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BATCH STUDIES FOR THE ADSORPTION OF LEAD (II) FROM AQUEOUS PHASE BY WASTE GENERATED FROM *CITRUS LIMETTIOIDES*

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ABSTRACT

The Pb (II) adsorption behaviour of carbon derived from *citrus Limettioides* seed, which is a novel waste material (CLSC), was investigated as a function of parameters such as agitation time, solution pH and temperature. The maximum uptake of lead (II) ion was obtained at pH 4.0-6.0. Adsorption equilibrium was established by 4 hr. The functionality of the CLSC was characterized by FT-IR spectra. The Freundlich, Langmuir, Temkin, Dubinin-Radushkevich, Redlich-Peterson and Sips models were applied to describe the equilibrium isotherms using nonlinear regression analysis. The equilibrium data fits well for the Langmuir, Redlich-Peterson and Sips adsorption isotherms. The Langmuir monolayer adsorption capacity of CLSC was found to be 142.86 mg/g. Thermodynamic parameters such as ΔG^o, ΔH^o and ΔS^o have also been evaluated and it has been found that the sorption process was feasible, spontaneous and exothermic in nature. Results indicate that CLSC can be used as an effective and environmentally friendly adsorbent to detoxify Pb (II)-polluted wastewaters.

Key words: Adsorption, *citrus Limettioides,* Lead (II), Isotherms, Thermodynamics.

INTRODUCTION

Lead is one of the important pollutants in wastewater, and it has become a public health concern because of its nonbiodegradable, toxic, and other adverse effects on human being as well as the fauna and flora. Many methods such as chemical precipitation, electrolysis, ion exchange, reverse osmosis, and membrane separation have been developed to remove lead from wastewater[1]. However, these technologies are either expensive for the treatment and disposal of the secondary toxic metal sludge or ineffective when lead is present in the water at low concentrations. Currently, activated carbon adsorption is a widely used technology because it is simple, low cost and effective for removing low lead

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concentration along with any inorganic and organic matter in waste streams. Activated carbon derived from various agricultural wastes such as *Tamarind* wood[2], hazelnut husks[3], coconut shell[4] and palm shell[5,6] 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 are used as flavouring and preservative in food and beverages, especially in soft drinks and the seeds are disposed off as waste materials. The *citrus limettioides* fruit is mainly composed of d-limonene, myrcene, citronellal and β-citronellol[7]. The purpose of this study aims to develop an activated carbon prepared from a novel waste material such as *Citrus Limettioides* seeds (CLSC) through H_2SO_4 activation and investigate its lead removal capability. The properties of the newly prepared CLSC were investigated by FTIR analysis. The effect of various experimental parameters such as agitation time, pH, and temperature were studied. Adsorption isotherms were analysed using the Freundlich, Langmuir, Temkin, Dubinin-Radushkevich, Redlich-Peterson and Sips isotherm equations. The thermodynamic adsorption data was also reported.

EXPERIMENTAL

Preparation of carbon adsorbent

The *citrus limettioides* seeds were collected from local juice manufacturing unit in Rasipuram and Namakkal (Dt). The material was washed with hot deionised water five to six times for removing water soluble, extractable organics and acids. The washed material was dried in sun light for 24 hr and sieved to 20-50 ASTM mesh size (average 0.575 mm diameter). The dried raw material was then treated with concentrated sulphuric acid in 1:2 weight ratios and kept in an air-oven at 160 ± 5°C for 24 hr. The carbonized material was washed with distilled water and soaked in 1% sodium bicarbonate for 24 hr. The material was again washed, dried and sieved to 20-50 ASTM mesh size and used for experiments (CLSC).

Preparation of the Pb (II) solutions

Stock aqueous solution of Pb (II) having concentration of 1000 mg/L was prepared by dissolving 1.59 g of $Pb(NO_3)_2$ in 1000 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 by using 0.1 N HCl or 0.1 N NaOH solutions.

