


Contemplating the feasibility of vermiculate blended chitosan for heavy metal removal from simulated industrial wastewater

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Abstract Wastewater contaminated by heavy metals pose great challenges as they are non biodegradable, toxic and carcinogenic to the soil and aquifers. Vermiculite blended with chitosan have been used to remove Cr(VI) and Cd(II) from the industrial wastewater. The results indicate that the vermiculite blended with chitosan adsorb Cr(VI) and Cd(II) from industrial waste water. Batch adsorption experiments were performed as a function of pH 5.0 and 5.5 respectively for chromium and cadmium. The adsorption rate was observed to be 72 and 71 % of chromium and cadmium respectively. The initial optimum contact time for Cr(VI) was 300 min with 59.2 % adsorption and 300 min for Cd(II) with 71.5 % adsorption. Whereas, at 4–6 there is saturation, increasing the solid to liquid ratio for chitosan biopolymers increases the number of active sites available for adsorption. The optimum pH required for maximum adsorption was found to be 5.0 and 5.5 for chromium and cadmium respectively. The experimental equilibrium adsorption data were fitted using Langmuir and Freundlich equations. It was observed that adsorption kinetics of both the metal ions on vermiculite

blended chitosan is well be analyzed with pseudo-second-order model. The negative free energy change of adsorption indicates that the process was spontaneous and vermiculite blended chitosan was a favourable adsorbent for both the metals.

Keywords Chromium(VI) · Cadmium(II) · Chitosan mixed vermiculite · Adsorption isotherms · Kinetics

Introduction

Chromium and cadmium are highly toxic heavy metals and these have to be removed from the water sources. These metals are from various industrial effluents such as tanneries, electroplating and paints. The chromium toxicity is mainly induced from its hexavalent form, Cr(VI) which is readily soluble in water. Its concentration should not exceed 0.05 mg l^{-1} in drinking water and become more toxic with potential carcinogenic effects (Baird and Cann 2005). Cadmium belongs to the hazardous metal group. It is fairly mobile in soil and is primarily present as an organically bound, exchangeable and water soluble species (Holm et al. 1995; Chlopecka 1996). The removal of cadmium from the wastewater by various techniques such as chemical precipitation, electro deposition, electro coagulation process, ion exchange and emulsion liquid membrane (Vasudevan et al. 2011; Elkady et al. 2011; Ahmad et al. 2012). These techniques are expensive and ineffective at low concentration of metal ions. Adsorption method is reported to be a favourable method owing to its low cost and high efficiency for high and low concentration of metal ions (Nghah and Hanafiah 2008).

Novel adsorbents prepared from orange peel and Fe_2O_3 nano particles have been used (Gupta et al. 2012) to

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remove cadmium from aqueous solutions. The removal of cadmium from the electroplating industry effluent is reported and is shown to have desorption and reusability without loss of efficiency. Material from the low cost fertilizer industry viz., carbon slurry, has been chemically treated, activated and used as adsorbent to remove hexavalent chromium from aqueous solutions (Gupta et al. 2010) and the kinetics of adsorption follows pseudo second order rate equation based on batch experiments. The removal of lead and chromium from aqueous solutions, has been reported using inexpensive red mud, an aluminium industry waste and bagasse fly ash. The blast furnace waste generated in steel plants has been used for the removal of lead and chromium (Srivastava et al. 1997) and the authors concluded that the efficiency is higher for lead than that of chromium.

Low cost adsorbents have been investigated from agricultural and fishery wastes such as rice hull and saw dust (Asadi et al. 2008), peanut husk (Li et al. 2007), pumpkin waste (Horsfall et al. 2006), Nipah palm (*Nypa fruticans* Wurmb), shoot biomass (Wankasi et al. 2006), prawn shell (Chu 2002), crab shell (Dahiya et al. 2008), chitin (Jayakumar et al. 2009) and chitosan (Tao et al. 2009) to remove metal ions from wastewater. Chitosan biopolymer (Kumari et al. 2009; ShahinHydari et al. 2012; Prakash et al. 2011) and vermiculite clay (Malandrino et al. 2006; Maria Rosaria Panuccio et al. 2009) are being explored recently for the removal of heavy metals from wastewater.

