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Adsorptive removal of chromium (VI) from aqueous solutions and its kinetics study

[a]M. Souundarrajan, [b]T. Gomathi and [b*]P.N.Sudha

[a]Manonmaniam Sundaranar University, Tirunalveli, Tamil Nadu, India
[b]Department of Chemistry, DKM College for Women, Vellore, Tamil Nadu, India

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ABSTRACT

Removal of heavy metals from wastewater is absolutely essential to avoid water pollution. In the present study, performance of chitosan coated carbon was evaluated for the removal of chromium (VI) from aqueous solution. Batch adsorption experiments were performed in order to examine the removal process under various factors like the effects of initial concentration, adsorbent dose, pH, and contact time. The metal ion removal was pH dependent and reached optimum at pH 5.0. Experimental data were analysed by Langmuir and Freundlich adsorption isotherms. The characteristic parameters and related correlation coefficients have been determined. The isotherm study revealed that the adsorption equilibrium is well-fitted to the Freundlich isotherm. Pseudo-first- and -second-order kinetic models were used for describing kinetic data. It was determined that removal of Cr (VI) was well-fitted by second-order reaction kinetic. The results showed that chitosan coated carbon are favorable adsorbent of Cr (VI) from aqueous solution.

Keywords: Chromium (VI); Chitosan coated carbon; Adsorption isotherms; Kinetics.

INTRODUCTION

Aqueous pollution with heavy metals is the most serious environmental problem, due to their toxic effect and accumulation tendency. Among heavy metals, chromium (VI) having high toxicity should be the first to be removed from aqueous environments [1-3]. Environmental contamination induced by chromium arises mainly *via* various sources like chrome pigments, leather tanneries, chrome plating, metal finishing industries and some textile plants are considered to contaminate the environment with chromium. Besides these, ores are believed to be the major donors of chromium through various processes like melting, roasting and extraction [4].

Although Chromium is an essential micro nutrient [5] when present as Cr(III) ion, there are suggestive evidences that its Cr(VI) can cause cancer in human body [6-8]. In addition to this, occupational exposure to chromium (VI) may be a cause of asthma [9] high levels of exposure produce acute tubular, glomerular damage [10, 11] and adverse effect in urinary system. Accumulation of chromium and some other transition metals in the breast tissues is considered as the cause of breast cancer [12], also an increased amount of chromium leads to the sperm death that in turn reduces the motility of live sperms and defects in DNA are also increased due to chromium poisoning [13, 14].

The conventional methods for the removal of chromium(VI) from waste waters include chemical precipitation, membrane separation, ion exchange adsorption and biosorption [15-19]. However, many of them have some disadvantages, such as incomplete removal of chromium ions, low selectivity and high amount of toxic sludge, high cost and energy consumption. Adsorption is now reorganized as an effective and economical process for a wide variety of applications, especially for the removal of heavy metals from waste waters. The most widely used adsorbent is activated carbon, [20, 21] but it is quite expensive and, possibly, no cost-effective in the treatment of large waste water volumes. That is why, an alternative low-cost biosorbents has been paid the considerable attention.

Many naturally occurring materials have been investigated for assessing their suitability in controlling water pollution. Peat [22, 23] lignin [24], fungi [25], chitin, chitosan are well known as low-cost biosorbents for removing heavy metals from aqueous solutions. Several studies have shown that chitosan is very efficient in removing various toxic and strategic metals, such as chromium, cadmium, mercury, molybdenum, uranium, vanadium, platinum and palladium [26, 27].

Chitosan, a hydrophilic natural polymer produced by alkaline deacetylation of chitin, obtained mainly by extraction from shrimp and crab shells. It is the most abundant biopolymer occurring in nature, after cellulose [28]. It is characterized by a high content of nitrogen, present as amine groups capable of adsorbing the metal ions through several mechanisms – including chemical interactions, such as chelation, electrostatic interactions or ionexchange. The interaction type depends on the metal ion, its chemistry and initial solution pH.

