



Chitosan coated silica as biosorbent to remove Cr(VI) from aqueous solutions

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Received: 1st January, 2010 ; Accepted: 11th January, 2010

ABSTRACT

This study investigated the feasibility of using chitosan coated silica as a novel type of biosorbent for Cr(VI) removal from aqueous solution through adsorption technique. The biosorbent was characterized by FTIR spectra, TGA, porosity and surface area analyses. The removal of Cr(VI) from aqueous solution was studied by using the biosorbent under batch equilibrium experimental conditions. The research parameters included the effect of pH, contact time, concentration of Cr(VI) and amount of biosorbent was investigated in order to optimize the process at room temperature. The equilibrium data were used to study the kinetics of Cr(VI) removal process such as pseudo first order, pseudo second order and Weber-Morris intraparticle diffusion models. The data were fitted to Langmuir and Freundlich adsorption isotherms. The maximum monolayer adsorption of Cr(VI) on chitosan coated silica was found to be 294.1 mg/g. The SSE and χ^2 analysis, used to correlate the equilibrium kinetic models and isotherms. The experimental results demonstrated that chitosan coated silica could be used as an effective biosorbent for the Cr(VI) removal.

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KEYWORDS

Cr(VI);
Biosorption;
Chitosan coated silica;
Equilibrium modeling.

INTRODUCTION

Heavy metals are defined as those metals and metalloids generally considered to be of sufficient distribution and abundance as to be in some way environmentally or biologically significant as toxic substance^[1]. These include metals such as lead (Pb), chromium (Cr), Copper (Cu), Cadmium (Cd), Nickel (Ni) and Zinc (Zn). Chromium pollution in our environment has attracted more and more attention in recent years because of its harmful effects to ecosystems and human beings. These

chromium species are commonly found in wastewater produced from leather tanning, dye, wood preservation and electroplating industries and their concentrations could range from tens to hundreds of mg/L^[2]. Hexavalent chromium Cr(VI) is more toxic than the trivalent form Cr(III) because of its carcinogenic and mutagenic effects. A variety of diseases such as bronchogenic carcinoma, asthma, pneumonitis and dermatitis have been reported to associate with occupational Cr(VI) exposure^[3]. Hence, the discharge of Cr(VI) to surface water is regulated below 0.05 mg/L by the U.S.

EPA, and total Cr including Cr(III), Cr(VI) as well as its other forms is regulated below 2 mg/L^[4].

Chemical precipitation, membrane separation, ion exchange, electrochemical treatment, evaporation and carbon adsorption are among the variety of treatment processes widely used for the removal of toxic heavy metals from the waste streams. In recent years biosorption has been recognized as an effective method of reduction of metal contamination in surface water and in industrial effluents^[5]. Biosorption is defined as the removal of metal or metalloid species, compounds, and particulates from solution by biological material^[6]. Olin et al.^[7] and Bailly et al.^[8] conducted an extensive literature search to identify low cost sorbents with potential for treatment of heavy metal contaminated water and waste streams. They identified 12 potential sorbents for lead, cadmium, copper, zinc and mercury. Among the sorbents identified, chitosan has the highest sorption capacity for metal ions^[9].

Chitosan is a partially deacetylated product of chitin, which is extracted from shrimp, crab, some fungi, and other crustaceans, has many useful features such as biocompatibility, biodegradability and antibacterial property^[10-12]. Chitosan is not only inexpensive and abundant in nature, but it also is a good adsorbent for heavy metals. Chitosan chelates five to six times greater amounts of metals than chitin. Several investigators have attempted to modify chitosan to facilitate mass transfer and to expose the active binding sites to enhance the adsorption capacity^[13,14]. Grafting specific functional groups onto native chitosan backbone allows its sorption properties to be enhanced. To overcome some of the problems associated with its softness and tendency to agglomerate or to form a gel in aqueous solutions, in this study a new biosorbent is prepared by coating chitosan, a glucosamine biopolymer over silica, and formed into beads. It is expected that the more active sites of chitosan will be available due to coating, thus enhancing the adsorption capacity.