Chitosan, poly (β (1-4)-2-amino-2-deoxy-D-glucose is obtained from partial *N*-deacetylation of chitin with a strong alkali solution such as sodium hydroxide. It is characterized by a high content of nitrogen, present as amine groups capable of binding the metal ion through several mechanisms, including chemical interactions, such as chelation, electrostatic interactions (or) ion-exchange. The interaction depends (Ng et al. 2003; Dzul Erosa et al. 2001) on the metal ions and initial pH of the medium. The chemical stability of chitosan is enhanced by several techniques such as cross linking (Du et al. 2009) carboxymethylation (Xu et al. 2009) grafting (Morimoto et al. 2002) blending (Wang and Kuo 2008; Ngah et al. 2004) coating (Popuri et al. 2009) and sulphonation (Holme and Perlin 1997). Among all the techniques cross linking is mainly focused because of its simple procedure and there are enormous opportunities to form macromolecular super structures for various specific applications (Crini 2005). Several studies have emphasized that chitosan and its modified form (cross linking coating and blending) is a very efficient adsorbent to remove various toxic and strategic metals (Gerente et al. 2007; Chang et al. 2007).

Vermiculite refers to a class of hydrated ferromagnesium–aluminum silicates that contains various

mineral groups. It looks like mica and has a lattice layer of Mg^{2+} (or) K^+ with water molecules (McBride 1994). Vermiculite can adsorb metals via two mechanisms: (1) cation exchange at the planar sites, resulting from the interaction between metal ions and negative permanent charge (outer-sphere complexes) and (2) formation of inner-sphere complexes through Si–O- and Al–O-groups at the clay particle edges. Removal of toxic metals such as Cd(II), Pb(II) and Cu(II) by vermiculite (Allan et al. 2007; Prakash et al. 2012) has also been reported.

Multiwall carbon nanotubes with the magnetic properties of iron oxide have been used as a composite adsorbent for the adsorption of Cr(III) and it has been shown (Gupta et al. 2011) that the adsorption of Cr(III) is strongly dependent on contact time, agitation speed and pH in the batch mode and on flow rate and the bed thickness in the fixed bed mode. Chemical treatment technologies for wastewater recycling has been reviewed in (Gupta et al. 2012) and a brief guideline for the selection of the appropriate technologies for specific applications has been neatly evaluated. The carbon occurs adsorbent prepared from carbon slurry is reported (Jain et al. 2003) to be efficient and can be used for the removal of dyes from solution.

Bottom ash and despoiled soya have been used as adsorbents for the removal of a hazardous azodye and reported in Mittal et al. (2008). A hazardous textile dye, safranin-T, has been successfully photo degraded using TiO_2 as catalyst and reported in Gupta et al. (2007). The adsorption performance of the materials namely bottom ash, a power plant water and de-oiled soya waste has been appreciable while employing batch and column methods as reported (Mittal et al. 2010). The hexavalent chromium, Cr(VI) has been successfully bioadsorbed on raw and acid treated *Oedogonium hatei* from aqueous solutions (Gupta et al. 2010c).

From the available literature reports, it is observed that the investigations on ternary blends with the presence of cross linking agents likely to enhance the thermal and chemical stability for the removal of heavy metals are scanty and inadequate. Hence, in the present study an attempt has been made to investigate the possibility of the vermiculite blended chitosan in the presence of glutaraldehyde as the cross linking agent for the adsorption of Cr(VI) and Cd(II) ions from the aqueous solution. Vermiculite is mixed with chitosan was prepared in ratios of (1:1), (3:1) in the presence and absence of cross linking agent glutaraldehyde. The blend was characterized by using FT-IR, XRD, TGA and DSC techniques. The kinetic adsorption studies of these blends with chromium and cadmium in aqueous solution were evaluated using different isotherms.