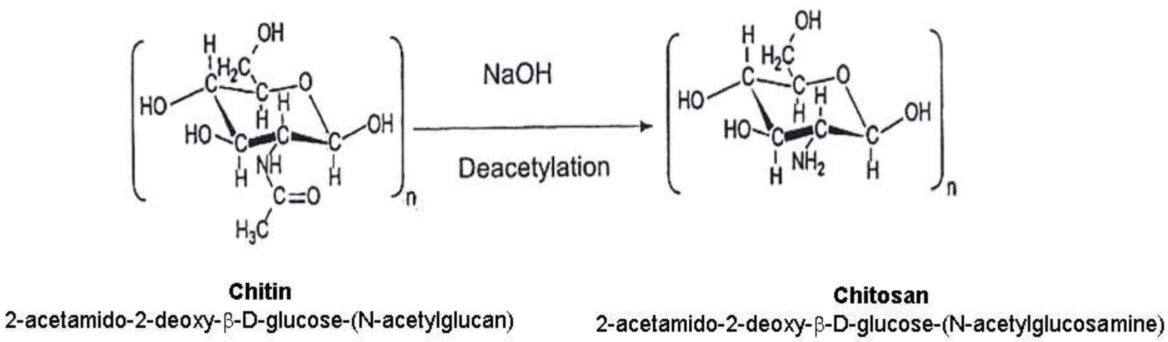

Figure 1. Deacetylation of chitin to chitosan

Carbon , Activated carbon, also called **activated charcoal** or **activated coal** is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. Due to its high degree of micro porosity, just 1gram of activated carbon has a surface area in excess of 500 m^2 (about one tenth the size of an American football field), as determined typically by nitrogen gas adsorption. Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment often enhances the adsorbing properties of the material. Activated carbon is usually derived from charcoal. Activated carbon is used as excellent low cost adsorbent for removal of toxic metal ions from industrial waste water.

The objective of the present investigation is to find out the optimum conditions for removing the chromium (VI) ions from aqueous solutions by adsorption on chitosan coated carbon and to evaluate the equilibrium adsorption studies.

MATERIALS AND METHODS

2.1 Preparation of carbon

The cocoanut shell was cut in to small pieces, ground. This was burnt at very high temperature for 2-3 hours. The surface of carbon obtained was activated by shaking the same with 7% sulphuric acid for 24 hours. The carbon was then washed several times with deionised water till there is no acid in the water. The sulphonated carbon was dried in hot air over for 5 hours at 110◦C

2.2 *Surface coating of carbon with chitosan*

About 400ml of chitosan gel was diluted with water (400ml) and heated to 40-50◦c. about 400 gms of activated cocoanut shell carbon as slowly added and mechanically agitated using a rotary shaker at 150 rpm for 24 hours. This gel coated activated carbon was washed with deionised water and dried. This process was repeated to get 1, 2, 3, 4& 5th. Coating at chitosan on activated carbon 3, 4 & 5th coating carbon used for the studies.

2.3 Stock solution

A stock solution of chromium (VI) ions, containing 200 mg Cr (VI)/L, was obtained by dissolving the potassium dichromate in twice-distilled water and standardized after preparation. 1:1 Hydrochloric acid and 1% sodium hydroxide solutions were used for pH adjustment. The exact concentration of each metal ion solution was calculated on mass basis and expressed in terms of mg L^{-1}. The required lower concentrations were prepared by dilution of the stock solution.

2.4 Adsorption experiments

The batch experiments were performed by adding Chitosan coated carbon with different concentrations of potassium dichromate to investigate the extent of adsorption. Synthetic solution of Cr(VI) ion taken in stoppered bottles and agitated at 30^oC for about 1 hr in orbit shaker at fixed speed of 210rpm. The extent of heavy metal removal was investigated separately by changing adsorption dose, contact time and changing pH of the solution. After attaining the equilibrium adsorbent was separated by filtration using filter paper and aqueous phase

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concentration of metal was determined with atomic adsorption spectrophotometer (Varian AAA 220FS).