The objectives of this study were to prepare chitosan coated silica biosorbent, to characterize the sorbent, and to evaluate the removal of Cr(VI) from synthetic samples. The adsorption capacity of the biosorbent was evaluated by studying the equilibrium adsorption isotherms and kinetics of Cr(VI) in batch method. Further the equilibrium data were fitted to Langmuir and

Freundlich adsorption isotherms and pseudo first order, pseudo second order and Weber-Morris kinetic models and the values of parameters of the isotherms and kinetics were obtained.

EXPERIMENTAL

Materials

Analytical grade potassium dichromate from Qualigens Fine Chemicals was used as source of chromium(VI). Hydrochloric acid and sodium hydroxide used for pH adjustment were obtained from Aldrich Chemicals Company. Sulphuric acid, potassium permanganate and sodium azide of analytical grade were from Loba Chemie, Mumbai. Chitosan and silica, used for preparation of chitosan coated silica, were obtained from Loba Chemie, Mumbai, India. Doubly distilled water was used in all experimental work.

Preparation of biosorbent

Chitosan gel was prepared by adding 4 g of chitosan to 100 mL of 2% acetic acid and stirring for about 4 h. Ten grams of silica, washed with 2% acetic acid solution were added to 100 mL of 4% chitosan gel while stirring with a magnetic stirrer for 4 h. This process led to the formation of silica / chitosan suspension. Spherical shaped beads were formed by drop wise addition of silica / chitosan suspension into a 0.1 M NaOH precipitation bath. The purpose of adding silica / chitosan suspension to a NaOH solution is to assist rapid neutralization of acetic acid, so that the spherical shape could be retained. These spherical beads were taken from NaOH bath, and washed several times with deionized water to a neutral pH. The beads were dried in freeze drier, oven and by air. The average size of the bead was found to be 2.05 mm.

FTIR, TGA and surface area analysis

The biosorbent was characterized by FTIR (Fourier transform infrared spectroscopy), TGA (Thermo gravimetric analysis) and surface analysis. FTIR spectrum of biosorbent was recorded in a Perkin-Elmer-283B FTIR spectrometer over the wave range 4000-400 cm⁻¹. The samples were formed into pellets with KBr. Thermal stability of the biosorbent was examined, using Seiko 220TG/DTA analyzer, from 25 to 700°C

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at heating rate of 10 °C/min with continuous flushing with pure nitrogen gas at 200 mL/min. Surface area of the biosorbent was measured by single point BET (Brunauer, Emmett and Teller) method using thermal conductivity detector (Carlo Ebra Soptomatic-1800) with in the range of 0.1-2000 m² g⁻¹ with the sample size of 2-10 mg. Pore volume of the biosorbent was measured using Pycnomatic ATC (Thermo Electronic Corporation).

Analytical procedure

The sorption and reduction capacities of chitosan coated silica was studied by adding 0.1 g of adsorbent to 100 mL of Cr(VI) solutions of different concentrations in 125 mL Erlenmeyer flasks. The flasks, sealed with glass stoppers and para film, were placed in an oscillating shaker and shaken for 4h at 150 rpm. Initial adsorption experiments showed that this period of time was adequate to ensure equilibrium between chromium adsorbed and chromium unadsorbed. After the equilibrium period, samples were filtered through Whatmann No. 5 filter paper. The first portion of the filtrate was discarded to eliminate the effect of any adsorption of chromium on filter paper.

The filtrate was then divided into two parts and first part was used to determine equilibrium concentration of Cr(VI) and the second part was used to determine Cr(VI) reduced to Cr(III). The concentration of Cr(VI) was determined spectrophotometrically by using diphenyl carbazide as a complexing agent. 10 mL of solution from first part was pipette into 100 mL standard flasks and made up to the mark with 1:1 H₂SO₄, diphenyl carbazide and double distilled water. The concentration of Cr(VI) was determined spectrophotometrically at 540 nm.

