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Comparative studies on the removal of chromium(VI) from aqueous solutions using raw and modified *Citrus Limettioides* peel

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Citrus Limettioides peel (CLPC) has been modified with sulphuric acid to increase the quantity of sulphonic acid groups improving its metal adsorption capacity. The effect of various parameters such as solution *p*H, contact time, adsorbent dose and presence of other cations and anions under ambient conditions along with raw *citrus limettioides* peel (CLP) has been studied. According to the experimental results, the optimal equilibrium time and *p*H for Cr(VI) ions are found to be 3 h and 2.0 for CLPC and CLP, respectively. The equilibrium data agree well with Langmuir model, which confirm the monolayer coverage of Cr(VI) ions onto CLPC and CLP. The Langmuir monolayer adsorption capacity of the CLPC is found to be 176.50 mg/g which is significantly about 1.8 times greater than that of CLP (99.50 mg/g) at 300 K. The thermodynamic analysis reveals that the adsorption process was spontaneous and exothermic in nature. The kinetic data follow pseudo-second order model with film diffusion process. A single-state batch adsorber has been designed to estimate the amount of adsorbent required to treat the known volume of the effluent using the Langmuir adsorption isotherm. Regeneration study show that CLPC could be effectively utilized for the removal of Cr(VI) ions for seven cycles of operation under study when compared with CLP.

Keywords: Chromium, *Citrus Limettioides* peel, Kinetics, Isotherms, Regeneration

Water is an essential life sustaining element. It pervades our lives and is deeply embedded in our cultural background. Water is required by all living creatures for survival. It is also required for economic growth and development. Clean and fresh drinking water is essential to human and other lives. Chromium compounds are widely used in stainless steel, plating, leather tanning, paints, pigments, printing inks, textile dyeing, and also in wood preservation[1]. Because of its widespread use in industries, huge quantity of wastewater is being generated. The wastewater containing Cr(III) and Cr(VI) affects the soil and water bodies. The Cr(VI) compounds are known to be toxic and mutagenic for most living organisms. Inhalation and ingestion of Cr(VI) over a period can cause cancer in digestive track and lungs[2]. The US EPA requires 0.05 and 0.1 mg/L of Cr(VI) in drinking water and inland surface waters, respectively[3]. Accordingly, chromium containing wastewaters must be treated to lower the Cr(VI) to allowable limits before discharging into the environment.

Conventional methods utilized to remove the Cr(VI) from industrial wastewaters include reduction followed by chemical precipitation, ion exchange, solvent extraction, reverse osmosis and adsorption[3,4] etc. These processes apart from being economically expensive have disadvantages such as high reagent and energy requirements, incomplete metal removal, and generation of a large quantity of toxic waste sludge, which necessitates careful disposal in further steps[5]. Recently, activated carbon adsorption is a commonly used technology because it is simple, inexpensive and effective for removing low chromium concentrations and any organic matter in waste streams. Some of the activated carbons from low-cost materials that have been exploited to remove the chromium(VI) ions from the aqueous solutions such as coconut shell[6], rice husk carbon[7], *Ricinus communis* seed shell[8], *Canarium schweinfurthii* seed shell[9], wood apple shell[10], pomegranate husk[11], *Trapa natans* husk[12] and hazelnut shell[13], etc.

The aim of this study is to investigate the activated carbon prepared from *Citrus Limettioides* peel (CLPC) and compared with raw peel (CLP) for the removal of Cr(VI) from aqueous solutions. The influence of various parameters such as contact time, solution pH, carbon dose and effect of cations and anions in the medium were investigated. The kinetic data were fitted to different models and the isotherm equilibrium data were fitted to Freundlich and Langmuir equations at different temperatures. Thermodynamic parameters were also carried out to estimate the standard free energy (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o). A single-stage batch adsorber was designed for different carbon dose/effluent volume ratios using the Langmuir equation.

Experimental Section

Preparation of adsorbent

The *Citrus limettioides* peel was collected from a local juice manufacturing unit in Rasipuram (Tk), India and consequently, 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 for 2 days and cut into small pieces using a cutter machine. The dried raw material was subsequently digested with sufficient quantities of perchloric acid to break down the fibers and then subsequently treated with concentrated sulfuric acid in a 1:2 ratio by weight and kept at 160 ± 5 ºC in an air-oven for 24 hr. The carbonized material was washed with distilled water and soaked in 1% sodium bicarbonate for 24 hr 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 raw peel at the same particle size as the carbon was also evaluated.

Preparation of Cr(VI) ions solution and analysis

The stock solution containing 1000 mg/L of Cr(VI) was prepared by dissolving 2.83 g of potassium dichromate in 1000 mL distilled water. Required initial concentration of Cr(VI) standards were prepared by appropriate dilution of the above stock Cr(VI) solution. The pH of the solution was adjusted to the required value by using 0.1N HCl or 0.1N NaOH solutions. All the chemicals used were of analytical reagent grade. The concentrations of chromium(VI) ions in the solution before and after equilibrium were determined by Atomic absorption spectrophotometer (Elico, Model-SL163). Fourier transform infrared (FTIR) spectrometer analysis was used to identify the different functional groups present on the surface of the CLP and CLPC from 400 to 4000 cm^{-1} while using KBr as the background. A scanning electron microscope (JOEL JSM 6360) was used to visualize the surface morphology of the CLP and CLPC. The FTIR and SEM details of the prepared adsorbent were discussed in our previous research article[14,15].