RESULTS AND DISCUSSION

3.1 Initial solution pH

The initial solution pH plays an important role in the adsorption of metal ions on various adsorbents, once it affects both the dissociation degree of the functional groups from the adsorbent surface and the solubility of the metal ions. In the study, the initial solution pH was varied between 4.0 and 8.0. The Figure 2 shows the effect of the initial solution pH on Cr (VI) adsorption onto chitosan coated carbon, at a constant dosage of chitosan (1 g/L), for a 1 hr contact time. The adsorption of chromium increases initially and reaches the optimum pH of about 5. The influence of the initial solution pH on the chromium(VI) adsorption is explained by the ionic state of the functional groups from chitosan coated carbon , involved in metal binding, as well as by the occurrence of the hydrated cation (Cr^{6+}), as a predominant ionic species. At low pH values, the adsorption is low, due to the competition between the H^+ ions and Cr^{6+} ions for the adsorption sites of chitosan coated carbon (dissociation of the – OH groups is strongly inhibited, while –NH2 protonation determined electrostatic repulsions). By increasing the initial pH, the dissociation degree of the hydroxyl groups and the negative charge density on the chitosan surface, respectively, are increasing, resulting in a higher adsorption ratio by the electrostatic interaction with cations (Cr^{6+}). Based on these results, an initial solution pH of 5 was selected as the optimum value, for analyzing the influence of other parameters on chromium (VI) ions removal from aqueous solutions, through adsorption on chitosan coated carbon.

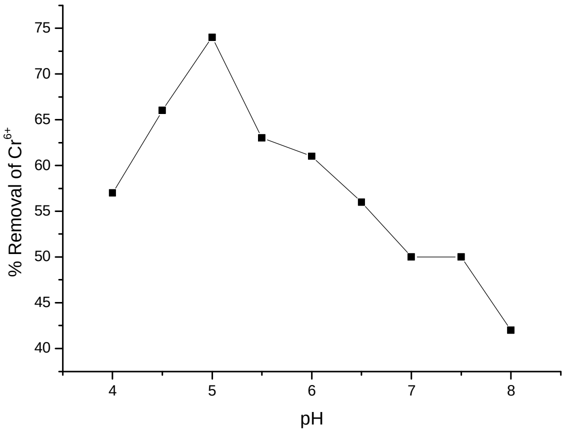


Figure 2. Removal of Cr (VI) onto chitosan coated carbon as a function of pH

3.2 Contact time

The influence of the contact time for the removal of Cr^{6+} from the aqueous solution using the adsorbent (chitosan coated carbon) was analyzed under keeping the initial solution concentration 200 mg Cr (VI)/L, pH 5, and adsorbent dosage 1g as constant. The results presented in Figure 3 evidence a slow increase in the adsorption in the first 300 min of the contact time, when an adsorption 59.1 % is attained. The equilibrium state is practically obtained after 330min. According to Qin *et al.*,[29] the fast initial adsorption could be the result of a very high transfer rate of the metal ions to the surface of adsorbent particles, while the slow adsorption in the second step is a consequence of the low diffusion rate of metal ions into the intra-particles pores of the adsorbent.

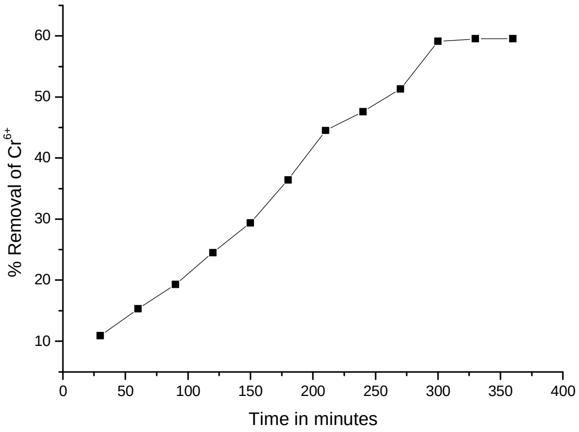


Figure 3. Removal of Cr (VI) onto chitosan coated carbon as a function of contact time