Batch adsorption experiments

Adsorption experiments were conducted in plastic bottles of 300 mL capacity on a temperature controlled shaker. 100 mg of CLSC were added to 100 mL of Pb (II) solutions of 10 mg /L 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 to 7 hr, and pH between 2 to 12. The effect of temperature (300-320 K) was studied by adjusting initial pH at 5.0 using 100 mL of Pb (II) solution containing the concentration of 10 mg/L, respectively. Adsorption isotherm parameters were obtained by varying the initial Pb (II) concentrations at pH 5.0, CLSC dosage 100 mg and equilibrated for 24 hr at room temperature. The batch experiments were 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:

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \qquad \ldots(1)$$

The adsorption capacity of Pb (II) ions adsorbed per gram of adsorbent (mg/g) was calculated by –

$$q_e = \frac{C_o - C_e}{M} \times V \qquad \ldots(2)$$

where C_o and C_e are the initial and equilibrium Pb (II) concentrations (mg/L); V is the volume of the Pb (II) solution (L); M is the mass of the adsorbent used (g), respectively.

RESULTS AND DISCUSSION

FI-IR 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, carboxylic and sulphonic acid groups were identified as potential adsorption sites, which are responsible for binding the metal ions to the adsorbent. FT-IR spectrum of CLSC is shown in Fig. 1. The strong absorption peaks at 3433, 1710 and

1359 cm^{-1} confirms the presence of the hydroxyl, carboxylic and sulphonic acid groups in the CLSC.

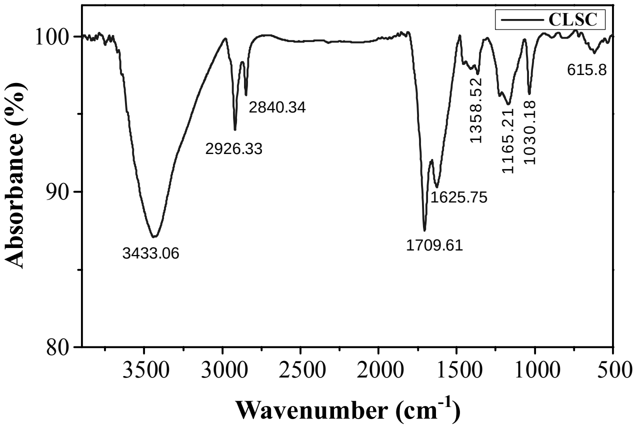

Fig. 1: FT-IR spectrum of CLSC

Effect of agitation time

The effect of agitation time on the removal of Pb (II) ions from aqueous solutions in the concentration of 10 mg/L at pH 5.0 is shown in Fig. 2. The results obtained from the adsorption of Pb (II) ions onto the CLSC showed that the adsorption increased rapidly with time and attains equilibrium at 4 hr. 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. Hence, the optimum equilibrium time was taken as 4 hr for subsequent experiments.

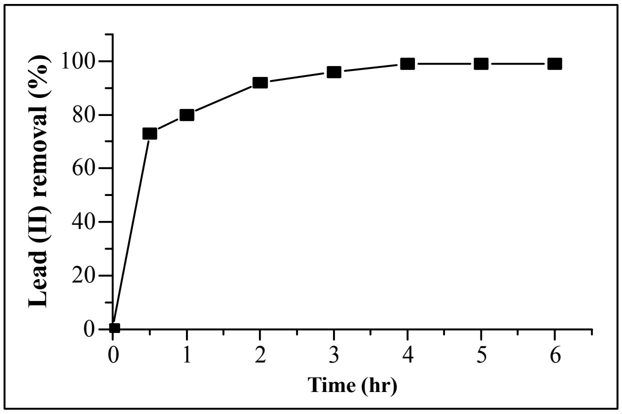

Fig. 2: Effect of agitation time on the adsorption of Pb (II) onto CLSC

Effect of pH

The effect of pH on metal adsorption is considered as a very important parameter in adsorption process. The functional groups are responsible for binding of metal ions in the adsorbent and the competition of metal ion that gets adsorbed to active sites of adsorbent are affected by pH. Fig. 3 shows that the lead removal increases with increase in pH and attains a maximum removal of 99% over a pH range 4.0-6.0 for CLSC, respectively. The adsorption of Pb (II) ions is very 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.