Batch mode adsorption studies

Batch adsorption studies were carried out by shaking the plastic bottles of 300 mL capacity which contains specified amount of chromium(VI) ions concentration and adsorbent dose at 125 rpm for a fixed period of the time using a temperature-controlled shaker. After the equilibrium period, the solutions were centrifuged and the Cr(VI) concentrations were determined with an atomic absorption spectrophotometer. Each determination is repeated thrice and the average results are presented in this study. The chromium(VI) removal (%) was calculated using the following equation[16] :

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \text{X } 100 \qquad \dots (1)$$

where C_0 and C_e are the initial and equilibrium concentration of chromium(VI) ions (mg/L) respectively.

Adsorption isotherms

Isotherm studies were conducted with 10-60 mg/L of Cr(VI) solutions by adding 0.1 g of CLPC and 0.3 g of CLP and equilibrated for 24 h at 300, 310 and 320 K. The Cr(VI) concentration of the solution was measured by AAS. The amount of Cr(VI) ions adsorbed at equilibrium, q_e (mg/g), was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad \dots (2)$$

where, V is the volume of the Cr(VI) solution (L) and m is the mass (g) of the adsorbent. The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a suitable description of the equilibrium separation between two phases. To determine the adsorption capacity of Cr(VI) ions onto CLPC and CLP, the equilibrium adsorption data were applied to the Freundlich and Langmuir isotherm equations at different temperatures by nonlinear regression analysis using MATLAB R2010b.

Freundlich isotherm

The Freundlich isotherm is an empirical equation that is based on the sorption of a sorbate on a heterogeneous surface of a sorbent as given by the equation[17]:

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

where q_e is the amount of sorbate sorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K_F ((mg/g)(L/mg)$^{(1/n)}$) and n (g/L) are the Freundlich empirical constants indicate the sorption capacity and sorption intensity, respectively.

Langmuir isotherm

The theoretical Langmuir isotherm relies on the chemical or physical interaction (or both) postulated to occur between the solute and the available vacant sites on the sorbent surface, which may be described as below[18]:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad \text{... (4)}$$

where q_m (mg/g) is the maximum metal uptake capacity, and K_L (L/mg) Langmuir constant related to adsorption energy. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, "R_L", expressed as in the following equation[19]:

$$R_L = \frac{1}{1+K_L C_0} \qquad \text{... (5)}$$

where K_L is the Langmuir constant and C_0 is the initial concentration of Cr(VI) ions. The value of R_L indicated the type of Langmuir isotherm to be irreversible (R_L=0), favorable (0<R_L<1), linear (R_L=1), or unfavorable ((R_L>1).

Thermodynamic studies

The thermodynamic considerations can be investigated through the Gibbs free energy, enthalpy and entropy. The change in the standard free energy (ΔG^o) is calculated using the following relationship:

$$\Delta G^o = -RT \ln K_c \qquad \text{... (6)}$$

where K_c (L/ g) is an equilibrium constant obtained by multiplying the Langmuir constants q_m and K_L[20]. T is the absolute temperature (Kelvin), and R is the gas constant (8.314 kJ /mol K). The relationship between the changes in the Gibbs free energy, entropy (ΔS^o) and enthalpy (ΔH^o) can be expressed as follows:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad \text{... (7)}$$

ΔS^o and ΔH^o were obtained from the slope and intercept after plotting ΔG^o versus T.

Adsorption kinetics

Adsorption kinetics were carried out by adding 0.1 g of CLPC and 0.4 g of CLP with 100 mL of different concentrations of chromium(VI) solutions (5-10 mg/L) at an optimum pH and equilibrated for 0.5 to 6 h. The amount of Cr(VI) ions adsorbed at time t, q_t (mg/g), was calculated by the following expression:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad \text{... (8)}$$

where C_t is the concentration of Cr(VI) ion solution at any time t (mg/L). Kinetic models are used to examine the controlling mechanism of the adsorption process, i.e. mass transfer or chemical reaction. In the present study, the adsorption kinetic data were applied using pseudo-first order, pseudo-second order and intraparticle diffusion model equations.

The linear form of the pseudo-first order rate equation by Lagergren[21] is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad \text{...(9)}$$

where q_e (mg/g) and q_t (mg/g) 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) versus t.

The Pseudo-second order model proposed by Ho and Mckay[22] was based on the assumption that the adsorption follows second order chemisorptions. The linear form of pseudo-second order model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{... (10)}$$

where k_2 (g/mg/min) 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/min) is defined as[23]:

$$h_0 = k_2 q_e^2 \qquad \text{... (11)}$$

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:

$$\text{P (\%)} = 100/\text{N}\sum\left[\frac{q_{e(exp)} - q_{e(theo)}}{q_{e(exp)}}\right] \qquad \text{... (12)}$$

where $q_{e(exp)}$ and $q_{e(cal)}$ are experimental and calculated value of Cr(VI) 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[24].

The kinetic data were analysed by an intra-particle diffusion model to expose the diffusion mechanism[25]:

$$q_t = k_d\, t^{1/2} + I \qquad \text{... (13)}$$

where q_t is the amount of sorbate on the surface of the sorbent at time t (mg/g), k_d (mg/g/ min$^{1/2}$) is the intra-particle diffusion rate constant and I (mg/g) a constant that gives idea about the thickness of the boundary layer. According to this model, the plot of q_t versus ($t^{1/2}$) is linear and passes through the origin, and then intraparticle diffusion is the sole rate-limiting step.

