



Adsorption of Cr(VI) ions onto *Pongamia pinnata* leaves carbon from aqueous solutions –A Kinetic study

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Abstract

A systematic exploration on the kinetic and equilibrium studies of adsorption of Cr(VI) ion from aqueous solution by activated carbon prepared from leaves of *Pongamia pinnata* was carried out in batch process. The potential of adsorbent was evaluated by varying various parameters such as effect of initial concentration, adsorption dose, contact time and temperature. Experimental data were fitted into linearised form of Lagergren and Ho kinetic equations for pseudo first order and pseudo second order models respectively. The kinetic parameters have been discussed in detail. The results revealed that the adsorption of Chromium (VI) ion onto chosen adsorbent followed the pseudo second order kinetics. The adsorption process was controlled by intra particle diffusion and it was confirmed using Webber Morris plot parameters.

Keywords: Adsorption, Kinetics, Chromium (VI) ion, *Pongamia pinnata*.

1. Introduction

Heavy metals ions such as Pb(II), Cu(II), Zn(II), Hg(II), Co(II), Ni(II) and Cr(VI) have been used by human for thousands of years and excessively released in to environment due to rapid industrialization and cause several adverse health effects and severe environmental problems. Cr(VI) found to be present in mining and metal plating, steel production, photographic materials, corrosive paints and cement industries[1]. Cr(VI) has been reported to be toxic to humans, animals and also is known to be carcinogenic[2]. The utmost permissible limit of Chromium (VI) for the discharge into inland surface water is 0.1 mg/L[3]. The mass usage of metals could cause rigorous environmental troubles. Consequently, industrial waste waters contain high levels of heavy metals and in order to avoid water pollution treatment is required before discarding. Therefore effective removal of heavy metals from waste waters still remains a major topic of present research [4].

Conventional methods such as precipitation, coagulation/flocculation, ion exchange, cementation, complexation/ sequestration, eletrochemical operation and biological treatment have been used for the removal of Cr(VI) from aqueous solution. Removal of Chromium by activated carbon would be the cheap and practical alternative to conventional process [5,6].

2. Materials and Methods

2.1 Preparation of Adsorbent

The leaves of *Pongamia pinnata* were cut into smaller pieces and soaked in concentrated H₂SO₄ with 1:1 ratio (W/V) for 48 hour and activated at 160°C for 6 h. The activated carbon was repeatedly washed with distilled water until the pH of the wash water become neutral. The carbon obtained was dried at 110° C for nearly 2 h to remove the moisture.

The above prepared carbon was designated as *Pongamia pinnata* Leaves Carbon there after referred to as PLC and it is kept in a desiccator.

2.2 Adsorption Studies

The adsorption experiments were carried out by a batch equilibrium technique. The effect of contact time and initial concentration of Chromium (VI) ions were investigated at five different initial concentrations viz. 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L and 30 mg/L of Chromium (VI) ion. 75 mg of adsorbent was taken in 100 mL iodine flask. 50 mL of the adsorbate solution was added to the flask. This aliquot was shaken in rotary shaker at 150 rpm for predetermined time. Then the solution was centrifuged and the adsorbate concentration in the centrifugate was measured by Diphenylcarbozide method. The kinetic experiments were performed with the working pH 2 and for contact times 5, 10, 20, 40, 60, 80, 100, 120, 140, 160 and 180 minutes.

Diphenylcarbozide method

A 0.25% (W/V) solution of diphenylcarbozide was prepared in 50% (V/V) acetone. 1 mL of the sample solution was pipette out into 25 mL standard flasks. To this 1 mL of 6 N H₂SO₄ was added followed by 1 mL of diphenylcarbozide and the total volume was made up to 25 mL using double distilled water. Concentration of Cr(VI) was estimated by the intensity of the reddish brown color developed due to complex formation using Systronics Double Beam UV-visible Spectrophotometer: 2202 at the wave length of 540 nm [7, 8].

