COMPARATIVE REMOVAL OF CHROMIUM TOXIC METAL FROM WATER USING VERMICULITE BLENDED CHITOSAN COATED CARBON BIOPOLYMER COMPOSITES

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ABSTRACT

A specific amount of chromium is required for normal body functions. Its higher concentration it may cause toxicity, including liver and kidney problems-genotoxic carcinogen. Hence it should be removed from waste water before discharging it. In this study chitosan blended vermiculite and chitosan coated carbon based bio-sorbents were prepared and used to remove chromium heavy metal ion ($Cr^{6+)}$ from water by changing various parameters such as adsorbent dosage, contact time and pHBoth the adsorbents exhibit maximum chromium ion removal at optimum pH=5, adsorbent dose 5g/100 ml and contact time 300 min. Sorption data were analyzed by sorption isotherm and kinetic study and thus, data well fitted with Frenundlich's isotherm model and follows pseudo-second order *kinetics.*

Key words: Toxic metal, Biosorption, Chitosan blended Vermiculite (CV), Chitosan Coated Carbon(CCC), Isotherm modeling and Kinetics study

1. INTRODUCTION

Chromium compounds generally exists in the environment as trivalent (III) and hexavalent (VI) ions. The trivalent chromium ion is a micro nutrient in trace amount, but hexavalent chromium ion is 500-1000 times toxic than Cr(III) and suspected carcinogen [1]. Daily intake of chromium by human is less than 100µg mostly from food and water [2].

Major sources for chromium such as, electroplating, metal finishing, leather tanning, magnetic tapes, wood production, pigments, brass, chemical manufacturing, electrical and electronic instruments and catalysis will contaminate the water[3]. Besides these, ores are believed to be the major donors of chromium through various processes like smelting, roasting and extractions[4].

The toxic action of Cr(VI) is due to the negatively charged hexavalent chromium ion complexes, which can easily cross cellular membranes by means of sulphate ionic channels, and then undergo immediate reduction reactions leading to formation of various reactive intermediates. These intermediates are harmful to cell organelles, proteins and nucleicacids[5]. Chromium also interferes with many metabolic processes of plants which cause reduced growth and phytomass, foliar chlorosis, stunting and finally plant death [6]. Bio-molecules such as, lipids and proteins are oxidatively damaged by this heavy metal [7]. It modifies the activity of enzymes which, includes antioxidants enzyme, nitrate reductase and ribonuclease [8] and change plant water status.

Chitosan, a hydrophilic natural polymer produced by alkaline deacetylation of chitin, obtained mainly by the extraction from shrimp and crab shells, is the most abundant biopolymer occurring in nature, after cellulose [9]. Chitin is a linear polymer mainly consisting of β-(1-4)-linked-2-acedamido-2-deoxy-β-d-glucopyranose units and partially of β-(1-4)-linked 2- amino- 2-deoxy-β-d-glucopyranose. It is composed of both glucosamine and acetyl-glucosamine as a monomer in the heteropolymeric network. 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 ion exchange. The interaction type depends on the metal ion, its chemistry and initial solution pH [10].Unprotonated amine groups in the chitosan adsorb metal ions by coordination [11]. Several studies of metal ion adsorption by chitosan have been carried out in the recent years such as removal of chromium and cadmium [12], nickel and lead ions from aqueous solutions [13]. In order to increase the adsorption capacity of chitosan and to improve the adsorption selectivity of metal ions, several chemicals with certain functional groups have been loaded on chitosan such as istatin [14-16]. The above properties of chitosan can also be enhanced by grafting with new functional groups which includes poly (ethylenimine) [17-20] through cross-linked chitosan backbone.