From the second part, 10 mL of the solution was pipette out into a conical flask followed by addition of 90 mL double distilled water. The contents were heated to boil and about 6 drops of 0.1 N potassium permanganate solution was added to oxidize Cr(III) to Cr(VI). To this about 4-5 drops of 0.5% azide was added to remove excess potassium permanganate. The concentration of Cr(VI) was determined spectrophotometrically which gave the total unadsorbed chromium. Chromium adsorbed was equal to the difference between the initial concentration of Cr(VI) and total unadsorbed

chromium and chromium reduced was equal to the difference between the total chromium unadsorbed and Cr(VI) present in solution.

Batch adsorption studies

In order to explore the effect of influencing factors, such as solution pH, contact time, quantity of the adsorbent and the initial concentration of Cr(VI), a series of batch experiments were conducted with solutions of initial concentrations of 50, 100 and 150 mg/L. The pH of the suspension at the start of the experiment was adjusted using 0.1 N HCl and 0.1 N NaOH. After agitating the samples for 3 hours, the samples were filtered through Whatmann No.5 filter papers to eliminate any fine particles. Then the concentrations of Cr(VI) and Cr(III) in the filtrate were determined as discussed earlier. The adsorption on the glassware was found to be negligible and was determined by running blank experiments.

The amount adsorbed per unit mass of adsorbent at equilibrium was obtained using the equation,

$$Q_e = \left(\frac{C_i - C_e}{m} \right) V \quad (1)$$

where Q_e (mg/g) is the adsorption capacity at the equilibrium, C_i and C_e denoted respectively the initial and equilibrium concentration of Cr(VI). V is the volume of the solution in liters and m is the mass of the adsorbent in grams.

RESULTS AND DISCUSSION

Characterization of biosorbent

The FTIR spectrum of chitosan coated silica beads before adsorption indicates the presence of predominant peaks at 3351.7 cm⁻¹ (-OH and -NH stretching), 2987.2 and 2901.4 cm⁻¹ (-CH stretching), 1638.2 cm⁻¹ (-NH bending in -NH₂), 1393.3 cm⁻¹ (-NH deformation vibration in -NH₂), and 1065.5 cm⁻¹ (-C-O-C stretching). This reveals that all functional groups such as -NH₂, -OH, originally present in chitosan, are intact even after coating on silica and are available for interaction with the metal ion. A broad peak around 1092 cm⁻¹ may be due to the merging of peaks relating to Si-O-Si, Si-O-H, and C-O groups. Another broad peak around 3439 cm⁻¹ is attributed to -NH and O-H stretch-

ing vibrations. The FTIR spectra of sorbent after adsorption indicate a shift in absorption frequency of amino and hydroxyl groups. This may be attributed to the deformation of O-H and N-H bands as result of interaction between the functional groups and metal ion.

The sample was subjected to thermo gravimetric analysis (TGA) to determine the thermal stability and decomposition characteristics. The thermal degradation behavior of chitosan coated silica was examined following weight loss as function of temperature. The thermo gravimetric curve (Figure 1) of chitosan coated silica showed a broad transition with a relatively less weight loss. The weight loss was about 3% around 150 °C and about 6% at 360 °C. Thermo gram of chitosan coated silica indicates that about 8% of chitosan is coated on silica. From the TGA analysis of the biosorbent, it may be concluded that the biosorbent could be used even at higher temperatures in water treatment. The influence of surface properties on the extent of adsorption was evaluated by measuring the surface area (160.8 m²/g), porosity (46.2 %) and pore volume (0.224 cm³ g⁻¹). Porosity is one of the factors that influence the activity and physical interaction of solids with liquids and gases.