Materials and methods

Instrumentation

FT-IR studies

Fourier Transform Infra Red spectra of all the adsorbents of various combinations were recorded in the frequency range of 400–4000 cm^{-1} using Thermo Nicolet AVATAR 330 spectrophotometer. The samples were pressed into pellets with KBr.

X-ray diffraction studies

X-ray diffractograms of powdered samples were obtained using a X-ray powder diffractometer (XRD-Shimadzu XD-D1) with Ni-filter, Cu K α , radiation source. The relative intensity was recorded in the scattering range 2θ of 10° – 90° .

Thermogravimetric analysis

Thermo gravimetric analysis of all the adsorbents with various combinations was conducted by SOT Q600. V8. This analysis is to find out the thermal stability of the synthesized polymer and the heating range is 20–50 $^\circ\text{C}$ and the heating rate is 20 $^\circ\text{C}$ per min.

Differential scanning calorimetric analysis

The thermal behaviour of the adsorbents was studied using NET 2 SCH DSC thermal analyzer. The sample was inserted into the Al pan and DSC scan was made from 30 to 300 $^\circ\text{C}$ in a nitrogen atmosphere at a heating rate of 20 $^\circ\text{C min}^{-1}$. The results were recorded and analyzed.

Stock solution

Stock solutions of chromium(VI) ions and cadmium ions were prepared (Dean 1995). All other concentration values, varying between 40 and 670 mg l^{-1} of Cd(II) were prepared by dilution from the stock solution. The initial pH of the working solution was obtained by adding small volumes of 0.5 N HNO_3 (for pH 2.0 and 3.0), or acetate buffer ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$), for $3.0 < \text{pH} < 6.0$.

Preparation of adsorbent: chitosan mixed vermiculite

The chitosan polymer solution was prepared by dissolving 1 g 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 (10 ml) as a

cross linking agent at room temperature for 1 h. Then the above prepared mixture were poured into a petri dish and dried in vacuum for 10 h to remove the solvent completely.

Methodology for batch process of adsorption studies

For the study of equilibrium isotherms, the adsorption studies were done at varying concentrations of the metal, i.e., 30, 60, 90, 120, 150, 180, and 210 mg l^{-1} of chromium and cadmium and keeping the amount of chitosan (2.0 g l^{-1}) constant at pH 5.0. Polymer blended solutions (30 ml) were added to the reactor vessel. Solutions were stirred magnetically throughout the experiments. Samples (100 μl) were taken from the feed cell into which metal was adsorbed and the solution is estimated for chromium and cadmium using the usual EDTA method (Prakash et al. 2012). Chromium and cadmium (30 mg l^{-1}) were added to the reactor vessel. The reactor vessel is stirred magnetically throughout the experiments. Following the chromium and cadmium concentrations were estimated, the equilibrium isotherm was prepared by plotting uptake in mg g^{-1} versus the equilibrium concentration of chromium and cadmium in mg l^{-1} .

Removal of chromium and cadmium

Synthetic solutions of Cr(VI) ions and Cd(II) ions were taken in stopper bottles and agitated with the prepared adsorbents separately at 30 $^\circ\text{C}$ in orbit shaker at fixed speed of 160 rpm. The extent of heavy metal removal was investigated separately by changing the amount of adsorbent, contact time and different pH of the solution. After attaining the equilibrium the adsorbent was separated by treating it with suitable reagents after leaching the metals from the adsorbents. Analysis of the concentration of the metals has been done using atomic adsorption spectrophotometer (Varian AAA 220 FS). Chromium has been determined from the analysis by fixing the wave length at 357.9 nm and cadmium has been obtained by fixing the wavelength at 228.8 nm.

Results and discussion

Characterization

Vermiculite blended chitosan were characterized by IR spectroscopy, X-ray diffraction, thermal gravimetric analysis (TGA/DTA), Differential Scanning Calorimetry (DSC). Further, kinetic analysis have also been reported and discussed.