Vermiculite is the typical clayand consists of tetrahedral–octahedral–tetrahedral sheets. The two tetrahedral silicate layers are bonded together by one octahedral magnesium hydroxide-like layer and the structure is often referred to as 2:1 phyllosilicate. When tetravalent silicon is substituted by trivalent aluminum in the tetrahedral layer of the vermiculite sheet, a negative charge is generated on the layer and, thus, hydrated magnesium is adsorbed on the tetrahedral layer between the sheets to maintain electro neutrality. These magnesium ions can be easily cation-exchanged with other cationic species such as copper, which partly contribute to the high cation-exchange capacity of vermiculite [21].Vermiculite has a high cation exchange capacity and surface area with their small particle size. Hence, it is used as an efficient and low cost adsorbent for the metal ion removal [22]

In this study, chitosan biopolymer is blended with vermiculite (CV) in the presence of glutaraldehyde as cross-linker and coated on activated carbon (CCC). These two biosorbents were used for the biosorpative removal of chromium metal ion from water comparatively, in changing various factors such as adsorbent dosage, contact time and pH. Sorption data were analyzed with sorption isotherm and kinetic study.

2. MATERIALS AND METHODS

2.1. Chemicals and Reagents

Chitosan (deacetylation 92% and MW 120,000) was procured from India Sea Foods, Cochin, Kerala, India. Vermiculite, Carbon and Potassium dichromate, cadmium chloride, hydrochloric acid, sodium hydroxide and acetic acid of AR grade were used without any further purification.

2.2. Preparation Biosorbents

Chitosan Blended Vermiculite(CV)

Chitosan biopolymer solution was prepared by dissolving 1g of chitosan in 2% acetic acid and mixed with a known weight of the vermiculite. The mixture was then stirred thoroughly in the presence of glutaraldehyde (10ml) as a crosslinking agent at room temperature for one hour. Then the above prepared mixture was poured into a petri dish and dried in vacuum for 10 hr to remove the solvent completely.

Chitosan Coated Carbon(CCC)

About 400ml of chitosan gel was diluted with water (400ml) and heated to 40-50ºC. About 400 g of activated coconut shell carbon (by 7% sulphuric acid) was slowly added and mechanically agitated using a rotary shaker at 150 rpm for 24 hours. This gel coated activated carbon was washed with deionized water and dried. This process was repeated to get multi coating.

2.3. Preparation of Stock Solutions

Stock solutions of chromium (VI) were prepared separately by dissolving potassium dichromate of 200 mg each per liter using double-distilled water and standardized after preparation. 1:1 Hydrochloric acid and 1% sodium hydroxide solutions were used forpH 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. Heavy Metal Removal by Batch Adsorption Study

Synthetic solutions of Cr(VI) ions were taken in stoppered bottles and agitated with the prepared adsorbents separately at 30ºC in orbit shaker at the fixed speed of 160 rpm. The extent of heavy metal removal was investigated separately by changing adsorbent dose, contact time of shaking and changing pH of the solution.After attaining the equilibrium, the adsorbent was separated by the filtration using filter paper and aqueous phase concentration of metal was determined with atomic absorption spectrophotometer (Varian AAA 220 FS).

3. RESULT AND DISCUSSION

3.1. Effect of Contact Time

This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system [23]. The equilibrium was attained due to the limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of the adsorbent [24].After optimum contact time, there was no change in the adsorption of metal ions. This is due to decrease of easily available active sites for the binding of metal ions, and the equilibrium attained between adsorption and desorption. Qin et al., [25] has reported that 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 (**Fig.1**).CCC bio-sorbent shows optimum removal of Cr(VI) ions from water at 300 min and CV at 270 min. In the effect of contact time CCC removes maximumCr(VI) ions than CV.