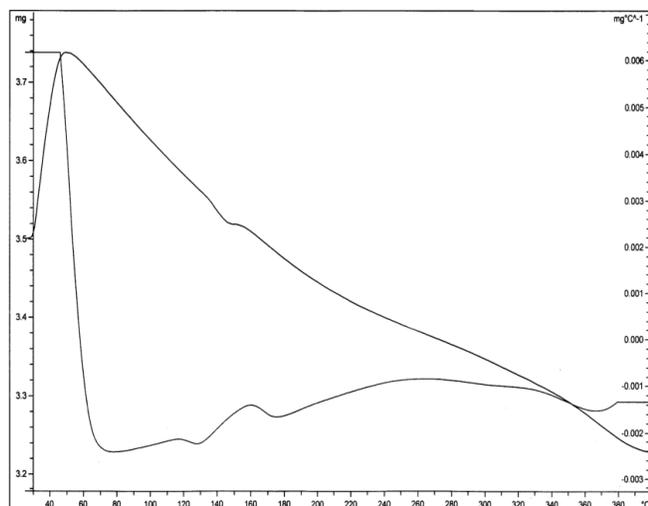


Figure 1 : Thermo gravimetric curve of chitosan coated silica
Effect of pH

In order to optimize the pH for maximum removal efficiency, experiments are conducted with 100 mL of 100 mg/L of metal solution containing 0.1 g of chitosan coated silica in the pH range of 3 to 8 for Cr(VI) at room temperature. The results are depicted in Figure 2. From the figure it is clear that the adsorption capac-

ity (87.95 mg/g) is maximum at pH 3 and decreases at higher pH values. Similar behavior was observed by de Dantas et al.^[15] and Schmuhl et al.^[16]. Chromium(VI) forms stable complexes such as Cr₂O₇²⁻, HCrO₄⁻, CrO₄⁻², and HCr₂O₇⁻¹ depending on the pH of the solution^[17]. The actual species of chromium present in solution depends on pH of the solution and the concentration of chromium. In a solution of acidic pH the predominant species present are Cr₂O₇²⁻ and HCrO₄⁻. The fraction of any particular species depends upon the chromium concentration and pH of the solution^[17].

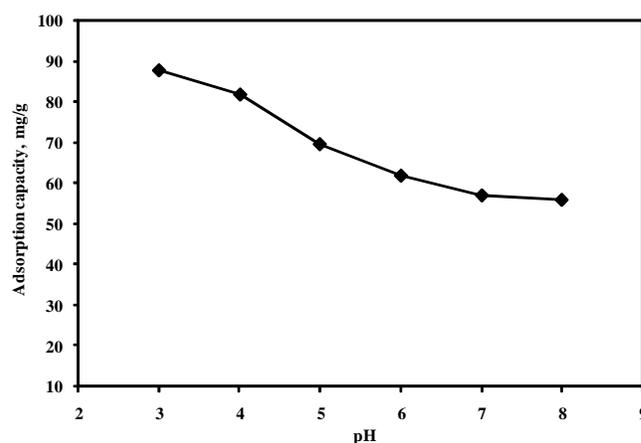


Figure 2 : Effect of pH on biosorption of Cr(VI) on chitosan coated silica

At lower pH the sorbent is positively charged due to the protonation of amino groups, while the sorbate, dichromate ion, exists mostly as an anion leading to the electrostatic attraction between sorbent and sorbate. This results in increased adsorption at low pH. As the pH of the solution increases the sorbent undergoes deprotonation and the adsorption capacity decreases. In view of this all experimental data were conducted at pH 3.

Effect of contact time and kinetic studies

The effect of contact time on the extent of adsorption of Cr(VI) at different concentrations at pH 3 was shown in Figure 3. The extent of adsorption increases with time and attained equilibrium for all the concentrations (50, 100 and 150 mg/L) of Cr(VI) studied at 180 min. After this equilibrium period, the amount of Cr(VI) adsorbed did not change significantly with time. The amount of Cr(VI) adsorbed versus time curves are smooth and continuous. The changes in the rate of removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient

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was high. Later, the Cr(VI) uptake rate by adsorbent had decreased significantly, due to the decrease in number of adsorption sites.