FT-IR spectra analysis

The FT-IR spectrum of chitosan gave a characteristic band at 3450 cm^{-1} which is attributed to $-\text{NH}_2$ and $-\text{OH}$ stretching vibration and the band for amide I at 1652 cm^{-1} is observed in the infrared spectrum of chitosan. The characteristic carbonyl stretching of chitosan observed at 1733 cm^{-1} and the broader peak at 1635 cm^{-1} corresponding to the chitosan NH_2 band. In 3:1 ratio the peaks observed at 3421 cm^{-1} are due to OH stretching, $-\text{NH}$ stretching and intermolecular hydrogen bonding. The peaks at 2935 , 1640 and 1579 cm^{-1} indicate asymmetric C–H stretching, C=O stretching and N–H bending respectively. The peaks at 1386 , 1254 , 1029 and 452 cm^{-1} arises due to C–H bending, O–H bending, Si–O stretching, Al–O stretching vibrations respectively. The IR spectrum of chitosan:vermiculite (1:1) shows the peak at 3430 cm^{-1} corresponding to the $-\text{OH}$ stretching, $-\text{NH}$ stretching, which may be due to intermolecular hydrogen bonding and polymeric association. The peaks at 2927 , 1605 cm^{-1} correspond to the asymmetric C–H stretching and N–H bending. The peaks at 1383 , 1021 and 460 cm^{-1} are due to the C–H bending, C–OH was stretching, Si–O and Al–O stretching vibrations.

The spectrum of chitosan:vermiculite+Glu (1:1), blend has a peak at $3000\text{--}3600\text{ cm}^{-1}$, which is due to OH stretching, NH stretching and intermolecular hydrogen bonding. The peak positions are slightly modified in the presence of cross linker. The peaks at 2938 , 1713 , 1583 and 1381 cm^{-1} correspond to the asymmetric C–H stretching, C=O stretching, N–H bending and C–H bending vibrations. The peak at 1020 , 681 , 499 and 450 cm^{-1} indicate the C–O stretching, N–H deformation and Al–O & Si–O stretching vibration respectively. The IR spectrum for the ratio of chitosan:vermiculite+Glu (3:1) has stretching and due to intermolecular hydrogen bonding. The peaks at 2927 cm^{-1} to aldehydic asymmetric and symmetric CH stretching, the peaks at 1716 , 1383 cm^{-1} the corresponds to C=O stretching, N–H bending and C–H bending vibrations respectively. The peaks at 1022 and 449 cm^{-1} correspond to C–OH stretching and Al–O, Si–O stretching vibrations respectively.

The sharp peak observed at 1610 cm^{-1} may be due to C=N (amide I band) of the Schiff's base formed between the free amino groups from the chitosan and aldehyde groups from glutaraldehyde which acts as a cross linking agent. In addition, the observed decrease in the intensity of the broad peak around may be attributed to the cross linking via acetalization reaction the glucosamine units of chitosan and aldehyde groups of glutaraldehyde. Similar observations were reported by Ruiz et al. (2000). An intensity of the sharp peak was observed at 1624 cm^{-1} which may be due to the N–H bending (amide II band).

The increase in the chitosan composition in blend leads to more number of $-\text{NH}$ functional groups. When chitosan was mixed with vermiculite the absorption peaks were observed at lower frequencies, due to the intermolecular hydrogen bonding of chitosan with vermiculite (Xie and Wang 2009).

When chitosan was blended with vermiculite in the presence of glutaraldehyde as cross linking agent an intensity of the sharp peak was observed at 1610 cm^{-1} which may be due to the C=N (amide I band) of the formed Schiff's base between the free amino groups that are present in the chitosan and aldehyde groups of the cross-linker glutaraldehyde (Ruiz et al. 2000).

X-ray diffraction studies

Figure 1a, b show the XRD spectrum of chitosan:vermiculite (1:1) and (3:1). From the XRD spectrum, the appearance of short sharp peaks at $2\theta = 19^\circ$, 33° and 36° for 1:1 and three sharp peaks at $2\theta = 11^\circ$, 15° and 25° for 3:1 indicates high crystalline nature of blends.