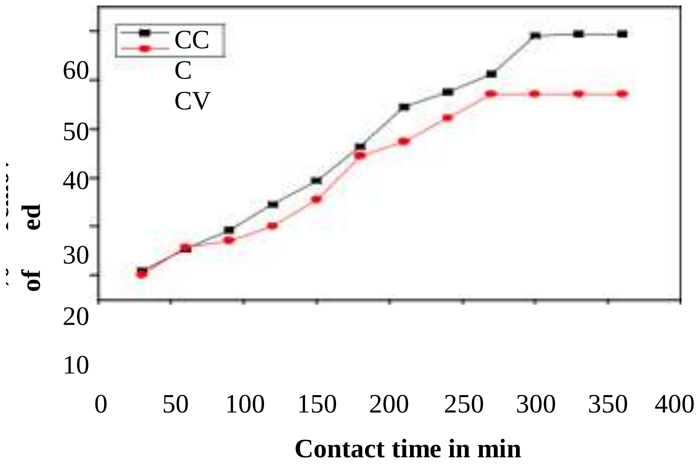

Figure 1 Effect of contact time

3.2. Effect of Adsorbent Dosage

The effect of the adsorbent dose was studied at room temperature by varying the sorbent amounts from 1 to 6 g. For all these runs, initial concentration of the metal ions was fixed.Fig.2 shows that the adsorption of Cr(VI) ion increases rapidly with the increase in the amount of adsorbent.This observed increase with the increase in the weight of adsorbent was due to the greater availability of the surface area. The significant increase in the uptake was observed when the dose was increased from 1 to 5 g. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This may be due to the overlapping of adsorption sites as a result of overcrowding of adsorbent particles. These results indicate that the removal efficiency is directly related to the number of available adsorption sites. Once equilibrium is attained, there is no effect on adsorption efficiency. Similar result was observed in studies done by Omar et al [26, 27]. Both biosorbents show optimum removal of Cr at 5g/100ml. CCC remove 68.5% and CV removes 71.4% of Cr(VI) ions from water.In the effect of adsorbent dosage, CV shows maximum removal of Cr(VI) ions than CCC.

These results also suggested that after a certain dosage of adsorbent, the maximum adsorption sets in and hence the amount of adsorbed ions and free ions in the solution remains as constant even with further addition of adsorbent. This was due to the overcrowding of adsorbent particles [28] and the screening effect on the dense outer layer of the cells, by shielding the binding sites from metals [29].

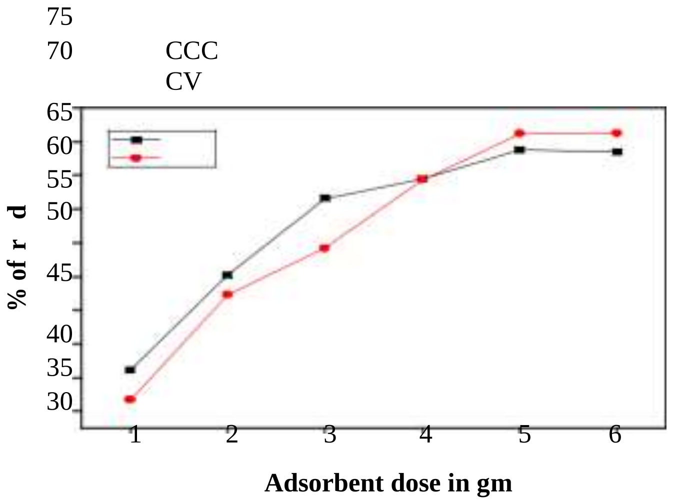

Figure 2 Effect of adsorbent dose

3.3. Effect of p^H

It is well known that p^H significantly influences the adsorption processes by affecting both the protonation of the surface groups and the degree of the ionization of the adsorbates [30].The effect of p^H change on adsorption was studied for both metals by changing the p^H of the contents from 4-8, using dilute solutions of HCl and NaOH.From Fig.3, At low p^H lower adsorption capacity of Cr(VI) ions was observed. This was due to the fact that at low p^H, amine groups in the chitosan gets protonated (surface active sites) and there will also be a repulsion force between heavy metal ions and active sites.This repulsion was reduced with the rise in the p^H, whichfavors the adsorption, Hence, it shows the increase in the adsorption of Cr(VI) ions with increase the pH [31].After p^H 6 adsorption of Cr(VI) ions decreased which may be due to the precipitation of metal ions as insoluble hydroxides [32, 33] Both biosorbents show maximum sorption of Cr(VI) ions at optimum p^H 5.