Regeneration studies

Desorption of Cr(VI) ions was performed using 0.5 N HCl solution as a desorbing agent to estimate the reversibility of adsorbent and recovery of Cr(VI) ions. Experiments were carried out 100 mL of 50 mg/L of Cr(VI) solution containing under the optimum conditions and equilibrated for 3 h. At the end of equilibration period, the solutions were centrifuged and the concentrations of (VI) ions were determined by using the AAS.

Results and Discussion

Effect of *p*H

The *p*H is a dynamic and imperative environmental factor controlling heavy metals' site dissociation, speciation, adsorption, accessibility and solution chemistry[26]. The effect of solution *p*H was determined by studying the removal of Cr(VI) at an initial concentration of 10 mg/L with an adsorbent dose of 0.1g of CLPC and CLP per 100 mL over the *p*H range 1.0-7.0 and the results are shown in Fig. 1a. Figure 1a shows that the optimum uptake occurred at the pH of 2.0 for CLPC and CLP and attaining a maximum Cr(VI) removal of 99% for CLPC and 75 % for CLP respectively. The decrease in the adsorption with the increase in solution pH may be attributed to the decrease in electrostatic force of attraction between the sorbent and the sorbate ions. The raw and modified Citrus Limettioides peel were analyzed using a Fourier transform infrared spectrometer (FTIR)[14] and the result shows that the presence of several functional groups such as hydroxyl and carboxyl and sulphonic acid groups are responsible for the binding of chromium(VI) onto the surface of CLPC and CLP. These functional groups were positively charged when protonated and may electrostatically interact with negatively charged metal complex.

At very low *p*H, chromium ions exist in the form of $HCrO_4^-$, at higher *p*H up to 6 different forms such as $Cr_2O_7^{2-}$, $HCrO_4^-$, and CrO_4^{2-}, coexists, of which $HCrO_4^-$ predominates. As the pH increases the equilibrium shifted from $HCrO_4^-$ to CrO_4^{2-} and $Cr_2O_7^{2-}$ [27]. At very low pH values, the surface of adsorbent would be surrounded by the hydronium ions which enhance the Cr(VI) interaction with binding sites of the adsorbent by greater attractive forces. As the *p*H increases, the overall surface charge on the adsorbents became negative and the adsorption decreases[28,29]. Hence, in the following experiments, the initial solution *p*H 2.0 was used.

Effect of contact time

The effect of the contact time on the removal of Cr(VI) ions from an aqueous solution by the CLPC

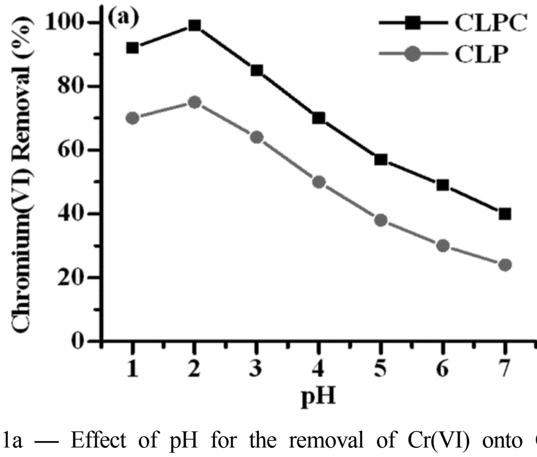

Fig. 1a — Effect of pH for the removal of Cr(VI) onto CLPC and CLP.

and CLP are shown in Fig. 1b. From Fig. 1b, it is evident that the removal of Cr(VI) ions increased with the increase in the contact time, the equilibrium is reached in 3 h and above that it was more or less constant. The fast removal of Cr(VI) at the initial stages may be due to availability of the uncovered surface and active sites on the adsorbent surface. Therefore, the optimum contact time was selected as 3 h for further experiments.

Effect of adsorbent dose

Adsorbent dose has significant influence on the percentage adsorption. Fig. 1c shows the effect of adsorbent dose on adsorption of Cr(VI) ions (range 0.05-0.4 g). The increase in adsorbent dose resulted in increase in adsorption up to a certain dose which then seemed to remain almost constant. Maximum adsorption occurs at an adsorbent dose of 0.1 g for CLPC and 0.3 g for CLP and this was fixed as optimal dose. The observed trend may be due to the fact that higher the dose of carbon greater the availability of surface area and functional groups for metal ions. These chemical groups play an important role in the formation of Vander Waals bonding as the functional groups play the main role in binding metals to the adsorbent during adsorption process. This provides more possibilities for adsorption to occur since there was less competition between metals for the binding sites. The data clearly shows that CLPC is 3 times more effective than CLP with respect to the adsorbent dose; this difference occurs because the ion-exchange capacity exhibited by CLPC is moderate compared with that of CLP.