2.3 Kinetics Studies

2.3.1 Pseudo First order kinetics

Lagergren equation is $\text{Log}(q_e - q_t) = \log q_e - (k_1 / 2.303) \times t$

Where q_e and q_t are the amounts of adsorbate adsorbed (mg/g) at equilibrium and at time

t respectively and k_1 is the pseudo first rate constant of adsorption (l/min) [9].

2.3.2 Pseudo Second order kinetics

Ho equation is $t/q_t = 1/k_2 \cdot q_e^2 + 1/q_e t$.

The pseudo second order constants k_2 (g/ (mg.min)) can be determined from the slope and intercept of plot of t/q_t versus t [10]. The initial adsorption rate, h (mg/(g min)), as $t \rightarrow 0$ can be defined as $h = k_2 q_e^2$.

2.3.3 Intra particle diffusion

Weber–Morris equation is $q_t = k_p t^{0.5} + C$

Where k_p is the intra-particle diffusion rate constant. Slope of the final straight line obtained in the plot of q_t versus $t^{0.5}$ is the rate constant for intra particle diffusion and intercept C is the thickness of the boundary film [11].

2.3.4 Test for kinetics models

The sum of error squares is given below

$$\text{SSE} = \sum [(q_e)_{\text{exp}} - (q_e)_{\text{cal}}]^2 / N$$

Where N is the number of data points, $(q_e)_{\text{exp}}$ is the experimental q_e , $(q_e)_{\text{cal}}$ is the calculated q_e .

3. Results and Discussion

3.1 Effect of Dose: The adsorption of Chromium (VI) ion onto PLC was studied by varying the dose of the adsorbent from 25 mg/ 50 mL to 105 mg/ 50 mL by taking 50 mg/ L of the adsorbate concentration. The percentage of removal of Chromium(VI) ions from aqueous solution increased with increase of carbon dose. The results are given in Table 1. This is due to the increased carbon surface area and availability of more adsorption sites. 75 mg of adsorbent per 50 mL of adsorbate solution was chosen for further studies.

Table 1 Effect of Dose
[C_i : 20 mg/L, pH:2]

Dose (mg/50 mL)	% of Removal
25	15.4
35	30.5
45	43.1
55	55.5
65	62.4
75	68.4
85	73.8
95	77.6
105	82.4

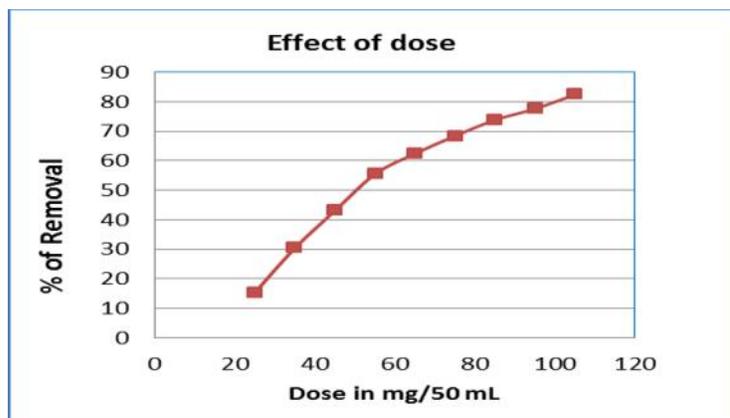


Figure 1 Effect of Dose

3.2 Effect of contact time for different initial concentrations: The experimental results for the adsorption of Chromium (VI) ion onto activated carbon for various contact times for various initial concentrations (10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L and 30 mg/L) at 303 K temperature was presented in Table 2 shown in Figure 2-4. The equilibrium data reveal that percentage of removal decreased with increase in initial Chromium ion concentration but the

actual amount of Chromium(VI) ion adsorbed per unit mass of carbon increased with increase in metal ion concentration. This means that the adsorption is highly dependent on the initial concentration of Chromium ion. This is because the ratio between the surface available on the adsorbent and the concentration of metal ion in the solution phase decrease with the increase of initial concentration of the solute [12].

