

## Removal of Cadmium(II) from Water using Modified *Citrus limettioides* Peels: Thermodynamic and Isotherm Studies

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The adsorption performance of sulphuric acid treated low cost adsorbent synthesized by using *Citrus limettioides* peel as an effective raw material for the removal of cadmium(II) from water. The batch adsorption method was carried out to optimize some parameters like contact time, pH and adsorbent dose. The nonlinear isotherm equations were used to calculate the different isotherm constant of five isotherm models namely Freundlich, Langmuir, Dubinin-Radushkevich, Redlich-Peterson and Sips. The Langmuir monolayer adsorption capacity of chemically modified *Citrus limettioides* peel was found to be 287.60 mg g<sup>-1</sup>. The negative values of  $\Delta G^\circ$  and  $\Delta H^\circ$  showed that the adsorption process is spontaneous and exothermic.

**Keywords:** Cadmium(II), Isotherms, *Citrus limettioides*, Sorption.

### INTRODUCTION

Water pollution with heavy metals has released into environment due increased in an industrial growth and human activities. The presence of toxic metals in the drinking water is very risky to all living organisms because they are non-biodegradable and must be removed to prior discharge in to water-bodies. The cadmium occurs in various industrial wastewaters as mining, refining processes, electroplating, fertilizer industries, silver-cadmium batteries and paints. The poisonous effect of Cd(II) causes liver damage, bone degeneration and renal dysfunction [1]. Long-term exposure to cadmium through water, soil, air, and food leads to cancer and organ system toxicity such as urinary, reproductive skeletal, cardiovascular, respiratory and central nervous symptoms. The maximum permissible limit of cadmium(II) in drinking water should not exceed 0.005 mg L<sup>-1</sup> as prescribed by WHO [2].

The chemical precipitation, adsorption, electrolysis, membrane filtration and ion exchange methods are applied to remove heavy metals from polluted industrial water. Compared with other techniques, adsorption technology is simple, low cost and can be effectively applied for removal of metal ions present at very low concentration in wastewater. In order to decrease

the experimental cost, several researchers have been attempted to identify low cost adsorbents from natural materials and agricultural wastes such as olive stone [3], cherry kernel [4], sunflower head carbon [5], *Albizia lebeck* pods [6], *Auricularia auricular* matrix waste [7], *Sorghumx drummondii* (Sudan grass) [8], red mud [9], wheat bran [10] and pigeon peas hulls waste [11] are successfully tested for removal of cadmium(II) in industrial wastewater.

The aim of this research focusses to remove cadmium(II) for the preparation of sulphuric acid treated adsorbent derived from *Citrus limettioides* peels and simultaneously evaluated by commercial activated carbon. The cadmium(II) removal efficiency was optimized to various process viz., effect of contact time, pH and carbon dose. The adsorptions isotherms models, thermodynamic parameters and desorption related process were also examined.

### EXPERIMENTAL

**Preparation of adsorbents:** The raw *Citrus limettioides* peel were collected from a local area in Rasipuram, India and washed with boiling deionized water to eliminate the acid content and dried in the sunlight and slash into little pieces. Then the content was treated with concentrated sulphuric acid

under a weight ratio of 1:2 and heated in the hot air-oven at  $160 \pm 5$  °C for 1 day. The material was washed thoroughly with deionized water and to remove the excess acid content by using 1 %  $\text{NaHCO}_3$ . The resulting material was washed, dried and sieved in the particle size range of 20-50 ASTM mesh and used in the further experiments named as sulphuric acid treated *Citrus limettioides* peel activated carbon (SCLP). The commercially activated carbon (CAC) was bought from the local shop and sieved to 20-50 ASTM mesh size and used for evaluation purposes.

**Batch adsorption studies:** The batch studies were carried out 100 mL of cadmium(II) solution containing a concentration of  $10 \text{ mg L}^{-1}$  were taken in the polythene bottle of 300 mL capacity and added 0.1 g of carbon. The reaction mixture was stirred into a temperature controlled shaker at room temperature for different time periods followed by filtration and the cadmium(II) concentrations were recognized by atomic absorption spectrophotometer.