Effect of Cr(VI) in presence of other cations and anions

Industrial wastewater and natural water often contain salt, which may interfere with the uptake of heavy metal ions by the adsorbents. For the determination of interference caused by the presence of other cations and anions such as Na^+, K^+, Ca^{2+}, Mg^{2+} and Cl^-, SO_4^{2-}, HCO_3^- were added to the Cr(VI) solution. These elements are major constituents of saline and hard waters and are likely to be encountered in most industrial effluents from which toxic metals are intended to be removed by adsorption. The dependence of chromium(VI) removal percentage of the sorbent (CLPC and CLP) in the presence of other common cations and anions which are commonly present in water was investigated with a fixed 0.1 g/100mL of these ions and by keeping 10 mg/L as initial Cr(VI) concentration at room temperature. As shown in Fig. 2 a and b the presence of Na^+, K^+ Cl^- and SO_4^{2-} have no antagonistic effect on sorption of Cr(VI) by CLPC and CLP and the effect of Ca^{2+}, Mg^{2+} and HCO_3^- was only marginal. Therefore, the effect of Ca^{2+}, Mg^{2+} is more evident compared with that of Na^+, K^+ because Ca^{2+}, Mg^{2+} can screen more negative charges on CLPC and CLP, thus exhibiting a higher inhibition of Cr(VI) adsorption than Na^+, K^+.

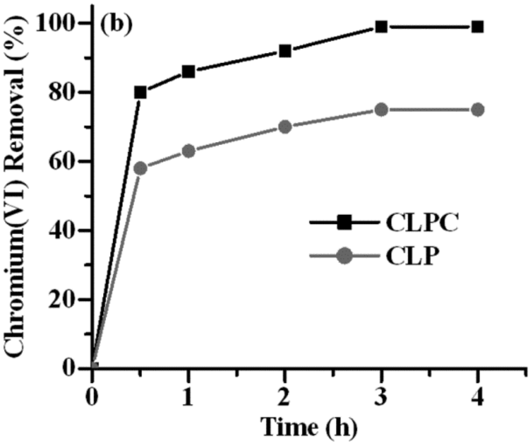

Fig. 1b — Effect of contact time for the removal of Cr(VI) onto CLPC and CLP.

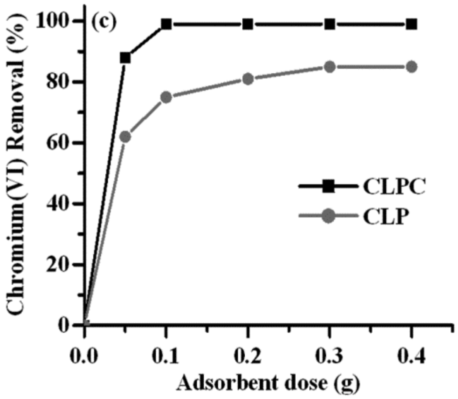

Fig. 1c. — Effect of adsorbent dose for the removal of Cr(VI) onto CLPC and CLP.

Adsorption Isotherms and thermodynamic studies

The nonlinearized Freundlich and Langmuir adsorption isotherms for the Cr(VI) ions were obtained at 300, 310 and 320 K, are shown in Fig. 3a and b. The isotherm constants, correlation coefficients (R^2), sum of squares error (SSE) and root mean squared error (RMSE) values are summarized in Table 1. The R^2 values closer to 1 and small SSE, RMSE values indicate better curve fitting. Based on the R^2, SSE and RMSE values from Table 1, the Langmuir model exhibited a better fit for the

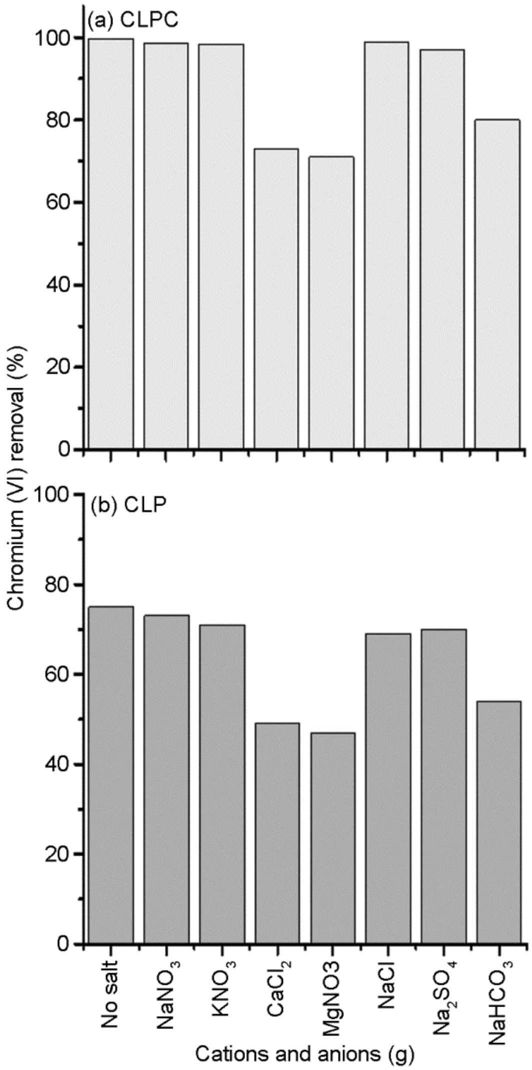

Fig. 2 — Effect of other cations and anions on the sorption of Cr(VI) by CLPC (a) and CLP (b).

adsorption of chromium(VI) ions onto CLPC and CLP, respectively. Furthermore, the R_L values for the Langmuir isotherm fall between 0 and 1 at different temperatures (Table 1), indicating a favorable adsorption process. Lower R_L values at higher initial Cr(VI) concentrations and lower temperature showed that adsorption was more favorable at higher concentration and lower temperature. Therefore, the active sites are distributed homogeneously on the adsorbent surface. The maximum monolayer adsorption capacity (q_m) decreases when increasing the temperature, revealing an exothermic process. According to the Langmuir equation, the maximum adsorption capacity (q_m) of Cr(VI) on CLPC was 176.50 mg/g at 300 K, which is significantly 1.8 times higher than that for CLP (q_m = 99.50 mg/g). The higher adsorption capacity of Chromium(VI) on CLPC than CLP may be related to the physical and chemical characterization of the adsorbents.