Table 2 Effect of initial concentration
[C_i : 20 mg/L, Dose : 75 mg, pH:2]

Initial Concentration (mg/L)	% of Removal	Equilibrium capacity(q _e) (mg/g)
10	75.00	5
15	72.67	7.27
20	68.00	9.07
25	65.60	10.93
30	63.67	12.73

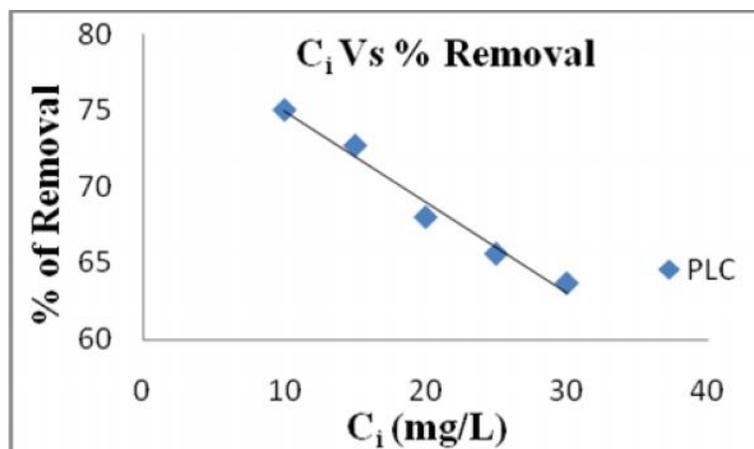


Figure 2 Initial Concentrations vs. % of Removal

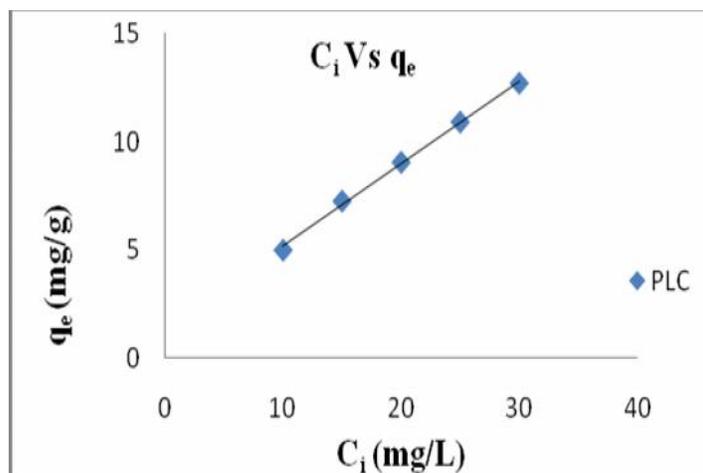


Figure 3 Initial Concentration vs. q_e

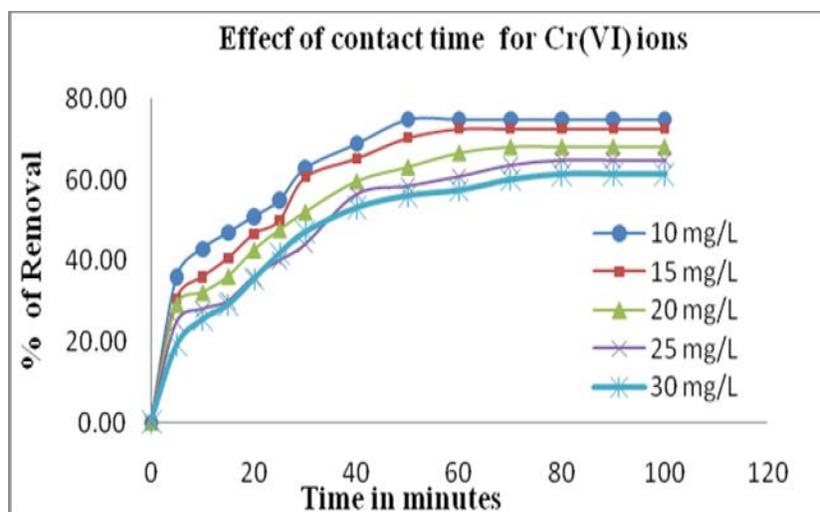


Figure 4 Effect of contact time

3.3 Kinetic models:

The results obtained from pseudo first order and second order kinetic models for Chromium (VI) ions were presented in Table 3. Concerned graphs at 305 K were shown in Figures 5 and 6. The pseudo first order rate constant k_1 (min^{-1}) ranged from 0.0461 to 0.962 and pseudo second order rate constant k_2 ($\text{g/mg}\cdot\text{min}$) ranged from 1×10^{-3} to 4.5×10^{-3} . The initial sorption rate 'h' increases directly with an increase of initial Chromium(VI) ion concentration at each temperature. Experimental $q_{e(\text{exp})}$, calculated $q_{e(\text{cal})}$ and SSE for the pseudo first order and pseudo second order kinetics were given in Table 3. It shows that $q_{e(\text{exp})}$ is close to

$q_{e(\text{cal})}$ for pseudo second order kinetics. It can be seen that SSE value is lower for the pseudosecond order kinetic model than that of pseudo first order kinetic model. This confirms the applicability of the pseudo second order kinetic model.

