	3.91
	5	4.79	0.014	2.30	0.998	51.98	0.010	4.98	0.25	0.999	3.97
	7	6.76	0.012	3.08	0.898	54.44	0.009	6.99	0.44	0.997	3.40
	10	9.30	0.021	4.74	0.914	49.03	0.006	9.50	0.54	0.995	2.15
CLPC	3	2.98	0.016	0.82	0.997	72.48	0.045	3.03	0.41	0.999	1.34
	5	4.93	0.016	1.25	0.996	74.65	0.030	5.03	0.76	0.999	2.03
	7	6.93	0.012	2.06	0.942	70.27	0.020	7.25	1.05	0.999	4.62
	10	9.98	0.018	3.36	0.974	66.33	0.010	10.42	1.09	0.999	4.41

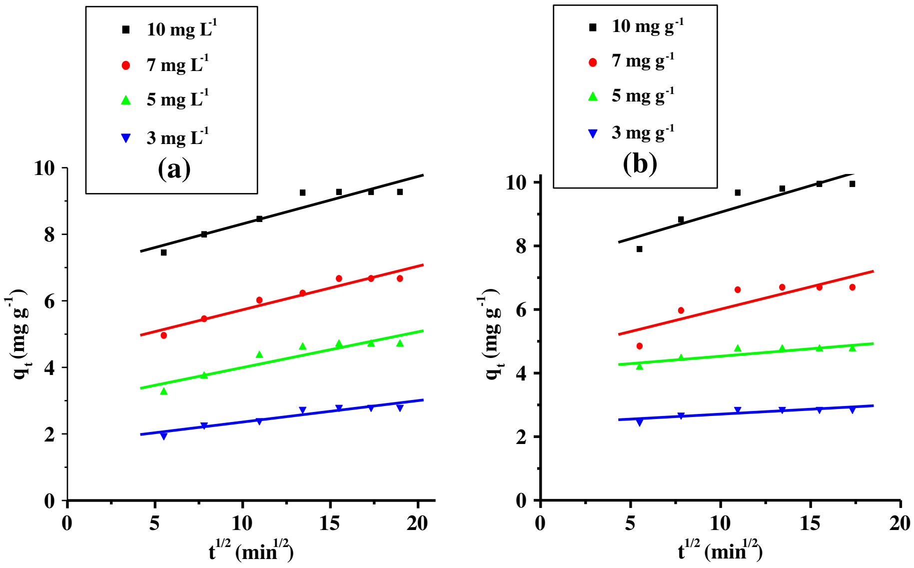

Fig. 6. (a) Intraparticle diffusion model for the adsorption of Pb(II) onto CLP and (b) intraparticle diffusion model for the adsorption of Pb(II) onto CLPC.

through sharing of electrons or by covalent forces through exchanging of electrons between adsorbent and adsorbate.

3.9. Adsorption mechanism

To gain insight into the mechanisms and rate-controlling steps affecting the kinetics of adsorption, the intraparticle diffusion model has been described by Weber and Morris [34] as:

$$q_t = k_d t^{1/2} + I \tag{15}$$

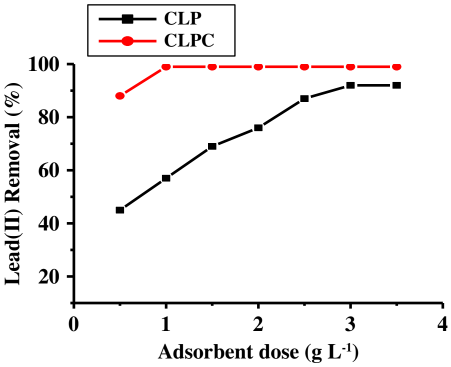

Fig. 7. Effects of the adsorbent dose on the removal Pb(II) ions from electroplating wastewater (C_0: 101 mg L^{-1}, pH: 5.0 and contact time: 3 h).