The percentage of cadmium(II) ions was determined as follows:

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

where  $C_o$  and  $C_e$  are the initial and equilibrium concentrations ( $\text{mg L}^{-1}$ ) of cadmium(II) ions.

The effect of contact time on adsorption behaviour of  $10 \text{ mg L}^{-1}$  of cadmium(II) ions was studied in different time intervals ranging from 0.5 to 3 h, 0.1 g of SCLP and CAC dose at pH of  $5.0 \pm 0.3$  and at 27 °C. To investigate the pH effect for the adsorption of  $10 \text{ mg L}^{-1}$  of cadmium(II) was tested in the pH range of 2.0 to 10.0, 0.1 g of carbon dose at a contact time of 2 and 3 h for SCLP and CAC, respectively. The carbon dose effect was also studied for the adsorption of  $10 \text{ mg L}^{-1}$  of cadmium(II) ions and differ the SCLP and CAC dose range from 0.05-0.4 g at an optimum pH and contact time of 2 h for SCLP and 3 h for CAC. After equilibration, the solutions were centrifuged and examined for cadmium(II) ion content was estimated.

To study the adsorption isotherms, the experiments were conducted with 100 mL of cadmium(II) solutions at the concen-

tration of 10 to  $60 \text{ mg L}^{-1}$ . The solution pH of cadmium(II) solutions was maintained at  $5.0 \pm 0.3$  °C for SCLP and at  $6.0 \pm 0.2$  °C for CAC, respectively. A constant dose of 0.1 g and 0.3 g for SCLP and CAC were added separately in each bottle and the solutions were agitated using a temperature controlled mechanical shaker for 24 h at  $27 \pm 0.5$ ,  $37 \pm 0.5$ ,  $47 \pm 0.5$  °C to attain equilibrium. After 24 h the solution was filtered and the adsorption capacity ( $q_e$ ) of cadmium(II) ions was calculated as follows:

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

where,  $C_o$  and  $C_e$  are initial and equilibrium concentration ( $\text{mg L}^{-1}$ ) of cadmium(II) ion,  $M$  = mass of the adsorbent,  $V$  = volume of cadmium(II) solution.

## RESULTS AND DISCUSSION

**FT-IR analysis:** Fig. 1 represents the FTIR spectra of SCLP and CAC. The band around at 3444 and  $3422 \text{ cm}^{-1}$  indicates the hydroxyl group of SCLP and CAC. The peaks observed at 2915, 2930 and  $1377 \text{ cm}^{-1}$  correspond to unsymmetrical aliphatic C-H stretching and aromatic C=C stretching vibrations. The band around at 1626 and  $1030 \text{ cm}^{-1}$  in SCLP is due to the C=O stretching vibrations in alcohols or carboxylic groups and S=O symmetric stretching vibration of sulphonic acid group. The presences of effective functional groups namely carboxyl, sulphonic and hydroxyl groups in SCLP is dependable for cadmium(II) adsorption.

**SEM and EDAX analysis:** The composition of elements and morphology of SCLP and CAC surface and its Cd(II) sorption was determined by SEM and EDAX techniques. The surface morphology of SCLP and CAC (Fig. 2) show that the pores are uneven and heterogeneous. Further, it could be concluded that pores on the SCLP and CAC assist the excellent ability for the adsorption of cadmium(II) ions.

The elemental composition of SCLP and CAC was analyzed using energy dispersive analysis system of X-ray (EDAX) to confirm the cadmium(II) ion adsorption. The EDAX spectra of unloaded SCLP and CAC do not show the peak of cadmium, while the presence of cadmium(II) ions was observed onto SCLP and CAC (Figs. 3b and 4b) after adsorption.