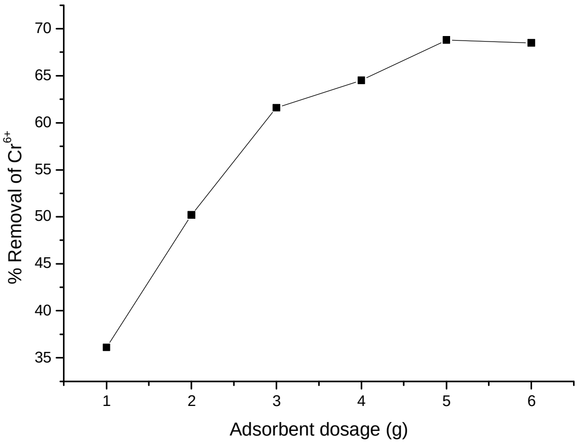


Figure 4. Removal of Cr (VI) onto chitosan coated carbon as a function of adsorbent dosage

3.3 Adsorbent dosage

Adsorbent dose seems to have a great influence on adsorption process. The Figure 4 shows the amount of adsorption increased with increasing the amount of adsorbent dosage to a maximum of 68.8 % removal in 5gm/100ml aqueous solution. These results indicate that removal efficiency is directly related to the number of available adsorption sites. This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent [30]. For lower values of adsorbent dose there was an increase in percent age removal of chromium. Amount of adsorbent added to the solution determines the number of binding sites available for adsorption. The decrease in the sorption capacity with the increasing adsorbent dose suggests that at constant concentration on increasing sorbent amount number of binding sites increases. Thus the effect of adsorbent dosage on percent age adsorption and uptake is important parameter. The results can be explained as a consequence of a partial aggregation, which occurs at high biomass concentration giving raise a decrease of active sites [31-33].

3.4 Adsorption isotherms – Langmuir and Freundlich

The adsorption isotherm is fundamental in describing the interactive behavior between solutes and adsorbent, which express the surface properties and affinity of the adsorbent [34, 35]. It also plays an important role in the design of an adsorption system. The Langmuir and Freundlich models are often used to describe equilibrium adsorption isotherms.

The most widely used Langmuir equation, is valid for monolayer sorption on to a surface with a finite number of identical sites. It is assumed that once a metal ion occupies a site, no further adsorption can take place at that site [36]. The Langmuir equation, which is also based on the assumption that there is no reaction between molecules adsorbed on neighboring sites [37], is given by:

$$Ceq/Cads = [1/Qb] + [Ceq/Q] \quad - (1)$$

where Q is the maximum adsorption at monolayer (mg g^{-1}), Ceq is the equilibrium concentration of Cr(VI) (ppm), Cads is the amount of Cr(VI) adsorbed per unit weight of chitosan beads at equilibrium concentration (mg g−1) and *b* is the Langmuir constant related to the affinity of binding sites (ml mg−1) and is a measure of the energy of adsorption. A linearized plot of Ceq / Cads against Ceq gives Q and b.

The widely used empirical Freundlich equation based on sorption on a heterogeneous surface is given by:

$$Cads = K\, Ceq^{1/n} \quad - (2)$$

The linearised form of this equation is expressed as

$$\log Cads = 1/n \log Ceq + \log K \quad - (3)$$

where *K* and *n* are Freundlich constants indicating adsorption capacity (mg g−1) and intensity, respectively. *K* and *n* can be determined from a linear plot of log Cads against log *C*e. The calculated results of the Langmuir and Freundlich isotherm constants are given in Table 1. It is found that the adsorption of Cr(VI) onto chitosan coated carbon correlates well ($R > 0.99$) with the Freundlich equation as compared to Langmuir equation under the concentration range studied. The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L that is used to predict if an adsorption system is “favourable” or “unfavourable” [38]. The separation factor, *R*L is defined by:

$$RL = 1/(1+bC_f) \quad - (4)$$

where C_f is the final Cr(VI) concentration (ppm) and *b* is the Langmuir adsorption equilibrium constant (ml mg−1). The parameter indicates the Effect of separation factor on isotherm shape