where k_d is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$), and I is the constant that gives an idea about the boundary layer thickness (mg g^{-1}). According to this model, if the plot of q_t vs. $t^{1/2}$ gives a straight line, then the adsorption process is controlled by intraparticle diffusion, while, if the data exhibit multi-linear plots, then two or more steps influence the adsorption process [35]. In the present study, the plots present multi-linearity (Fig. 6(a) and (b)), indicating that two steps occurred in the process. At the first, sharper portion may be considered as an external surface adsorption or faster adsorption stage. The second portion describes the gradual adsorption stage, where the intraparticle diffusion is rate controlled. This indicated that the rate of metal removal is higher in the beginning due to large surface area of the adsorbent available for the adsorption of metal ions. After the adsorbed material formed a thick layer, the capacity of adsorbent got exhausted and the uptake rate was controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. None of the plots passed through the origin (Fig. 6(a) and (b)), which revealed that the intraparticle diffusion is part of the adsorption but is not the only rate-controlling step. Some other mechanisms such as ion exchange may be also control the rate of adsorption.

4. Pb(II) removal from electroplating wastewater

Batch experiments with lead electroplating wastewater have been carried out to elucidate the

Table 5
Five cycles of Pb(II) adsorption–desorption with 0.7 N HCl as the desorbing agent

Cycles	Pb(II) concentration (mg L^{-1})	CLP Adsorption (%)	Recovery (%)	CLPC Adsorption (%)	Recovery (%)
1	101	93.42	61.41	99.50	98.90
2	101	90.39	36.57	99.17	98.35
3	101	90.18	34.14	99.22	97.74
4	101	89.15	33.54	99.10	94.80
5	101	85.35	30.25	99.20	92.13

applicability of both sorbents under batch mode operations. Fig. 7 shows the effect of the adsorbent dose on the removal of Pb(II) from electroplating wastewater. When removing Pb(II) from wastewater containing 101 mg L^{-1}, the optimum CLP and CLPC doses were 3 and 1 g reaching maximum removals of 87.42 and 99.50%, respectively. Therefore, CLPC is more effective than CLP when treating lead plating wastewater due to the moderate ion exchange observed with CLPC compared to CLP.

4.1. Desorption and regeneration of the adsorbent

To determine the applicability of the adsorbent over repeated uses, 0.7 N HCl was used to regenerate the peel and carbon over five cycles of operation. The results in Table 5 clearly show that CLPC can be used repeatedly for five cycles of operations without affecting its adsorption capacity for Pb(II). However, the recovery of Pb(II) ions decreased in CLPC from 98.90 to 92.10% during the fifth cycle because the Pb(II) ions were strongly bound to the new opening sites. In the case of CLP, both the adsorption and desorption values decreased rapidly. These results showed that CLPC has a greater potential for repeated use and recovery of Pb(II) ions. The attrition losses were also calculated at the end of the fifth cycle. The CLPC showed 3.0% losses on average, while CLP showed 5–6% losses at the end of the cycle during batch mode operations.

5. Conclusion

CLP and its CLPC can be used to remove 85 and 99% of the Pb(II) from aqueous solutions. The presence of hydroxyl, carboxylic and sulphonic acid groups in CLPC is confirmed by FT-IR spectroscopy, imparting ion-exchange properties to the CLPC. The equilibrium data agreed with the Langmuir isotherm, and the adsorption capacity (Q_0) of CLPC is 1.3 times larger than that of CLP. The thermodynamic parameters indicate that the adsorption process is spontaneous, feasible and exothermic. The kinetic studies show that the experimental data can be well fitted by pseudo-second-order rate equation. The experiments with lead(II) electroplating wastewater revealed that CLPC is more effective than CLP. The CLPC was tested for five adsorption and regeneration cycles for the removal of Pb(II) ions from wastewater, revealing lesser tendency towards attrition when compared to CLP. Therefore, the present studies reveal that the CLPC is a very effective and inexpensive adsorbent for removing Pb(II) from aqueous systems.

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