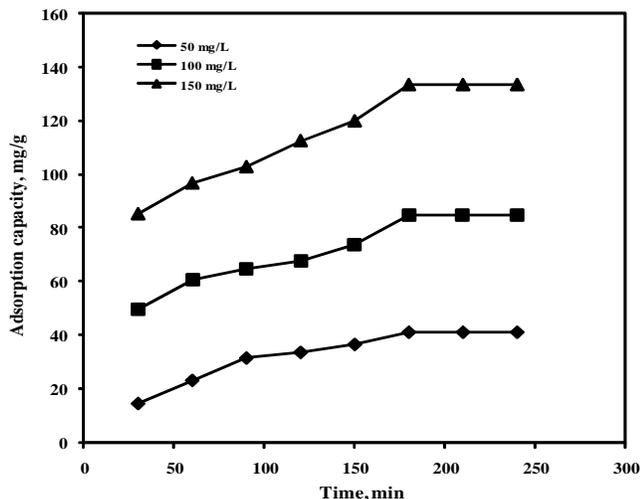


Figure 3 : Effect of contact time on biosorption of Cr(VI) on chitosan coated silica

In order to investigate the mechanism of sorption, the rate constants of sorption process were determined by using pseudo first order^[18,19] and pseudo second order^[20] kinetic models. The values of the first and second order rate constants are included in TABLE 1. In many cases the first order equation does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption process^[21]. The second order kinetic model assumes that the rate limiting step may be chemical adsorption^[22]. In many cases, the adsorption data could be well correlated by second order rate equation over the entire period of contact time^[23]. The results of the present study indicate that the adsorption of Cr(VI) on chitosan coated silica follows second order kinetics. It was found that the correlation coefficient r^2 values for this model was near to unity as compared to the r^2 values as obtained in the first order kinetics.

TABLE 1 : Pseudo first order and pseudo second order kinetic models of Cr(VI) biosorption on chitosan coated silica

Concentration of fluoride solution (mg/L)	First order model		Second order model			
	k_{ad}	r^2	$Q_e \text{ exp. (mg/g)}$	$Q_e \text{ cal. (mg/g)}$	k_2	r^2
50	0.01	0.99	41.2	57.8	0.0002	0.99
100	0.01	0.97	85.0	99.0	0.0002	0.98
150	0.01	0.97	133.7	153.8	0.0002	0.99

The adsorption process on porous sorbents generally described with four stages, and one or more of which may determine the rate of adsorption. These stages are described as bulk diffusion, film diffusion, intraparticle diffusion and finally adsorption of the solute on the surface. The experimental data were used to investigate whether the diffusion is the rate controlling step in adsorption of Cr(VI) on chitosan coated silica. The model proposed by Weber and Morris^[24] can be written as,

$$q_t = K_{id} t^{1/2} + C \quad (2)$$

where K_{id} ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$) is the rate constant of intra particle diffusion. C is the value of intercept of q_t versus $t^{1/2}$, which gives an idea about the boundary layer thickness, i.e. the larger the intercept; the greater is the boundary layer effect.

The plots of q_t versus $t^{1/2}$ obtained for the adsorption of Cr(VI) on chitosan coated silica at different concentrations (50, 100 and 150 mg/L) are shown in Figure 4. The intra particle rate constants (K_{id}) 2.70, 3.71 and 5.33 $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$ and intercept (C) values 2.79, 30.10 and 55.38 $\text{mg} \cdot \text{g}^{-1}$ for 50, 100 and 150 mg/L respectively. The kinetic results can be used to determine if particle diffusion is the rate-limiting step for Cr(VI) adsorption on chitosan coated silica. According to this model, the plot of uptake (q_t) versus the square root of time ($t^{1/2}$) should be linear and these lines should pass through the origin if intra particle diffusion is the rate controlling step^[25]. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and further shows that the intra particle diffusion is not the only rate limiting step, but also other kinetic processes may control the rate of adsorption.