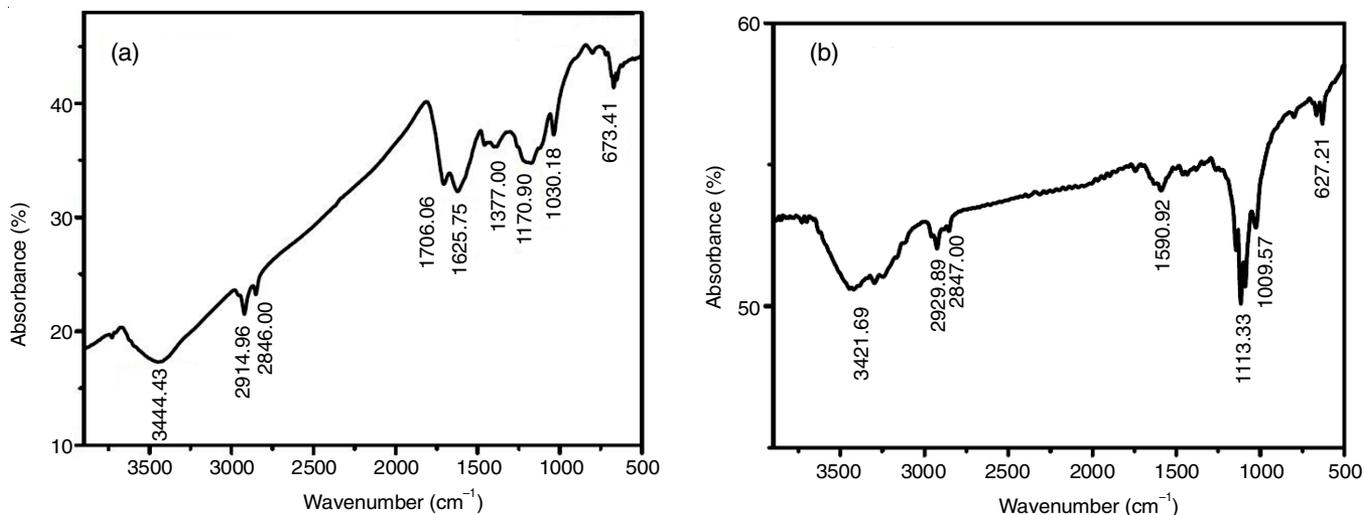


Fig. 1. FTIR image of (a) SCLP; (b) CAC

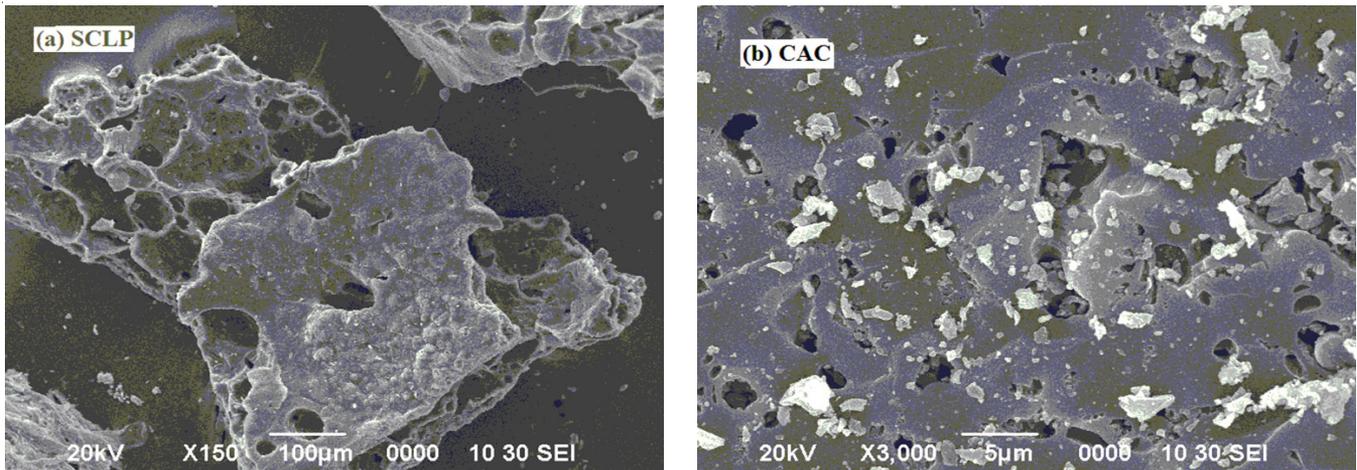


Fig. 2. SEM photographs for (a) SCLP; (b) CAC