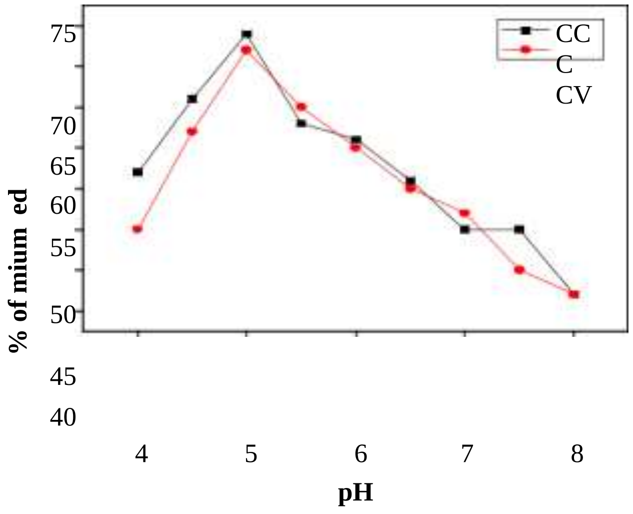

Figure 3 Effect of p^H

4. SORPTIONISOTHERM STUDY

The adsorption isotherm is fundamental in describing the interactive behavior between solutes and adsorbent [34, 35]. According to Ofomaja andHo the isotherm yields certain constant values, which express the surface properties and affinity of the adsorbent. It also plays an important role in the design of an adsorption system. The Langmuir and Frenundlich's models are often used to describe equilibrium adsorption isotherms (**Fig.4**).

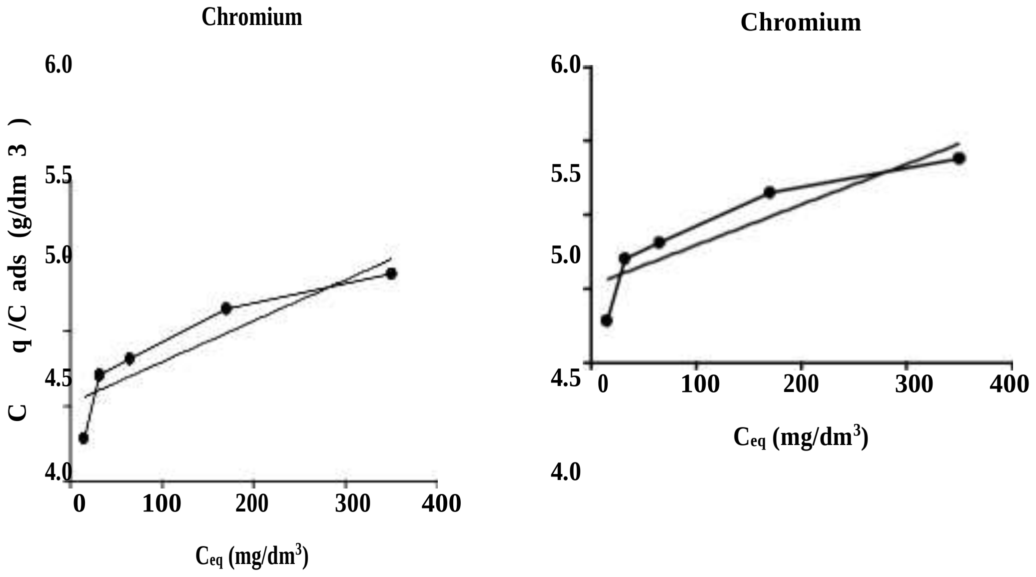

Figure 4 Langmuir plot for Cr (VI) adsorption onto (a) chitosan blended Vermiculite (b) chitosan coated carbon

The chromium sorption onto Vermiculite blended Chitosan coated Carbon Bio polymeric Compositeswere carried out by changing the initial metal ion concentration and thus verified for fitting in the Langmuir and Frenundlich's adsorption isotherm model (Fig.4).

4.1. Langmuir Sorption Isotherm

The most widely used Langmuir equation, is valid for monolayer sorption onto a surfacewith 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 the neighboring sites [37].