In the presence of glutaraldehyde, the XRD spectrum of chitosan:vermiculite for ratio (1:1) and (3:1) are shown in Fig. 1c, d. The XRD peaks are observed at $2\theta = 19^\circ$, 26° , 34° for 1:1 and at $2\theta = 25^\circ$, 39° for 3:1. From the XRD data it is clear that the nature of the sample is semi crystalline in nature for 1:1 ratio, where as in the case of 3:1, the observation of two long sharp peaks at $2\theta = 25^\circ$ indicate crystalline nature of the blend.

Thermo gravimetric analysis (TGA)

Figure 2a, b represents the thermogram of chitosan:vermiculite mixture for (1:1) and (3:1) ratios. The maximum weight loss takes place at the temperature range from 250 to 500°C . Around 54.57% of the sample had disintegrated at the temperature of approximately 731.25°C . At the end of the experiment, 45.43% of the sample was obtained as a residue. 12% of the sample had disintegrated at the temperature range of $510\text{--}860^\circ\text{C}$. It may be due to loss of water. In the case of 3:1 ratio, the maximum weight loss takes place at the temperature range from 200 to 663°C . Around 63.10% of the sample had disintegrated at the temperature of about 657.12°C . At the end of the experiment 36.90% of the sample remained as a residue. 15% of the sample had disintegrated at a temperature range of $450\text{--}200^\circ\text{C}$.

Figure 2c, d represents the thermogram chitosan:vermiculite (1:1)+Glu (10 ml) ratio. The maximum weight loss takes place at the temperature range from 150 to 375°C . Around 75.311% of the sample had disintegrated at the end of the experiment. 24.68% of the sample remained as a residue. 5% of the sample had disintegrated at the temperature range of $500\text{--}150^\circ\text{C}$. The weight loss