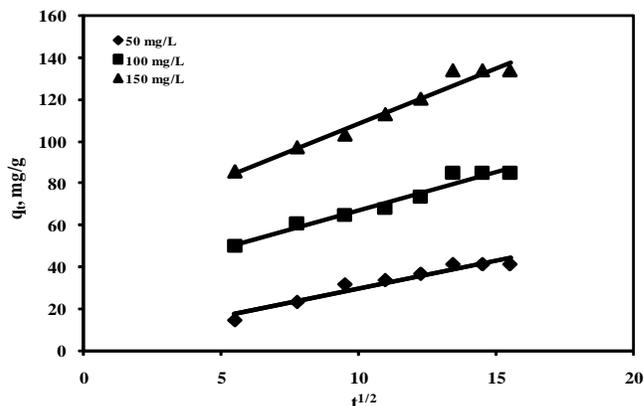


Figure 4 : Weber-Morris plots for biosorption of Cr(VI) on chitosan coated silica

The plots shown in Figure 4 are not passing through origin indicating that the intra particle diffusion is not the only rate determining factor and in addition other factors may be operating simultaneously.

Fitness of the sorption kinetic models

The assessment of the employed kinetic models for fitting the sorption data was made by calculating the squared sum of errors (SSE). Lower values of SSE show better fit to sorption data and can give an indication of the sorption mechanism.

$$SSE = \sum \frac{(q_{t,e} - q_{t,m})^2}{q_{t,e}^2} \quad (3)$$

where $q_{t,e}$ are the experimental sorption capacity of Cr(VI) (mg/g) at time t and the corresponding value which is obtained from the kinetic models. SSE values (Eq. (3)) of the pseudo first, second and Weber-Morris kinetic models were computed and summarized in TABLE 2. It is assumed that the model which gives the lowest SSE values is the best model for this system and then the mechanism of sorption can be explained based on that model. It was observed from TABLE 2 that pseudo second order model seems to be better fit than the other two models (pseudo first order and Weber-Morris models) for representing the kinetics of Cr(VI) sorption.

TABLE 2 : The sum of the squares of the error (SSE) values of the kinetic models employed for Cr(VI) biosorption

Models	50 mg/L	100 mg/L	150 mg/L
First order	1.00	1.00	1.00
Second order	0.16	0.03	0.02
Particle diffusion	0.87	0.83	0.76

Equilibrium modeling

Analysis of the equilibrium data is important to develop an equation which accurately represent the results and which could be used for design purposes. Several isotherm equations have been used for the equilibrium modeling of adsorption process. Two of these have been applied in this study, namely Langmuir and Freundlich isotherms. To obtain the isotherms, initial concentrations of Cr(VI) were varied from 50-150 mg/L while keeping the weight of chitosan coated silica and contact time constant at pH 3 of chromium solution.

The experimental data were fitted to the Langmuir isotherm^[26] of the form,

$$Q_e = \frac{Q^\circ b C_e}{1 + b C_e} \quad (4)$$

where the Q_e is the amount of Cr(VI) adsorbed (mg/g), C_e is the equilibrium concentration of Cr(VI) (mg/L), Q° is the amount of adsorbate at complete monolayer coverage (mg/g), which gives the maximum sorption capacity of the sorbent, b is the Langmuir isotherm constant (L/mg), that relates to the energy of adsorption evaluated from the linear plot (Figure 5), are presented in TABLE 3 along with the correlation coefficient.