The Langmuir equation (1),

$$C_{eq} / C_{ads} = [1/Qb] + [C_{eq}/Q] \qquad (1)$$

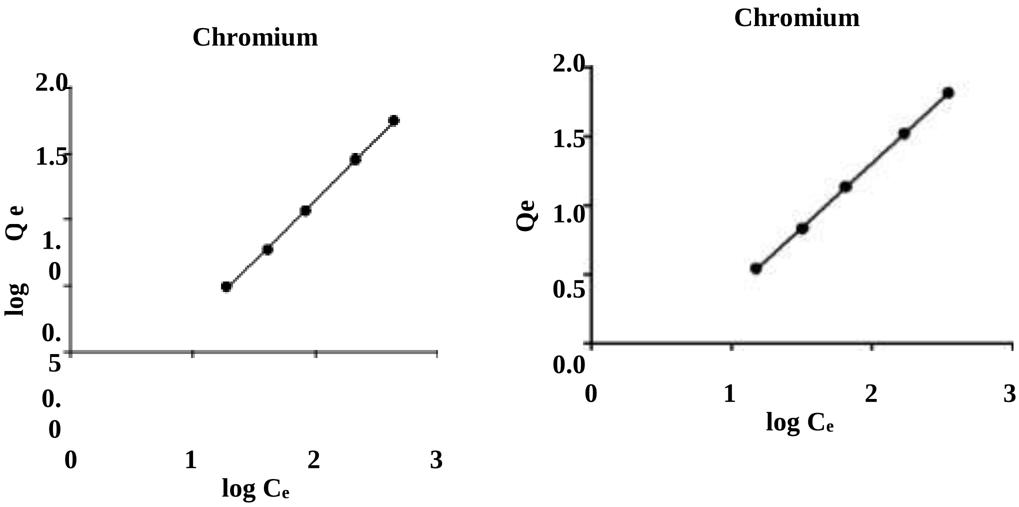

Figure 5 Frenundlich's plot for adsorption of Cr(VI) onto (a) chitosan mixed vermiculite (1:1) + glutaraldehyde (b) chitosan coated carbon

Where C_{eq} is equilibrium concentration of adsorbate in solution, (mgg^{-1}),Cads is amount adsorbed (mg.dm^{-3}), Q is maximum adsorption at monolayer (mg g^{-1}), b is Langmuir constant related to the affinity of binding sites (ml mg^{-1}) and is a measure of the energy of adsorption. In general for good sorbents, high values of Qand low values of b are required.A plot of C_{eq}/C_{ads} vs C_{eq} yields a straight line confirming the applicability of Langmuir adsorption isotherm (**Fig.5**).

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

Metal ions/Adsorbent	**Langmuir constants**			
	K_L (dm^3/g)	**b (dm^3/mg)**	**C_{max}(mg/g)**	**R^2**
Cr(VI)/CV	3.497	0.003822	914.96	0.6860
Cr(VI)/CCC	4.522	0.002745	1647.36	0.8107

4.2. Frenundlich's Sorption Isotherm

A brief empirical equation often used to represent adsorption data is called the Frenundlich's equation. The Frenundlich's isotherm describes the physical adsorption from liquids. The exponent 1/n is an index of the diversity of free energies associated with the adsorption of the solute by multiple components of a heterogeneous adsorbent.The Frenundlich's equation (3) which was used to describe heterogeneous surface energies was expressed as:

$$C_{ads}=K\ C_{eq}1/n \qquad (3)$$

The linearized form of this equation is expressed as

$$\log C_{ads}=1/n \log C_{eq} + \log K \qquad (4)$$

Whereas, 1/n is Frenundlich's characteristic constant related to energy, and K is maximum adsorption capacity. Both n and K are temperature dependent.By plotting log C_{ads} against log C_{eq}. If a straight line is obtained then the value of 1/n and K can be calculated from slope and intercept.The good fit of Frenundlich's isotherm to an adsorption system means there is almost no limit to the amount of adsorbed and there is a multilayer adsorption (**Fig.6**). The applicability of the Frenundlich's equation to a particular case was tested by log Cads against log C_{eq} from the logarithmic form of equation (4).