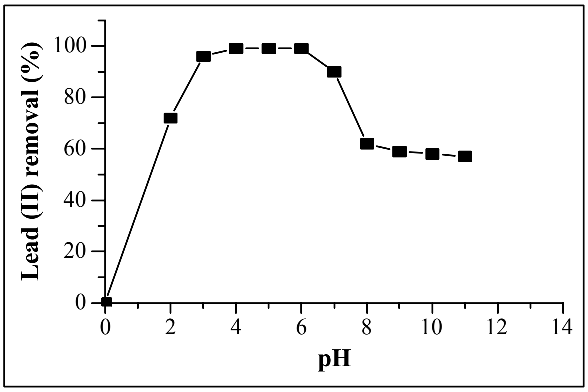

Fig. 3: Effect of pH on the adsorption of Pb (II) onto CLSC

Adsorption isotherms

Equilibrium data is a vital piece of information to design a particular adsorption process. At equilibrium condition, the chemical potential of the solute in liquid phase is equal to that in solid phase. The constant parameters of the isotherm equations for this adsorption process were calculated by nonlinear regression analysis using MATLAB R2010b. The lead (II) concentration data (Fig. 4) were analyzed using the following nonlinear forms of the Freundlich[8], Langmuir[9], Temkin[10], Redlich-Peterson[11], Sips[12] and Dubinin-Radushkevich[13] isotherm models:

$$q_e = K_F C_e^{1/n} \qquad \ldots(3)$$

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \qquad \ldots(4)$$

$$q_e = B \ln (AC_e) \qquad \ldots(5)$$

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \qquad \ldots(6)$$

$$q_e = q_{max} \frac{K_s C_e^\gamma}{1 + K_s C_e^\gamma} \qquad \ldots(7)$$

$$q_e = q_{mD} \exp[-\beta (RT \ln (1 + \frac{1}{C_e}))^2] \qquad \ldots(8)$$

where, C_e is the concentration of lead in the aqueous solution at equilibrium, K_F and n are the Freundlich constants, denoting the adsorption capacity and intensity; Q_m is the monolayer adsorption capacity, and K_L is the Langmuir constant related to binding energy; A (L/mg) is the equilibrium binding constant that corresponds to the maximum binding energy, and B is a Temkin constant related to the heat of adsorption (kJ/mol). K_R, a_R and g are the Redlich-Peterson constant related to the adsorption capacity, affinity of the binding sites and adsorption intensity; q_{max}, K_s and γ are the sips constant; q_{mD} is the D-R monolayer adsorption capacity and β is the adsorption energy. The β value gives the mean free energy (E) of adsorption per molecule of adsorbate, when it is transferred to the surface of the solid infinity in the solution, and can be computed using the following relationship:

$$E = [1/\sqrt{2\beta}] \qquad \ldots(9)$$

The isotherm parameters, correlation coefficients (R^2), sum of squares error (SSE), and root mean squared error (RMSE) values were estimated from the plot of q_e versus C_e (Fig. 4) and are listed in Table 1. Based on the R^2, SSE and RMSE values from Table 1, the Langmuir, Redlich-Peterson and Sips isotherm model exhibited a better fit to the adsorption equilibrium data of lead (II) ions onto CLSC, respectively. Note that the Redlich-Peterson and Sips model fit was superimposed on the Langmuir fit (Fig. 4). The values of g and γ in Table 1 are closer to 1 than 0, which means that the isotherm is approaching the Langmuir but not the Freundlich isotherm. Hence, the good fit of equilibrium data in Langmuir, Redlich-Peterson and Sips isotherm expressions confirms the monolayer adsorption of lead (II) ions onto CLSC. This may be due to the homogeneous distribution of active sites on the surface of CLSC. According to Langmuir isotherm, the monolayer saturation capacity (Q_m) of Pb (II) ion onto CLSC was found to be 142.86 mg/g. The calculated E value for the present study (Table 1) is below 8 KJ/mol, indicates that the adsorption of lead (II) ions onto the CLSC surface follow the physical adsorption type.

Table 1: Nonlinear fitting isotherm parameters for the adsorption of Pb (II) onto CLSC

Isotherm model	Parameter	CLSC
Freundlich	K_F (mg/g)	22.32
	n	1.388
	R^2	0.995
	SSE	1.246
	RMSE	6.205
Langmuir	Q_m (mg/g)	142.86
	K_L (L/mg)	0.210
	R^2	0.999
	SSE	0.288
	RMSE	0.331
Temkin	A	3.484
	B	8.914
	R^2	0.965
	RMSC	3.632
	SSE	52.77
Dubinin-Radushkevich	$q_{m\mathrm{D}}$ (mg/g)	58.00
	β (mg^2 J^{-2})	6.12 x 10^{-8}
	E (KJ/mol)	2.857
	R^2	0.932
	SSE	5.091
	RMSE	103.7
Redlich-Peterson	K_R (L/g)	27.43
	a_R (L/mg)	0.230
	g	0.958
	R^2	0.999
	SSE	0.325
	RMSE	0.316

Cont…

Isotherm model	Parameter	CLSC
Sips	q_{max} (mg/g)	132.1
	K_s (L/mg)	0.199
	γ	0.990
	R^2	0.999
	SSE	0.328
	RMSE	0.322

Note: SSE and RMSE denote the sum of square error and root mean square error, respectively

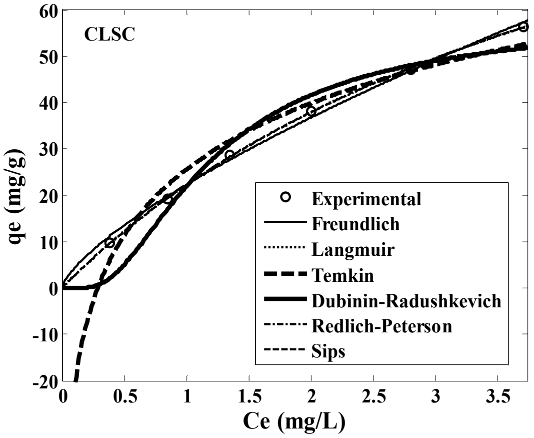

Fig. 4: Nonlinear adsorption isotherms for Pb (II) ion onto the CLSC

The comparison of maximum monolayer adsorption capacity (Q_m) of lead (II) ions onto various adsorbents such as *Tamarind* wood[2] (43.85 mg/g), hazelnut husks[3] (13.05 mg/g), coconut shell[4] (40.12 mg/g) and palm shell[5,6] (95.20 and 82.46 mg/g) shows that CLSC has high adsorption capacity of 142.86 mg/g, suggesting that it is a promising adsorbent to remove heavy metals from aqueous solutions.

Effect of temperature and thermodynamics parameters

The effect of temperature on the removal of lead (II) ions onto CLSC was studied using 100 mL of 10 mg/L of Pb (II) concentrations with an adsorbent dosage of 100 mg at pH 5.0 and at a temperature of 300-320 K for 4 hr and the results are shown in Fig. 5a. The percentage removal of lead (II) ions decreases with the increase in temperature. This is mainly due to the decrease in surface activity suggesting that the adsorption between lead (II) ions and CLSC is an exothermic process. The maximum removal of lead (II) ions was obtained at 300 K.