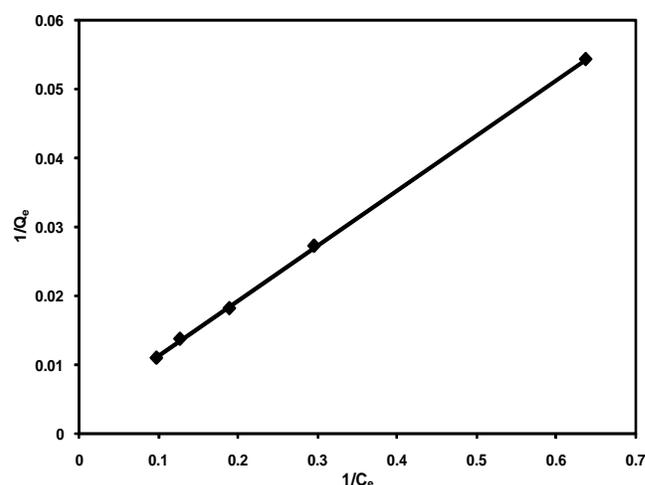


Figure 5 : Langmuir isotherm for biosorption of Cr(VI) on chitosan coated silica

TABLE 3 : Langmuir and freundlich isotherm parameters with chi-square analysis for Cr(VI) biosorption on chitosan coated silica

Langmuir				Freundlich				
Q° (mg/g)	b (L/mg)	r^2	χ^2	K_F (mg/g)	$1/n$ (L/mg)	n	r^2	χ^2
294.1	0.04	1.00	141.9	12.87	0.84	1.182	1.00	460.3

The Freundlich^[27] equation is expressed as,

$$Q_e = K_f C_e^{1/n} \quad (5)$$

where Q_e is the amount of Cr(VI) adsorbed per unit weight of the sorbent (mg/g), C_e is the equilibrium concentration of Cr(VI) (mg/L), K_f is a measure of adsorption capacity, and $1/n$ is adsorption intensity, evaluated from the plot (Figure 6) of $\log Q_e$ versus $\log C_e$. The values of Freundlich constants along with the correlation coefficient are presented in TABLE 3. Values of $1/n$

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are lying between 0.1 and 1.0 confirms the favorable conditions for adsorption. Adsorption capacities of chitosan and modified chitosan sorbents, collected from the literature, are included in TABLE 4 along with the values corresponding to chitosan coated silica for comparison. The sorbent developed in the present study exhibits higher adsorption capacity compared to chitosan in its natural and modified forms^[28].

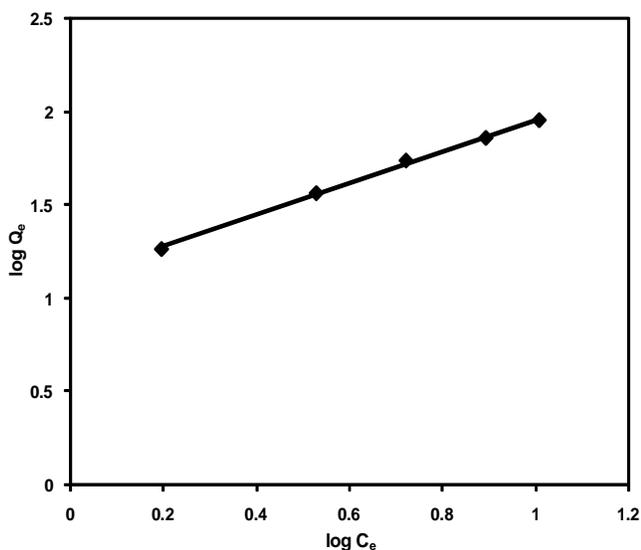


Figure 6 : Freundlich isotherm for biosorption of Cr(VI) on chitosan coated silica

TABLE 4 : Comparison of different biosorbents for Cr(VI) adsorption capacity (Langmuir model)

Adsorbent	pH	Adsorption capacity (mg/g)	Reference
sawdust	6.0	3.3	20
compost		101.0	22
chitosan	5.0	78.0	5
cross-linked chitosan	5.0	50.0	18
metal ion imprinted chitosan	5.5	51.0	14
chitosan cross-linked with epichlorohydrin	3.0	11.3	26
chitosan coated silica	3.0	294.1	Present work