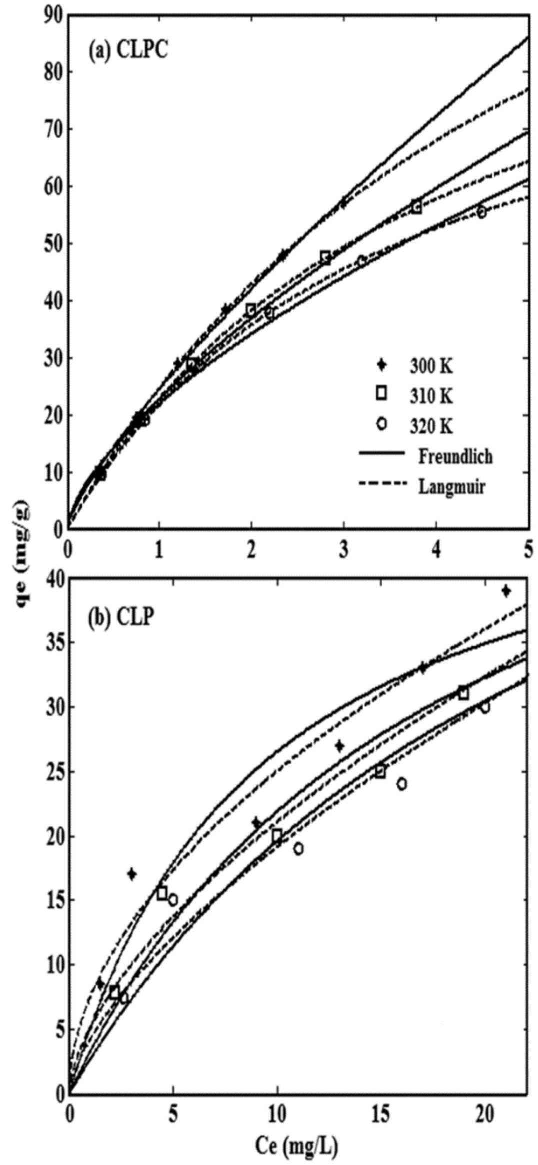

Fig. 3 — The nonlinear adsorption isotherm for Cr(VI) ions onto CLPC (a) and CLP (b).

The maximum adsorption capacity (q_m) of CLPC is compared with those of other adsorbents reported in the literature in Table 2. The high adsorption capacity of CLPC reveals that it should be promising adsorbent for removing Cr(VI) from aqueous system.

The calculated thermodynamic parameters for the CLPC and CLP for the adsorption of Chromium(VI) ions are given in Table 1 and Fig. 3c. The overall change in the free energy during the adsorption process was negative for the experimental

Table 1 — Nonlinear isotherm and Thermodynamic parameters for Cr(VI) removal from aqueous solutions

Isotherm models and Thermodynamic	Parameters	Temperature (K)					
		CLPC			CLP		
		300K	310K	320K	300K	310K	320K
	K_F (mg/ g)	34.17	31.20	29.94	7.449	5.093	4.181
Freundlich	n	1.384	1.448	1.575	1.90	1.62	1.51
	R^2	0.994	0.991	0.987	0.917	0.905	0.877
	SSE	4.012	6.402	10.81	30.23	35.66	43.23
	RMSE	0.978	1.265	1.644	2.766	2.789	3.880
	q_m (mg/g)	176.50	134.10	104.35	99.50	82.35	76.60
Langmuir	K_L (L/mg)	0.290	0.252	0.199	0.110	0.056	0.041
	R^2	0.999	0.999	0.999	0.991	0.987	0.983
	SSE	0.352	0.466	0.572	6.560	8.970	9.155
	RMSE	0.150	0.221	0.195	0.656	0.894	0.976
	R_L	0.26-0.05	0.28-0.06	0.33-0.08	0.48-0.13	0.64-0.23	0.71-0.29
	ΔG^0 (kJ/ mol)	-9.816	-9.073	-8.070	-5.968	-3.940	-3.045
Thermodynamic	ΔH^0 (kJ/ mol)		-36.04			-49.62	
	ΔS^0 (kJ / mol/ K)		-0.087			-0.146	

Table 2 — Monolayer adsorption capacities in the literature for Cr(VI) adsorption.