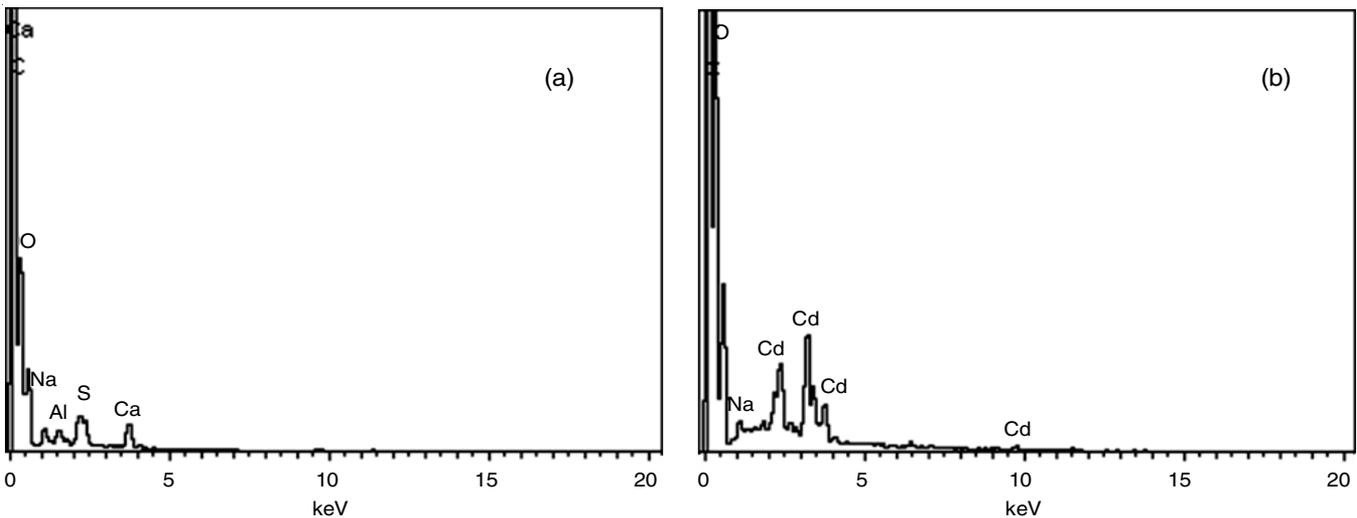


Fig. 3. EDAX image for SCLP (a) and (b) before and after adsorption of Cd(II), respectively