Chi-square analysis

To identify a suitable isotherm model for the sorption of Cr(VI) on chitosan coated silica this analysis has been carried out. The chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by

the corresponding data obtained by calculating from the models. The equivalent mathematical statement is

$$\chi^2 = \sum \left(\frac{(q_e - q_{e,m})^2}{q_{e,m}} \right) \quad (6)$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is the experimental data of the equilibrium capacity (mg/g). If the data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ; χ^2 will be a bigger number. Therefore, it is necessary also to analyze the data set using the non-linear chi-square test to confirm the best-fit isotherm for the sorption system^[29]. The χ^2 values are calculated using Eq. (6) and are given in TABLE 3. The χ^2 values of both the isotherms are comparable and hence the adsorption of Cr(VI) on chitosan coated silica follows both Langmuir and Freundlich isotherms and better fits to Langmuir as its χ^2 value is less than that of Freundlich model.

Effect of adsorbent dose

The dependence of Cr(VI) biosorption on chitosan coated silica was studied at room temperature by varying the adsorbent amount from 0.1 g to 0.8 g while keeping the other parameters such as pH (3), metal solution volume (100 mL), concentration (100 mg/L) and contact time (4h) constant. The results are graphically shown in Figure 7. It is apparent that the percent removal of Cr(VI) increases rapidly with increase in the dose of chitosan coated silica. This is expected due to the fact that the higher dose of adsorbent in the solu-

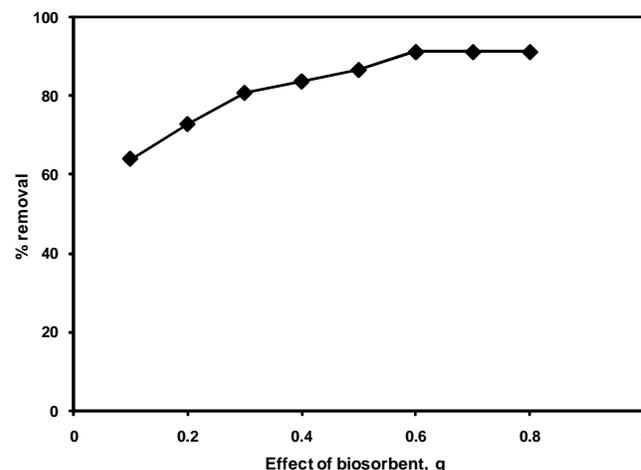


Figure 7 : Effect of biosorbent dose on percent removal of Cr(VI)

tion results in greater availability of exchangeable sites for the ions. The maximum Cr(VI) removal efficiency is 91.25 % at 0.6 g. This suggests that the Cr(VI) can be removed effectively by using <1 g of the biosorbent at pH 3. The reduction in adsorption capacity with increase in the biosorbent dose is mainly due to unsaturation of adsorption sites through the adsorption process.

CONCLUSIONS

In this study, chitosan coated silica beads were developed and used as a biosorbent for the removal of Cr(VI) from aqueous solution. The biosorbent was characterized on the basis of FTIR spectral study, TGA and surface area analysis. The equilibrium data fitted the Langmuir and Freundlich isotherms. The maximum adsorption capacity of chitosan coated silica was found to be 294.1 mg/g from Langmuir isotherm at pH 3 of chromium solution. Data revealed that Cr(VI) removal on chitosan coated silica is complex and both the surface adsorption as well as intraparticle diffusion contributes to the rate determining step. The kinetics of adsorption of Cr(VI) on chitosan coated silica follows pseudo second order model. The material is cheap and indigenous. The adsorption method is also very simple, does not cause any pollution, hence eco-friendly. The results obtained through this study support that the chitosan coated silica is an effective biosorbent for removal of Cr(VI).

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