Adsorbents	q_m (mg/g)
Wood apple shell[10]	13.74
pomegranate husk[11]	35.20
Tamarindus indica seed[29]	98.04
Mangosteen peel[30]	24.50
Hazelnut shell[31]	17.70
Walnut hull[32]	98.13
Bengal gram husk[33]	91.64
Rice husk carbon[34]	0.80
CLPC (Present study)	176.50
CLP (Present study)	99.50

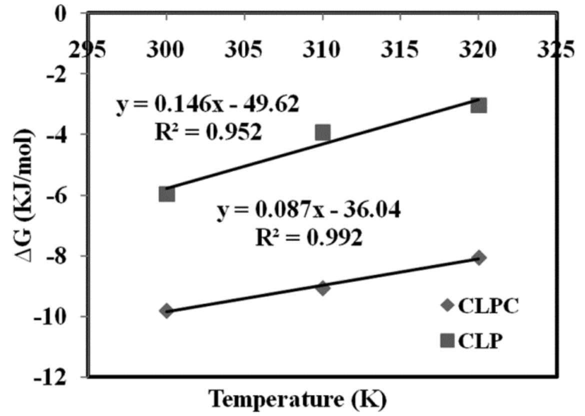

Fig. 3c — Thermodynamic plots for the adsorption of Cr(VI) ions onto CLPC and CLP.

temperature ranges (Table 1), indicate that the adsorption is spontaneous. The ΔG^o value is more negative when decreasing the temperature, suggesting that lower temperatures favor the adsorption. The negative ΔH^o value implies that the adsorption phenomenon is exothermic and explains the decrease in Cr(VI) ion adsorption efficiency that was observed as the temperature increased. The negative ΔS^o value suggests that the process is driven by enthalpy.

Designing batch adsorption from equilibrium data

The best fitted adsorption isotherm model was used to design a single stage batch adsorber for the treatment of aqueous solutions which contains Chromium(VI) ions. A schematic diagram of single batch adsorber is shown in Figure 4. The design objective is to reduce the chromium(VI) concentration C_o to C_e of solution volume V (L). The amount of adsorbent used is M (g) and the Cr(VI) ion loading changes from q_o to q_e. At time t=0, $q_0 = 0$ as time proceeds the mass balance equates the Cr(VI) removed from the solution to that picked up by the CLPC and CLP adsorbent is given by the following equation:

$$V (C_o - C_e) = M (q_e - q_o) = Mq_e \qquad \text{... (14)}$$

The Langmuir adsorption isotherm data may be applied to Eq. 14 since the Langmuir adsorption isotherm gave the best fit to experimental data.

$$\frac{M}{V}=\frac{C_0-C_e}{q_e}=\frac{C_0-C_e}{\frac{q_m K_L C_e}{1+K_L C_e}} \qquad \text{... (15)}$$

Figure 5 a and b shows the plot between the calculated amounts of CLPC and CLP required to remove chromium(VI) ions solution of initial concentration 60 mg/L for 75%, 80%, 85%, 90% and 95% Chromium(VI) removal at different solution

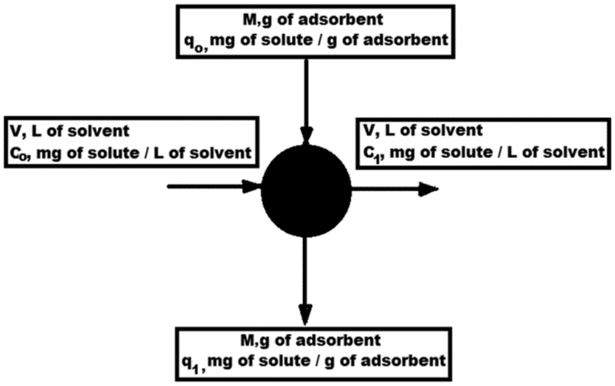

Fig. 4 — A single–stage batch adsorber design.

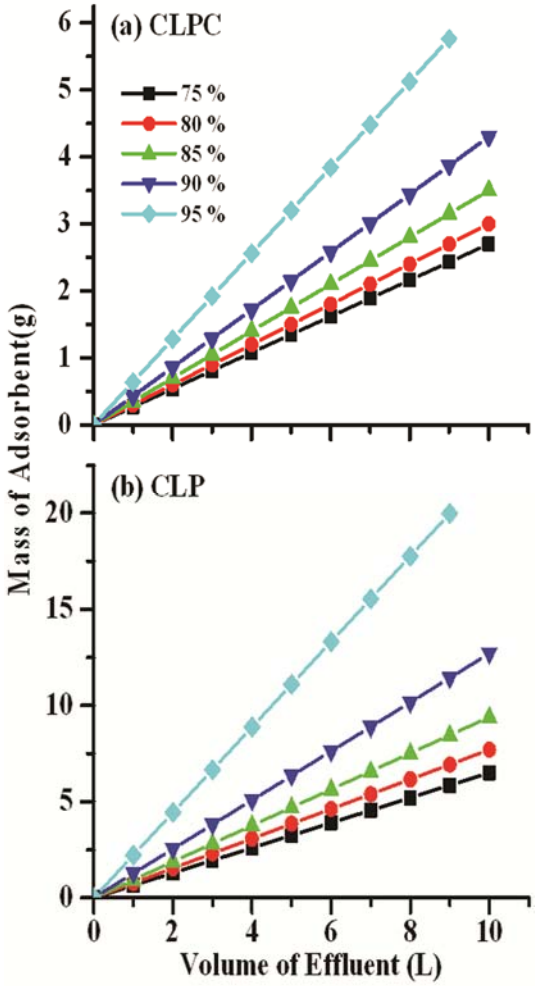

Fig. 5 — Design plot for the adsorption of Cr(VI) ions onto CLPC (a) and CLP (b).

volume (1 to 10L) for a single-stage batch adsorption system, for which the design procedure is outlined.