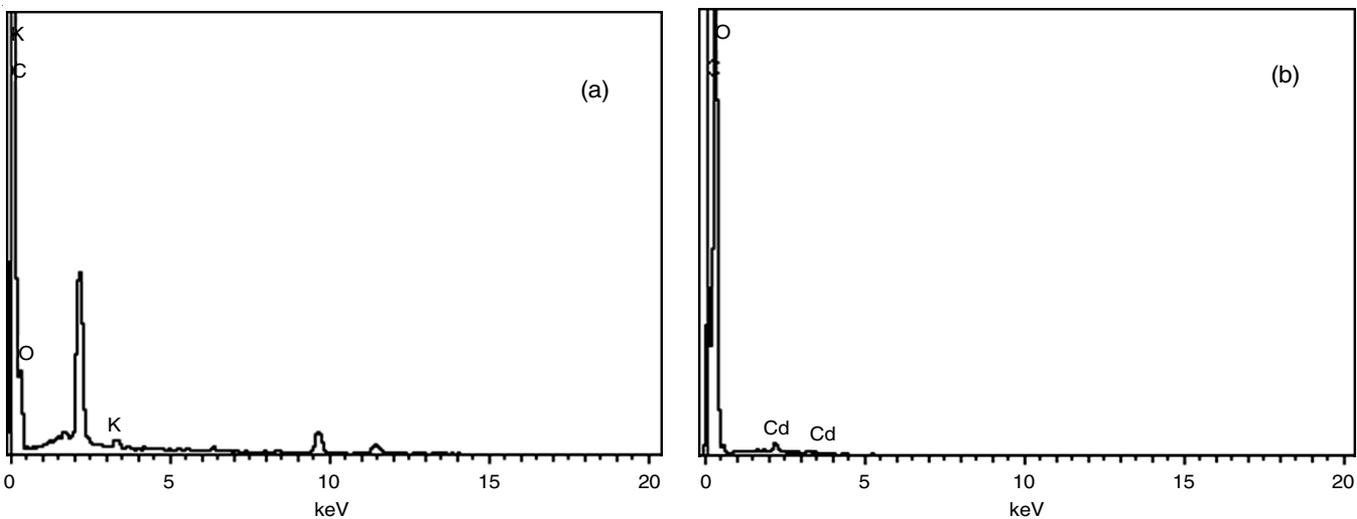


Fig. 4. EDAX image for CAC (a) and (b) before and after adsorption of Cd(II), respectively

**Effect of contact time:** It could be examined from Fig. 5, the rate of removal is faster at the initial stage and attaining equilibrium in 2 h for SCLP and 3 h for CAC. The faster rate at the initial stage is due to the greater availability of uncovered adsorption sites of SCLP and CAC [12]. Therefore, the contact

time was considered as 2 h for SCLP and 3 h for CAC in all subsequent experiments.

**Effect of pH:** Fig. 6 represents that uptake of metal ions are greatly dependent with pH and maximum removal of  $99.5 \pm 0.4\%$  of cadmium(II) ions against SCLP was achieved over

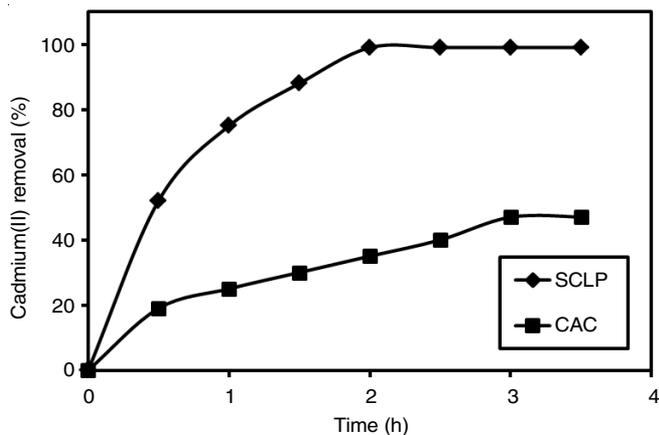


Fig. 5. Effect of contact time for the adsorption of Cd(II) ions

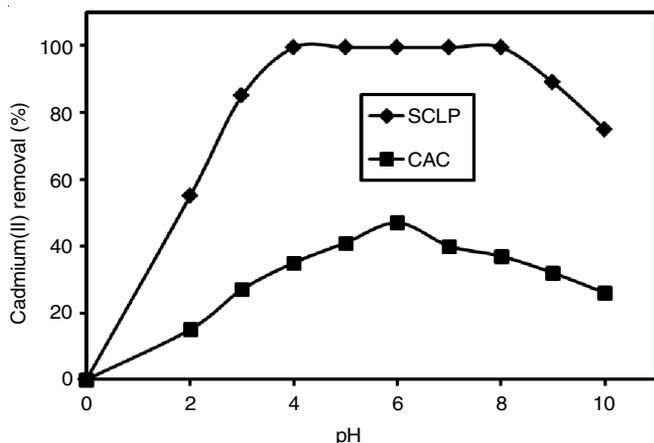


Fig. 6. Effect of pH for the adsorption of Cd(II) ions

a range of pH 4.0-8.0. However in case of CAC, the maximum cadmium(II) removal was determined to  $47 \pm 0.2\%$  at pH of 6. It could be observed that at low pH value, metal ion adsorption amount is very low, because the active adsorption sites remain protonated. As the pH increased, the concentration of  $H^+$  ions decreased, consequently they do not compete with metal ions on the adsorption sites and the adsorbent surface is higher negative charge will easily attract the positively charged metal ions [13,14]. When the pH values are higher, metal ions combined with  $OH^-$  ion to form metal hydroxide precipitate, thus stop the adsorption process. Therefore, further experiments were studied to take at an optimum pH value of 5 and 6 for SCLP and CAC, respectively.