Intra particle diffusion rate constant K_p values were found to increase with an increase of Chromium(VI) ion concentration that reveals the rate of adsorption is governed by the diffusion of Chromium (VI) ions within the pores of the adsorbent [13]. Present results show the pore diffusion limits the overall rate of the Chromium (VI) ion adsorption. The graphs of intra particle diffusion are shown in Figure 7.

Table 3 Kinetic study results.

[pH = 2; dose = 75 mg/50 mL; contact time = 180 min].

Pseudo First order						
Initial Concentration (mg/L)	k_1 (min^{-1})	$q_{e(\text{exp})}$ (mg/g)	$q_{e(\text{cal})}$ (mg/g)	q_e	R^2	SSE %
10	0.0276	5.0	2.9	2.1	0.604	1.08
15	0.0348	7.3	4.8	2.4	0.652	
20	0.0345	9.1	6.2	2.8	0.714	
25	0.0415	10.8	9.7	1.1	0.848	
30	0.0348	12.3	9.2	3.1	0.812	
Pseudo Second order						
Initial Concentration (mg/L)	k_2 (g/mg.min)	$q_{e(\text{cal})}$ (mg/g)	q_e	h	R^2	SSE %
10	0.0242	5.4	-0.4	0.72	0.991	0.81
15	0.0093	8.4	-1.1	0.66	0.992	
20	0.0065	10.6	-1.5	0.73	0.992	
25	0.0038	13.2	-2.4	0.67	0.984	
30	0.0036	14.90	-2.6	0.80	0.993	
Intra Particle Diffusion						
Initial Concentration (mg/L)	k_p (mg/g.min)	C	R^2			
10	0.51	1.42	0.995			
15	0.55	3.09	0.993			
20	0.57	4.35	0.997			
25	0.59	5.64	0.992			
30	0.63	6.63	0.993			