Kinetic studies

The kinetic parameters and correlation coefficients are listed in Table 3 and are given in Fig 6 a-f. From the Table 3, the correlation coefficients for pseudo-second order equation is much closer to unity. The calculated q_e values are very closer to the experimental q_e values. Furthermore, the percent 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 Cr(VI) ions onto the CLPC and CLP is mainly governed by pseudo-second order equation. This suggests that the rate-limiting step of this sorption system may be controlled by chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate. Figure 6 e and f shows a plot of the Weber and Morris intra-particle diffusion model for the adsorption of Cr(VI) onto CLPC and CLP. The deviation in the plots from origin for all concentrations indicated that pore diffusion was not the only sole rate-controlling factor but some other processes like film diffusion were also involved in the sorption process. The low correlation coefficient values obtained for the intra-particle diffusion model also indicate that adsorption is not occurring in the pores of sorbent in accordance with surface adsorption. Moreover, distinct ionic species might be present simultaneously in the solution and hence, each of them being adsorbed at variable rates as a function of their affinity to the individual functional groups and depends on the binding mechanism.

In order to further assess the nature of the diffusion process responsible for the adsorption of Cr(VI) on CLPC and CLP, attempts were made to calculate the pore and film diffusion coefficients for various concentrations of Cr(VI) using the following the equation[35]:

$$D_p = 0.03\ r_o^2 / t_{1/2} \qquad \text{... (16)}$$

where D_p is the pore diffusion coefficient (cm^2/s), r is the radius of the sorbent (cm), and $t_{1/2}$ is the half-life period (sec).

$$D_f = 0.23\ r_o\ d\ C^* / C\ t_{1/2} \qquad \text{... (17)}$$

where D_f is the film diffusion coefficient (cm^2/s), d is the film thickness (cm), and C*/C is equilibrium loading of the sorbent. According to Michelsen et al[36] if film diffusion to be the rate determining process in the adsorption of heavy metals on a sorbent, the values of film diffusion coefficient (D_f) should be between 10^{-6} and 10^{-8} cm^2/s. If pore diffusion D_p were to be rate determining process, its value should be in

Table 3 — Pseudo-first order, second order and intraparticle diffusion model parameters for the adsorption of Cr(VI) ions onto CLPC and CLP at different initial concentrations.

Kinetic model	Parameters	Concentrations (mg/ L)					
		CLPC			CLP		
		5	7	10	5	7	10
Pseudo-first order	$q_{e,}$exp (mg/g)	4.97	6.95	9.86	4.79	6.76	9.30
	k_1 (min^{-1})	0.016	0.023	0.014	0.014	0.012	0.021
	$q_{e,}$cal (mg/g)	2.55	4.14	4.33	2.30	3.08	4.74
	R^2	0.926	0.988	0.980	0.990	0.898	0.914
	P %	48.69	40.43	56.09	51.98	54.44	49.03
Pseudo-second order	k_2(g/ mg/min)	0.025	0.020	0.010	0.010	0.009	0.006
	$q_{e,}$cal (mg/g)	5.05	7.14	10.31	5.08	6.99	10.20
	h_0(mg/g/min)	0.638	1.020	1.063	0.258	0.440	0.624
	R^2	0.999	0.999	0.999	0.999	0.999	0.999
	P %	1.62	2.77	4.56	3.97	3.40	2.15
Intraparticle diffusion	K_d (mg /g/min$^{1/2)}$	0.110	0.143	0.169	0.107	0.131	0.142
	I (mg/g)	3.086	4.591	6.799	2.927	4.422	6.891
	R^2	0.648	0.663	0.850	0.857	0.938	0.884
Film diffusion	D_f (×10 $^{-8}$ cm^2/ sec)	1.353	1.489	1.087	0.550	0.670	0.615
Pore diffusion	D_p (×10^{-8} cm^2/ sec)	5.125	5.641	4.133	2.150	2.589	2.480