**Effect of adsorbent dosage:** The effect on SCLP and CAC dose on the removal percentage of cadmium(II) ions are shown in Fig. 7. At equilibrium, the effectiveness of cadmium(II) ion removal decreased with an increase in carbon dose and this may due to the gradient of concentration. The maximum removal of cadmium(II) ions was achieved at  $99.5 \pm 0.4\%$ , when 0.1 g of SCLP dose is used. However in case of CAC, the maximum removal of  $72.5 \pm 0.3\%$  was achieved at an optimum dose of 0.3 g. An increase in removal efficiency of cadmium(II) ions can be recognized that increase in surface area ensuing from the increase in SCLP and CAC mass or higher number of exchangeable sites for adsorption. This indicated that SCLP is three times more efficient with respect to dose of carbon than CAC.

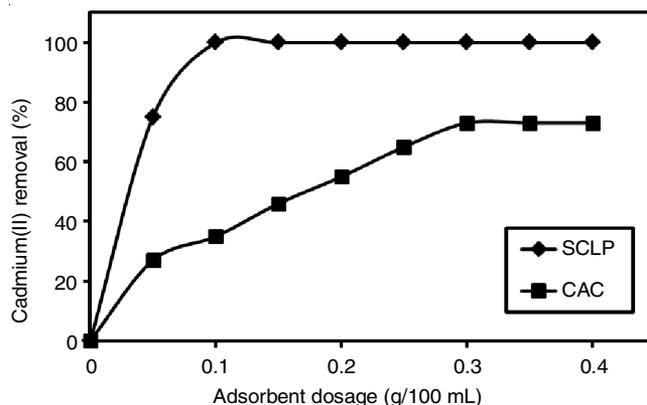


Fig. 7. Effect of adsorbent dose for the adsorption of Cd(II) ions

**Adsorption isotherms:** In the present work, several isotherm models *viz.* Freundlich [14], Langmuir [15], Dubinin-Radushkevich [16], Redlich Peterson [17] and Sips [18] were used to analyze the equilibrium data at different temperatures (27-47 °C) by using the following equations:

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

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = q_{mD} \exp \left[ -\beta \left( RT \ln \left( 1 + \frac{1}{C_e} \right) \right)^2 \right] \quad (5)$$

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

$$q_e = q_{max} \frac{K_S C_e^\gamma}{1 + K_S C_e^\gamma} \quad (7)$$

where,  $C_e$  is the sorbate equilibrium concentration,  $K_F$  is the Freundlich constants and  $n$  is the constant that represents the measure of non-linearity;  $q_m$  represent the Langmuir monolayer adsorption capacity and  $K_L$  is the Langmuir constant related to binding energy;  $K_R$ ,  $a_R$  and  $g$  are the Redlich-Peterson constants correspond to adsorption capacity, affinity of the binding sites and adsorption intensity, respectively. The  $q_{max}$ ,  $K_a$  and  $r$  are the sips constant;  $q_{mD}$  is the D-R monolayer adsorption capacity and  $\beta$  is the adsorption energy. The  $\beta$  value gives the mean free energy ( $E$ ) of adsorption per molecule of adsorbate, when it is transferred to the surface of solid infinity in the solution, and can be computed using the following relationship:

$$E = \left( \frac{1}{\sqrt{2\beta}} \right) \quad (8)$$

The non-linear regression analysis was used to calculate the various isotherm parameters such as correlation coefficients ( $R^2$ ), sum of squares error (SSE) and root mean squared error (RMSE) using MATLAB R2010b from the plot of  $q_e$  versus  $C_e$  (figures not shown) and the values are presented in Table-1.