From the Table.2 it was observed that the R^2 value for the metal Cr(VI) was found to be 0.9994 onto chitosan blended vermiculiteand 0.9998 ontochitosan coated carbon. From the above value, it was concluded that the adsorption of Cr (VI) ion onto the both biosorbents correlates well with the Frenundlich's equation as compared to the Langmuir equation under the various concentration ranges studied. These results indicate about the feasibility of multilayer adsorption onto the chitosan coated carbon and also the Frenundlich's constant 'n' shows the feasibility of heterogeneous adsorption.

Table 2 Frenundlich's Adsorption isotherm constant

Metal ions/Adsorbent	Frenundlich's constants		
	K	n	R^2
Cr (VI)/ CV	0.1948	1.0780	0.9994
Cr (VI)/ CCC	0.2760	1.0735	0.9998

5. KINETICS STUDY

In order to examine the controlling mechanism of the adsorption process such as mass transfer and chemical reaction, kinetic models were used to test the experimental data. The kinetics of metal ion adsorption on the chitosan coated carbon was determined using pseudo-first order and pseudo-second order model.The linearized form of the first order Lagergren equation was given as equation 5.

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

Where qe is the mass of metal adsorbed at equilibrium (mg/g), qt the mass of metal at time t(min.), k_{1ads} the first-order reaction rate of adsorption (per minute). The slope and intercept of plots of log (q_e-q_t) vs t (Fig.7)wereused to determine the pseudo-first order constant k_1 and q_e. The obtained values are presented in Table.3

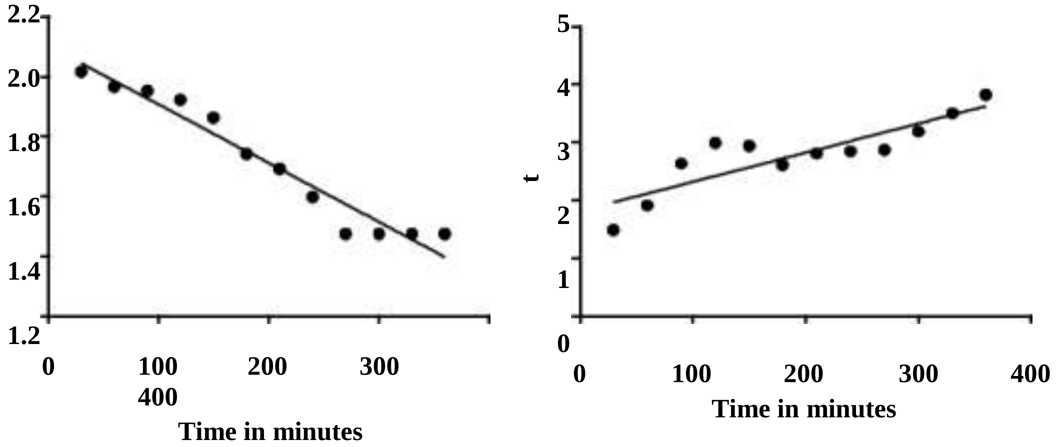

Figure 7 Pseudo-first-order kinetics plot of adsorption of Cr (VI) onto (a) chitosanblended vermiculite (b) chitosan coated carbon

The theoretical qe values estimated from the pseudo-first order kinetic model gave significantly different values and the correlation coefficients were also found to be lower. These results showed that the pseudo-first order kinetic model did not describe these sorption systems.The sorption data were also treated according to the pseudo-second-order kinetics (Equation 6) because it was shown to be more likely to predict the behaviour over the whole range of the adsorption being based on the assumption that the rate determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and sorbate [38].