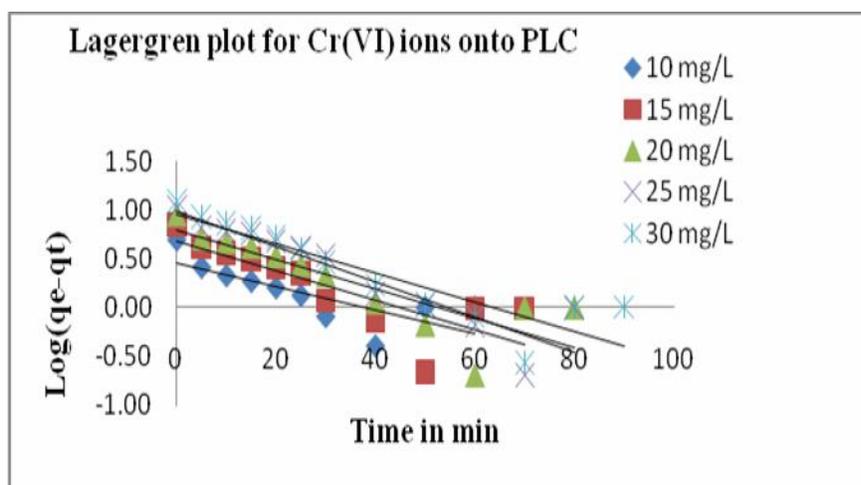


Figure 5 Lagergren plot for pseudo second order kinetics model

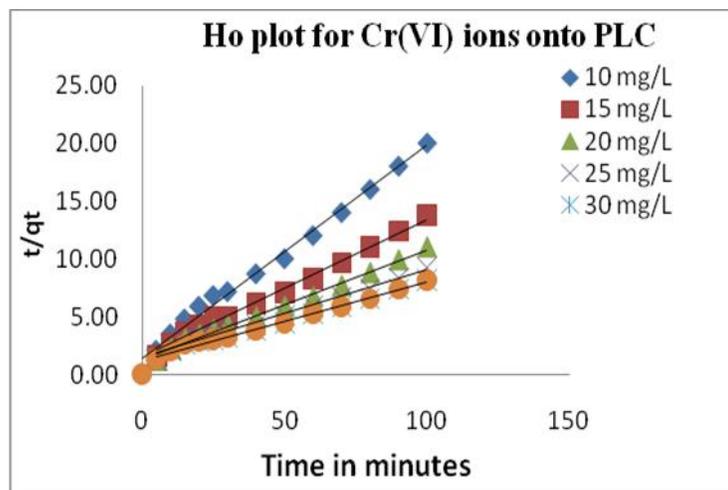


Figure 6 Ho plot for pseudo second order kinetics model

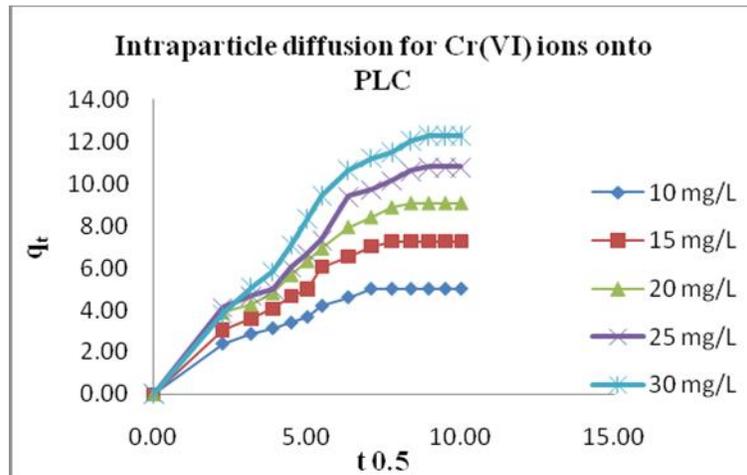


Figure 7 Intraparticle diffusion plot

4. Conclusion

The adsorption dynamics of Chromium (VI) ion onto *Pongamia pinnata* leaves Carbon (PLC) was studied. Adsorption experiments were carried out as a function of contact time, initial concentration in a batch mode process. Experimental data indicated that PLC adsorbent was effective in removing Chromium (VI) ion from aqueous solution. The percentage of removal increased with an increase in contact time and achieved equilibrium around 100 minutes when 75 mg PLC was used as adsorbents for 50 mL solution. Adsorption capacity of PLC was found to be higher at higher initial concentrations. In the kinetics studies, R^2 value and SSE revealed that the process of adsorption followed pseudo first order kinetics.

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