R_L value Type of isotherm
$R_L > 1$ Unfavourable
$R_L = 1$ Linear
$0 < R_L < 1$ Favourable
$R_L = 0$ Irreversible

isotherm shape according to Table 1. The values of R_L calculated for different final Cr(VI) concentration. The R_L values are in the range of $0 < R_L < 1$, it indicates that the adsorption of Cr(IV) onto chitosan coated carbon are favourable. Thus, chitosan coated carbon are favourable adsorbents. The mechanism of ion adsorption on porous adsorbents may involve three steps: (i) diffusion of the ions to the external surface of adsorbent; (ii) diffusion of ions into the pores of adsorbents; (iii) adsorption of the ions on the internal surface of adsorbent.

Table 1 - Adsorption isotherm constant, C_{max} and correlation coefficients

Metal ions	Langmuir constants				Freundlich constants		
	K_L (dm^3/g)	b (dm^3/mg)	C_{max} (mg/g)	R^2	K	n	R^2
Cr(VI)	4.522	0.002745	1647.36	0.8107	0.2760	1.0735	0.9998

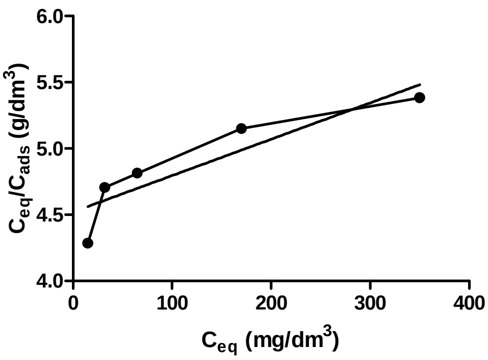
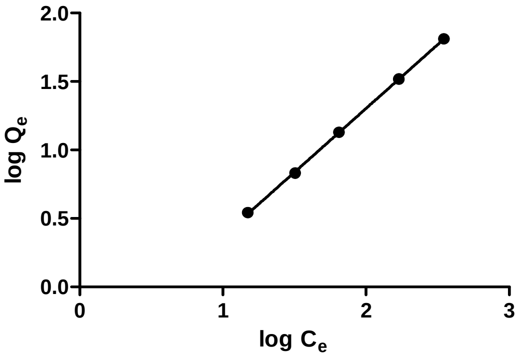


Figure 5. Langmuir isotherm model



Firuge 6. Freundlich isotherm model

3.5 Kinetics Study

The sorption data of Cr(VI) uptake by chitosan coated carbon adsorbent was fitted using Lagergren pseudo-first-order model (Figure7) and pseudo-second-order model (Figure 8). The linearized form of first order Lagergren equation is given as Eq.5

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,ads}}{2.303}t \qquad (5)$$

The pseudo-second-order equation Eq.6

$$\frac{t}{q} = \frac{1}{k_{2,ads}q_e^2} + \frac{t}{q_t} \qquad (6)$$

where qe is the mass of metal adsorbed at equilibrium (mg/g), qt the mass of metal at time t(min.), k_1,ads the first-order reaction rate of adsorption (per minute), k_2,ads the pseudo-second-order rate constant of adsorption mg/g min^{-1}. A comparison between two kinetic models suggested (Table 2) the coefficient of correlation (R^2) for the pseudo-second-order kinetic model is much higher in comparison to pseudo-first-order model (2) the close agreement between the experimental qe (mg/g) values and the estimated qe (mg/g) values from pseudo-second- order kinetic model. These facts suggest that obtained kinetic data followed the pseudo-second-order kinetic model which describes the biosorption as the rate limiting step [39].