Among five isotherms, the values of  $R^2$  is much closer to 1 and less RMSE, SSE value suggests that Langmuir isotherm provides the best fit for the adsorption of cadmium(II) ions by SCLP and CAC at different temperatures (27-47 °C). Langmuir

TABLE-1  
FIVE ADSORPTION ISOTHERM CONSTANTS AND THERMODYNAMIC  
PARAMETERS FOR THE Cd(II) REMOVAL BY SCLP AND CAC

Isotherm model	Constants	SCLP			CAC		
		27 °C	37 °C	47 °C	27 °C	37 °C	47 °C
Freundlich	$K_F$	14.55	7.510	5.542	5.232	4.015	2.790
	$n$ ( $\text{g L}^{-1}$ )	2.755	1.980	1.450	1.987	1.545	1.352
	SSE	32.96	19.42	37.15	15.32	16.12	18.55
	RMSE	3.306	2.926	3.021	2.104	2.039	1.961
	$R^2$	0.958	0.978	0.945	0.960	0.955	0.970
Langmuir	$q_m$ ( $\text{mg g}^{-1}$ )	287.60	235.45	220.50	45.07	36.88	29.55
	$K_L$ ( $\text{L mg}^{-1}$ )	0.385	0.255	0.156	0.097	0.085	0.070
	SSE	4.597	5.516	5.067	1.564	2.543	2.686
	RMSE	0.304	0.212	0.505	0.689	0.841	0.756
	$R^2$	0.998	0.992	0.993	0.995	0.993	0.995
Dubinin-Radushkevich	$q_{mD}$ ( $\text{mg g}^{-1}$ )	47.50	37.30	30.25	10.23	9.85	8.75
	$\beta \times 10^{-7}$ ( $(\text{mol K kJ}^{-1})^2$ )	1.814	2.312	2.668	3.709	6.640	7.834
	$E$ ( $\text{kJ/mol}$ )	1.642	1.471	1.370	1.163	0.869	0.800
	$R^2$	0.792	0.804	0.765	0.789	0.795	0.810
	SSE	35.45	39.67	45.59	32.30	40.50	45.80
	RMSE	4.588	3.789	5.670	3.678	4.350	4.860
Redlich-Peterson	$K_R$ ( $\text{L g}^{-1}$ )	0.979	0.865	0.823	0.350	0.245	0.211
	$a_R$ ( $\text{L mg}^{-1}$ )	8.560	8.025	7.560	3.780	2.970	2.230
	$G$	0.432	0.380	0.285	0.325	0.289	0.245
	$R^2$	0.919	0.920	0.934	0.911	0.925	0.922
	SSE	85.75	69.70	58.25	97.60	85.10	65.20
	RMSE	8.911	8.357	7.975	9.245	8.945	8.970
Sips	$q_{max}$ ( $\text{mg g}^{-1}$ )	11.65	10.10	9.75	3.150	3.010	2.975
	$K_s$ ( $\text{L mg}^{-1}$ )	0.456	0.564	0.478	0.225	0.178	0.120
	$\gamma$	0.439	0.574	0.538	0.389	0.315	0.275
	$R^2$	0.925	0.934	0.917	0.937	0.945	0.928
	SSE	34.56	25.75	40.15	29.26	38.53	32.47
	RMSE	3.575	3.879	2.918	4.789	4.257	3.457
Thermodynamic parameters	$\Delta G^\circ$ ( $\text{kJ mol}^{-1}$ )	-276.17	-154.74	-91.515	-10.90	-8.079	-5.503
	$\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )		-303.60			-91.870	
	$\Delta S^\circ$ ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )		-9.232			-0.270	

adsorption isotherm illustrate the removal of cadmium(II) ions onto SCLP and CAC was dominated by monolayer chemisorptions and homogeneity surface. The maximum adsorption capacity ( $q_m$ ) of cadmium(II) ions onto SCLP was estimated at  $287.60 \text{ mg g}^{-1}$ , which was about 6.4 times greater than that of CAC ( $45.07 \text{ mg g}^{-1}$ ) at  $27^\circ\text{C}$ . The  $q_m$  values decreased with increase in temperature representing the process is exothermic. Table-2 clearly shows that SCLP have higher sorption ability as compared with other adsorbents the removal of cadmium(II) ions.