Rate expression is$t/q = 1/k_{2ads}\, q_e^2 + t/q_t$ (6)

Where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t the mass of metal at time t(min.), k_{1ads} the first-order reaction rate of adsorption (per minute), k_2,ads the pseudo-second-order rate constant of adsorption mg/g min^{-1}.The values of q_e and k_2 were obtained from the slope and intercept of the straight line obtained by plotting t/q_t against t**.**

The results obtained from the pseudo-first-order kinetics demonstrated that the experimental q_e (mg/g) values did not agree well with the calculated value obtained from the linear plot. So adsorption process does not follow the first order kinetics. But there will be a close agreement between experimental qe value and calculated q_e value from the pseudo-second -order model. This confirms that it is appreciable to use Lagergren second order model to predict the adsorption kinetics for Cr(VI) onto both biosorbents, which is based on the assumption that the rate limiting step may be chemisorption involving valance forces through sharing and exchange of electrons.

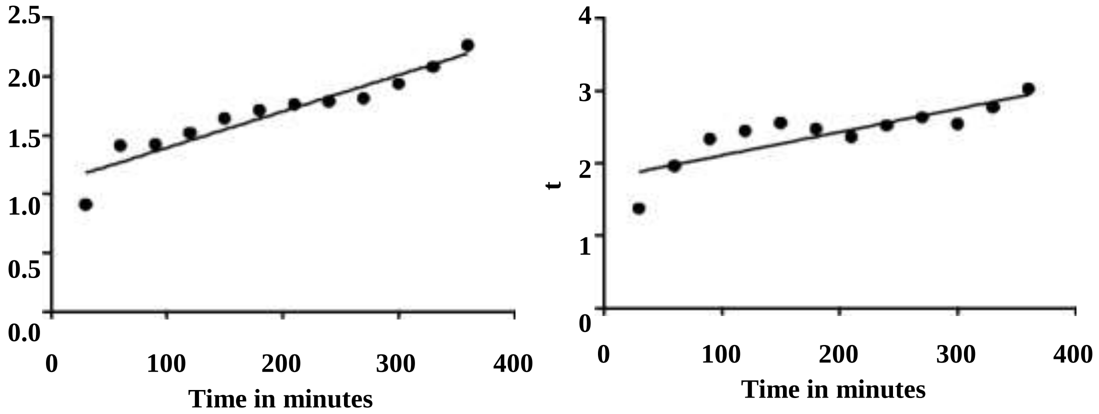

Figure 8 Pseudo-second-order kinetics plot of adsorption of Cr (VI) onto (a) chitosanblended vermiculite (b) chitosan coated carbon

Table 3 Comparison between Lagergren pseudo first-order and pseudo-second order kinetics models for Cr (VI) sorption.

Metal ion Cr(VI)	**Pseudo-first-order kinetic model**			**Experimental value**	**Pseudo-second-order kinetic model**		
	q_e (mg/g)	**k_1 (min^{-1})**	**R^2**	**q_e (mg/g)**	**q_e (mg/g)**	**k_2 (g mg^{-1} min^{-1})**	**R^2**
CS+VM	1071.86	0.001962	0.9483	124	360.73	0.005037	0.7539
CCC	767.10	0.002924	0.9485	135	555.79	0.003217	0.7040

6. CONCLUSIONS

Chitosan biopolymer blended vermiculite (CV) and coated on carbon (CCC) shows great tendency to remove Cr(VI) ions from water. The optimum p^H for the both adsorbent is 5at which CV removes 72% and CCC removes 74% of chromium ions. In the sorbent dose, CV removes maximum Cr(VI) ions than CCC at 5g/100ml. In contact time, CCC removes maximum Cr(VI) than CV at 300 min. All sorption dataare well fitted withFrenundlich's isotherm than Langmuir isotherm, which confirmed that multilayer adsorption of metal ions is possible. All the sorption processes follow pseudo second order kinetics. The negative free energy change of sorption process shows that sorption of Cr(VI) ions by both sorbent is spontaneous and a favorable one. Vermiculite blended chitosan coated carbon bio polymeric composites are favorable sorbent for the removal of Cr(VI) ions from water.

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