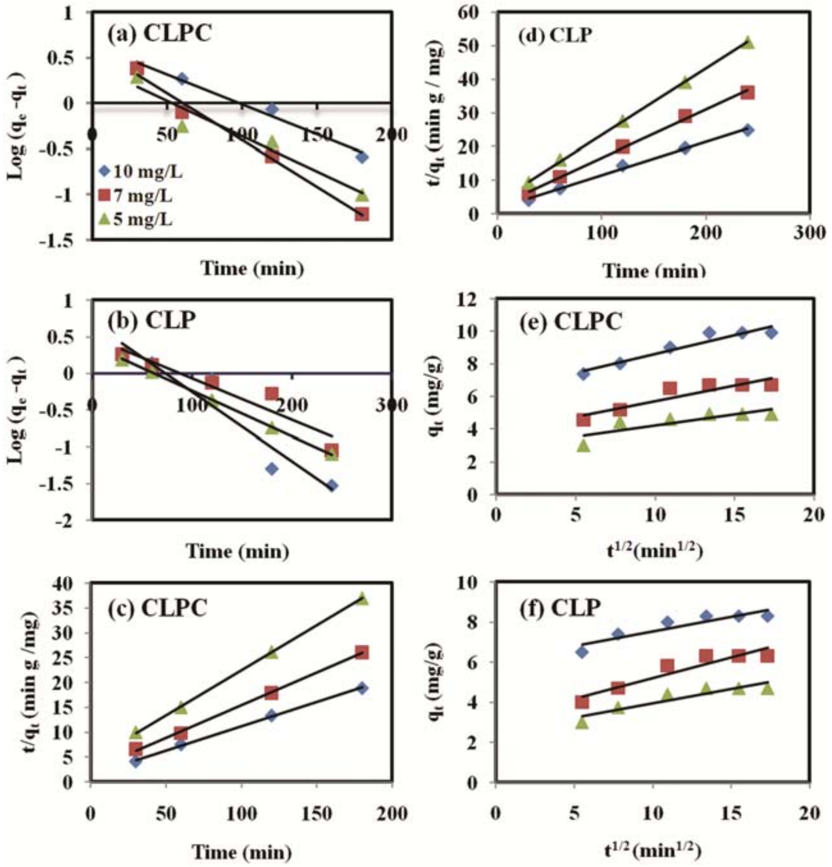

Fig. 6 — Kinetics for the adsorption of Cr(VI) ions onto CLPC and CLP at different initial concentrations; (a, b) pseudo-first order; (c, d) pseudo-second order; (e, f) intra-particle diffusion for CLPC and CLP\

the range of 10^{-11}-10^{-13}cm^2/s. The pseudo-second order rate constant (k_2) was applied to calculate the film and pore diffusion coefficients for the present study. It is evident from the Table 3 that the removal of Cr(VI) ions follows film diffusion process, since the coefficients values are closer to the range of10^{-6}-10^{-8} cm^2/s.

Desorption and regeneration studies

In order to make the sorption process more economical through repeated use of the adsorbent, desorption and regeneration potential of CLPC and CLP was investigated. The desorption studies are help in further elucidating the mechanism of adsorption and the feasibility of regenerating the spent activated carbon. The study of Namasivayam and Yamuna[37] showed that if the adsorbed ions on the solid surface can be desorbed by water, the attachment of the ion on the adsorbent can be verified by weak bonds such as Vander Waals forces. If acid or alkaline water desorbs the ion, then the adsorption occurs through an ionexchange. In this study 0.5 N HCl was used to regenerate the CLPC and CLP over seven cycles of operation. From the Fig. 7a clearly shows that the CLPC can be used repeatedly for seven cycles of operations without affecting its adsorption capacity for Cr(VI) ions. However, the recovery of Cr(VI) ions decreased in CLPC from 99.50 to 90.50 % during the seventh cycle because the Cr(VI) ions were strongly bound to the new opening sites. In the case of CLP (Fig. 7b), both adsorption and desorption values decreased rapidly. These results showed that CLPC has a greater potential for repeated use and recovery of Cr(VI) ions. The results additionally indicate that ion exchange was the main mechanism for Cr(VI) sorption with CLPC as compared with CLP.

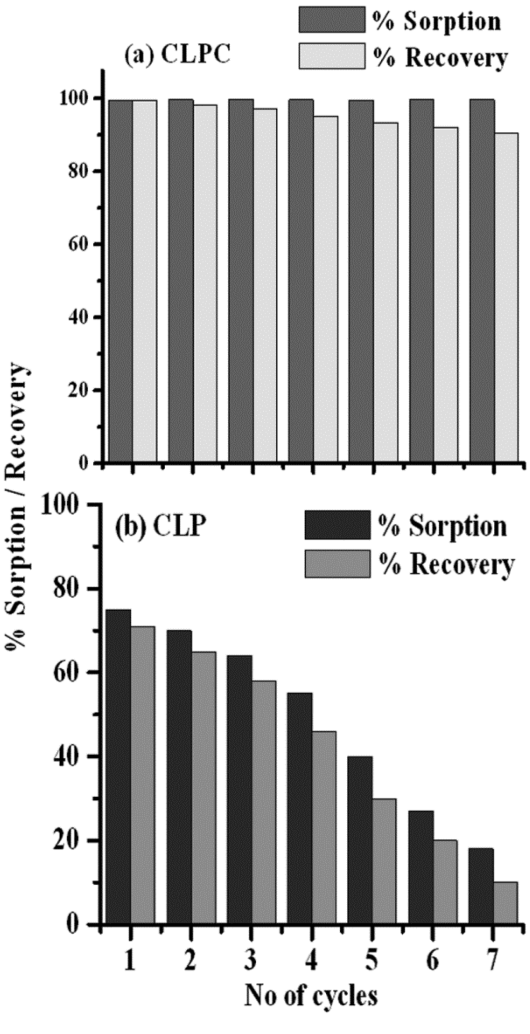

Fig. 7 — Regeneration and recycling by batch process for CLPC (a) and CLP (b).

Conclusion

The results of the present investigation show that CLPC adsorbent prepared from an agricultural waste has considerable potential for the removal of Cr(VI) ions from aqueous solutions. The removal of Cr(VI) ions from aqueous solution strongly depends on the solution pH, contact time and carbon dose. *Citrus limettioides* peel and its carbon derivative can be used to remove 75 % and 99 % of the Cr(VI) from aqueous solutions. The equilibrium data fit well with Langmuir isotherm and the adsorption capacity of CLPC is 1.8 times larger than that of CLP. Thermodynamic study shows that the adsorption was spontaneous and exothermic. The adsorption is followed by pseudo-second order kinetics, which indicates the chemisorptions with film diffusion process being essential rate controlling step. A single stage batch adsorber was designed using the best fitted adsorption isotherm equation, which is Langmuir adsorption isotherm equation. The CLPC can be regenerated and reused upto seven cycles of operation under study when compared with CLP. Therefore, it can be concluded that the CLPC is a good and effective adsorbent for the removal of Cr(VI) ions and could be used in water and wastewater treatment.

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