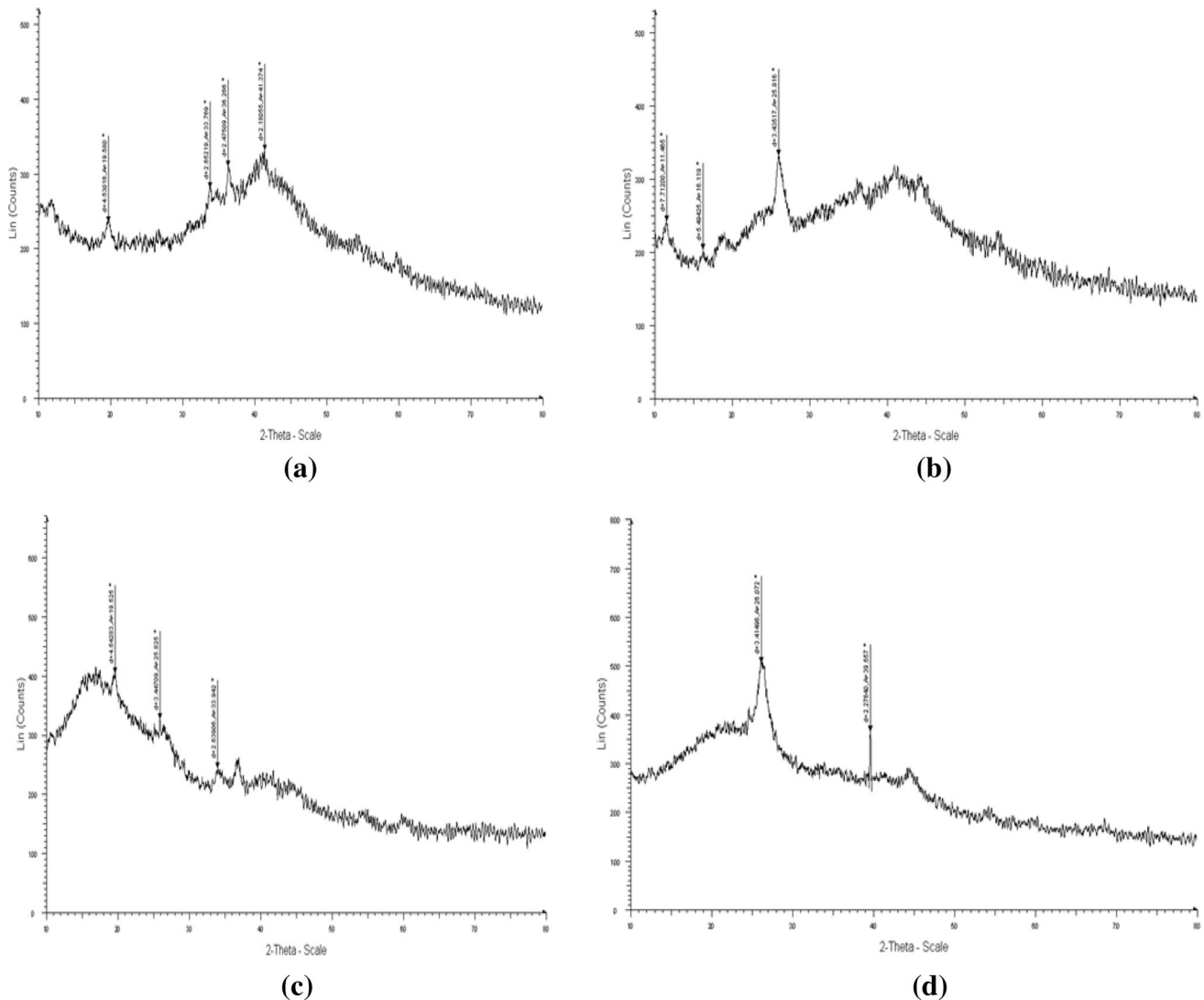


Fig. 1 **a** XRD diffractogram of chitosan mixed vermiculite (1:1), **b** XRD diffractogram of chitosan mixed vermiculite (3:1), **c** XRD diffractogram of chitosan mixed with vermiculite (1:1)+Glu, **d** XRD diffractogram of chitosan mixed with vermiculite (3:1)+Glu

between 50 and 150 °C may be due to water loss. The maximum weight loss occurs at 150 and 375 °C. The weight loss may be due to the decomposition of the $-\text{CH}_2-$ linkages, H-bonding and other interaction between the two polymers. After 400 °C there was a sudden rise in the decomposition of the pyranose ring of the polysaccharides. When we compare the thermal stability with or without cross linking agent, the cross linked chitosan was thermally more stable.

Based on Fig. 2d, the thermogram of chitosan:vermiculite+Glu (3:1), the maximum weight loss takes place at the temperature range from 200 to 400 °C. Around 63.552 % of the sample had disintegrated at the temperature range of 700 °C. At the end of the experiment, 36.448 % of the sample remained as a residue. The

maximum weight loss that occurred at 200–400 °C may be due to the decomposition of the $-\text{CH}_2-$ linkage, H-bonding and other interaction between the polymers.

Adsorption experiments

Experimental procedure

Series of experiments were performed to evaluate the influence of the following variables: initial pH value of the solution, contact time, and adsorbent dosage. The batch experiments were performed by adding chitosan mixed vermiculite to a 25 ml solution containing Cr(VI) ions and Cd(II) ions under intermittent stirring, at room temperature (25 ± 0.5 °C) and, with the exception of only