Thermodynamic parameters such as free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) change of adsorption can be evaluated from the following equations

$$\Delta G^0 = -RT \ln K_c \quad \text{...(10)}$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad \text{...(11)}$$

where, R is the gas constant (8.314 KJ/mol K), T is the absolute temperature (Kelvin) and K_c is the equilibrium constant (L/g). The values of enthalpy change (ΔH^0) and the entropy change (ΔS^0) were determined from the slope and the intercept from the plot of ln K_c versus $1/T$ (Fig. 5b) and are listed in Table 2.

Table 2: Thermodynamic parameters for the adsorption of Pb (II) ions onto CLSC

Adsorbent	Temp. (K)	Thermodynamic parameters		
		ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (kJ/mol / K)
CLSC	300	-11.473	-87.746	-0.255
	310	-8.196		
	320	-6.492		

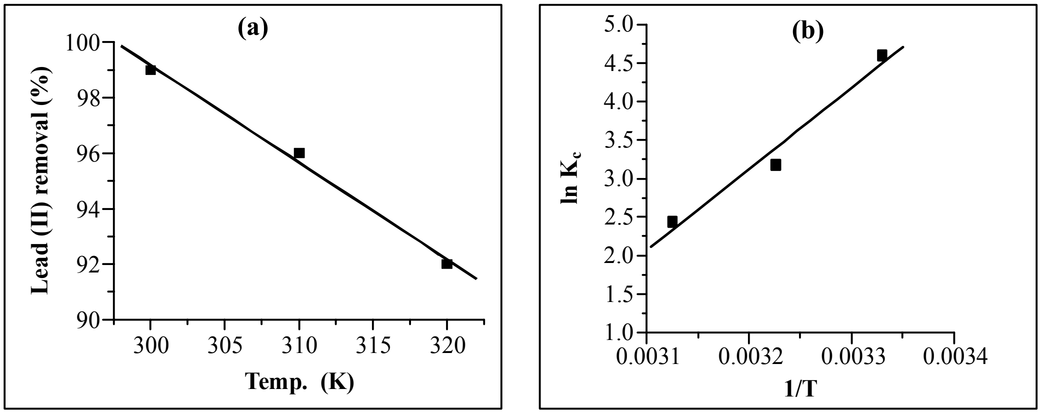

Fig. 5: (a) Effect of Temperature on lead (II) removal onto CLSC; (b) Thermodynamic plots for the adsorption of Pb (II) ions onto CLSC

The negative value of ΔG^o implies that the adsorption of lead (II) ions onto CLSC was spontaneous and feasible. The ΔG^o value is more negative when decreasing the temperature, suggesting that lower temperatures favor the adsorption.The negative ΔH^o value indicates the exothermic nature of adsorption and the ΔS^o can be used to describe the randomness at the CLSC- solution interface during the sorption.

CONCLUSION

The present study shows that the carbon prepared from a novel waste material, *citrus Limettioides* seed can be used as an adsorbent for the removal of lead (II) ions from aqueous solutions. The presence of hydroxyl, carboxylic and sulphonic acid groups are confirmed by FT-IR spectroscopy. The removal of Pb (II) from aqueous solutions strongly depends on the agitation time, solution pH and temperature. It was observed that the adsorption was pH dependent and the maximum removal of occurred at pH of 4.0-6.0 for an initial Pb(II) concentration of 10 mg/L. The percentage removal of lead (II) ion decreased with increase in temperature. Equilibrium data agreed well with the Langmuir, Redlich-Peterson and Sips isotherm models. The maximum monolayer adsorption capacity of CLSC was found to be 142.86 mg/g. Therefore, it can be concluded that carbon derived from *citrus Limettioides* seed is a very effective and inexpensive adsorbent; it may be treated as an alternative adsorbent for the treatment of wastewater containing lead (II) ions.

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