Table 2: Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Cr(VI) sorption by chitosan coated carbon

Metal ion	**Pseudo-first-order kinetic model**			**Experimental value**	**Pseudo-second-order kinetic model**		
	qe (mg/g)	**k_1 (min^{-1})**	**R^2**	**qe (mg/g)**	**qe (mg/g)**	**k_2 (g mg^{-1} min^{-1})**	**R^2**
Cr(VI)	767.10	0.002924	0.9485	135	555.79	0.003217	0.7040

Adsorption of Cr(VI) and onto chitosan coated carbon follows second order

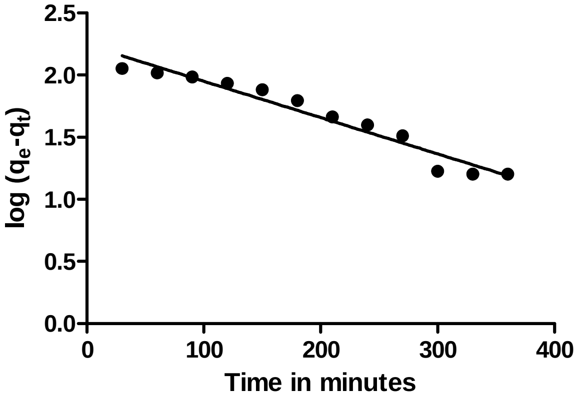


Figure 6. Pseudo-first-order kinetics plot of Cr (VI) on chitosan coated carbon

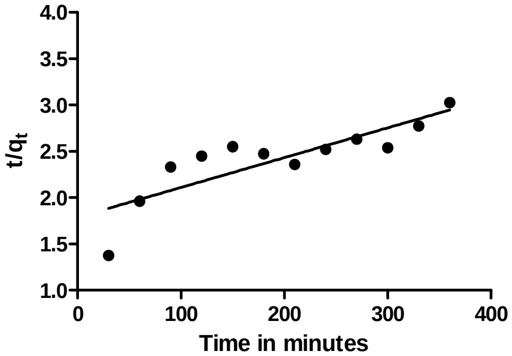


Figure 7. Pseudo-second-order kinetics of Cr (VI) on chitosan coated carbon

3.6 Free Energy Change(ΔG)

The change in the free Gibbs energy (ΔG) was calculated from the Langmuir constant using equation

$\Delta G = -RT \ln K_L$ - (6)

(where R is the universal gas constant (8.314 J/mol K), K_L is Longmuir constant and T is the absolute temperature). K_L=4.522(dm3/g). T= 25^0C.

Hence, ΔG= -313.636 KJ/mol

The negative value of ΔG indicates that the adsorption process of Chromium (VI) onto chitosan coated carbon is feasible and spontaneous

CONCLUSION

The adsorption of Cr (VI) from aqueous solutions onto chitosan coated carbon was investigated. The experiments were performed in batch system, at room temperature, on analyzing the effects of the following variables: initial solution pH, contact time and chitosan dosage. The results lead to the following conclusions:

- The adsorption of Cr(VI) on chitosan increases by changing the pH from acid towards neutral, while the optimum pH value for Cr(VI) removal was found to be 5.0;
- The equilibrium state of the interaction between chromium ions and the chitosan coated carbon surface is reached after 300-min contact time;
- The removal of Cr(VI) increases slightly with the chitosan coated carbon dosage, while the adsorption rate (Cr(VI)/g chitosan coated carbon) significantly decreases, and thus, at a chitosan coated carbon dosage higher than 4g/L, the process is not cost-effective;
- The application of the Langmuir and Freundlich isotherm models for the mathematical description of Cr(VI) adsorption onto chitosan coated carbon permits the following conclusions:
- Adsorption equilibrium data are very well fitted to Freundlich than the Langmuir isotherm, the maximum adsorption rate (Cmax) – of 1647mg/g – occurring under the experimental conditions studied;
- The value of the free Gibbs energy (ΔG), calculated from the Langmuir constant, is negative, indicating that the adsorption process of Cr (VI) onto chitosan coated carbon is feasible and spontaneous.
- Pseudo-second-order chemical reaction describes adequately the largest part of the process for the sorption of Cr(VI) ions onto chitosan coated carbon.

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