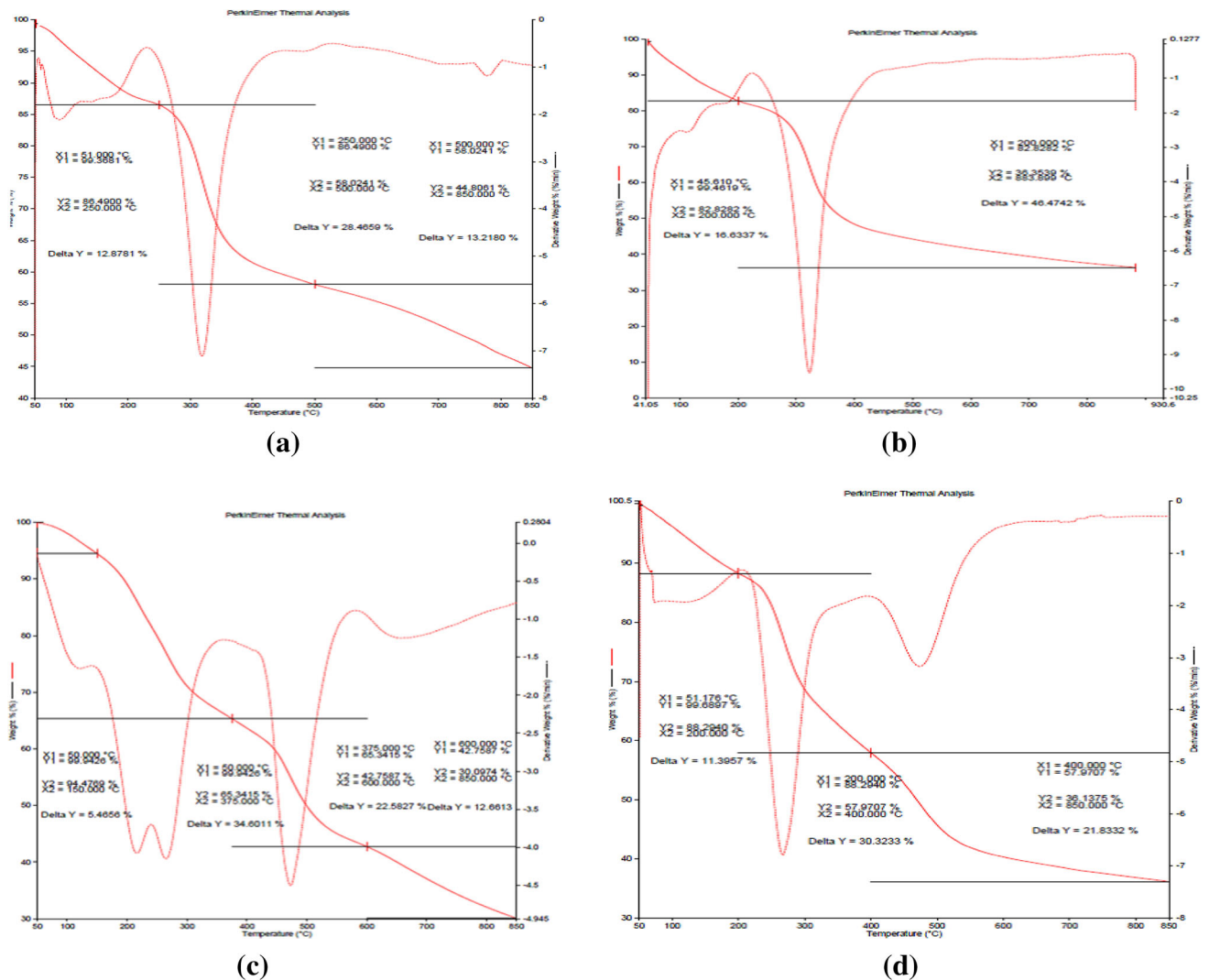


Fig. 2 a TGA of chitosan mixed with vermiculite (1:1), b TGA of chitosan mixed with vermiculite (3:1), c TGA of chitosan mixed with vermiculite (1:1)+Glu, d TGA of chitosan mixed with vermiculite (3:1)+Glu

one series, at a constant contact time of 24 h. The influence of the initial solution pH on Cr(VI) and Cd(II) ions capacity of adsorption onto chitosan mixed vermiculite was investigated over the 4.0–8.0 pH range, at a constant dosage of chitosan mixed vermiculite. To evaluate the effect of adsorbent dosage on Cr(VI) and Cd(II) adsorption, the metal ion solutions of a constant concentration (71.3 and 74.3 mg l^{-1}) was treated with variable dosages of chitosan mixed vermiculite. (Resulting in adsorbent concentrations in the mixture from 5 to 40 g l^{-1} , at pH 5.0 of the initial solution). The influence of contact time of both the metal ions concentration on chitosan mixed vermiculite adsorption capacity was studied over the 30–360 min range, at pH 5.0 of the initial solution and constant dosage of chitosan mixed vermiculite (5 g l^{-1} concentration in the reaction volume). It is seen from