**Thermodynamics adsorption:** Various thermodynamic parameters, such as standard Gibbs free energy ( $\Delta G^\circ$ ), standard enthalpy ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ) for the adsorption of cadmium(II) ions onto SCLP and CAC were estimated using the following equation:

$$\Delta G^\circ = -RT \ln K \quad (9)$$

where, R and T are the universal gas constant ( $8.134 \text{ kJ mol}^{-1} \text{K}$ ) and absolute temperature (K), while K ( $\text{L g}^{-1}$ ) is the equilibrium constant. This value can be obtained by multiplying the Langmuir constants  $q_m$  and  $K_L$  [32]. Similarly, the values of enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) can be calculated as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

Table-1 shows that the obtained values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are negative at different temperatures, which implies that

TABLE-2  
COMPARATIVE EVALUATION OF VARIOUS  
LOW-COST MATERIALS ON CADMIUM REMOVAL

Agricultural waste carbon	Cadmium(II) uptake capacity, $q_m$ ( $\text{mg g}^{-1}$ )	Ref.
Cherry kernel	198.7	[4]
Sunflower stem carbon	4.40	[5]
<i>Albizialebeck</i> pods	21.22	[6]
Red mud	12.05	[9]
Olive stone	7.80	[19]
Olive fruit stone	24.83	[20]
Silk cotton hull	100.00	[21]
Rice husk	125.94	[22]
Hazelnut husk	61.35	[23]
Hazelnut husk	20.90	[24]
Groundnut husk	29.78	[25]
Brewery spent barley husk	6.64	[26]
Saffron leaves	68.75	[27]
Firmiana Simplex Leaf	117.79	[28]
Bamboo powder	8.57	[29]
<i>Cicer arietinum</i> waste	18.00	[30]
Corn stalk	12.73	[31]
SCLP	287.60	Present study
CAC	45.07	Present study

the adsorption process is spontaneous and exothermic in nature towards the adsorption of cadmium(II) ions in SCLP and CAC.

**Desorption and reusability:** The desorption studies was tested onto SCLP and CAC adsorbents by mixing 100 mg L<sup>-1</sup> of Cd(II) ions in wastewater (1 L) using 0.5 M HCl as a regenerating agent at a dose of 1.0 (SCLP) and 3.0 g (CAC). Then the adsorbent was centrifuged, filtered and washed 3 or 4 times with distilled water and taken into another plastic bottles containing 100 mg L<sup>-1</sup> of cadmium(II) ions solution. Table-3 shows that after five cycles of operation, the adsorption and desorption percentage was almost same for SCPC, but in case of CAC, the adsorption and desorption percentage was decreased rapidly. It could be concluded that as compared to commercial activated carbon (CAC), sulphuric acid treated *Citrus limettioides* peel activated carbon (SCLP) is more effective which proved its suitability for the industrial purpose in large scale applications.

TABLE-3  
DESORPTION STUDY OF Cd(II) ONTO FIVE CYCLES

Cycles	Cd(II) conc. (mg L <sup>-1</sup> )	SCLP		CAC	
		Sorption (%)	Recovery (%)	Sorption (%)	Recovery (%)
1	100	99.50	99.00	70.50	62.35
2	100	99.20	99.10	65.10	51.30
3	100	99.40	99.20	50.30	31.55
4	100	99.60	99.40	39.65	23.34
5	100	99.50	99.20	25.65	19.78

## Conclusion

The modified adsorbent prepared from an agricultural waste viz. *Citrus limettioides* peel found to be a low cost and environment friendly adsorbent for decontaminating the wastewater containing heavy metals. The experimental data fitted well with Langmuir adsorption isotherms and the calculated adsorption capacity of SCLP was found to be 6.4 times greater as compared with CAC. The thermodynamic values of  $\Delta G^\circ$  and  $\Delta H^\circ$  indicated that the adsorption process is spontaneous and exothermic. Desorption studies also explored that *Citrus limettioides* peel activated carbon (SCLP) is effectively utilized for five cycle's operation as compared to commercial activated carbon (CAC).

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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