Fig. 3, that cadmium recovery is higher when compared to chromium recovery at all times. It is seen from the graph that the complexes of Cr^{6+} and Cd^{2+} behave in the same manner and cadmium and chromium complexes are stable during the studies. This may also be due to the stability of the complexes, cadmium complex is more stable compared to chromium complex (Prakash et al. 2012). The percentage of removal of cadmium is always higher compared to chromium at all contact time Fig. 3. Since cadmium is easily polarizable and charge to size ratio is less for cadmium compared to chromium the recovery of cadmium is more at all time compared to chromium. ($\text{Cr}^{6+} = 11.6 \times 10^{-24}$ and $\text{Cd}^{2+} = 7.2 \times 10^{-24}$) Fig. 3 also shows the effect of contact time on the removal of chromium and cadmium metals in the artificial wastewater.

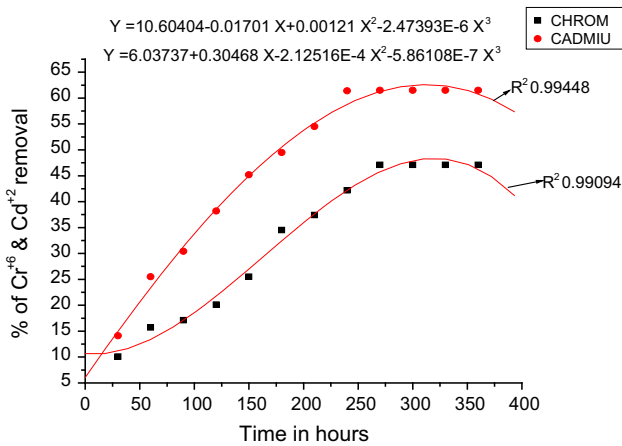


Fig. 3 Percentage of metal removal as a function of time

Percentage of metal removal as a function of pH

The adsorption process is strongly affected by the pH of the solution. The effect of pH change on adsorption was studied for both the metals by changing the pH of the contents from 4 to 8, using dilute solutions of HCl and NaOH. The observation shows that the maximum adsorption of both the metals took place in acidic media and this is evident from Fig. 4. The maximum adsorption for Cr(VI) was observed at pH 5 (72 % removal) and for cadmium at pH 5.5 (71 % removal) (Prakash et al. 2012). In general, at very high and very low pH values, the surface of the adsorption is surrounded mainly by H⁺ and OH⁻ ions respectively. These positively and negatively charged ions may compete with the metal ions and as a result, adsorption decreases. That’s why metal ions show low adsorption at very high and low pH values (Saeed and Iqbal 2003). Influence of pH on adsorption phenomenon is also related with the functional groups present on the bio-adsorbent.

The percentage removal of chromium and cadmium using chitosan mixed with vermiculite at different adsorbent dosage

Various operational parameters like solid/liquid ratio, pH, contact time, metal ion concentration and temperature were employed to determine the adsorption characteristics of chitosan biopolymers for heavy metal ion adsorption from aqueous solutions. The effect of the solid/liquid ratio for chromium adsorption on chitosan biopolymer was examined. In these experiments, operational parameters were kept constant $T = 298\text{ K}$, $C_0 = 200\text{ mg l}^{-1}$ and the pH was varied initially for various time intervals. Figure 5 indicates that the percentage of adsorption of chromium and cadmium increases steadily with, solid to liquid ratio of 1–3 %. Whereas, at 4–6 there is saturation, increasing

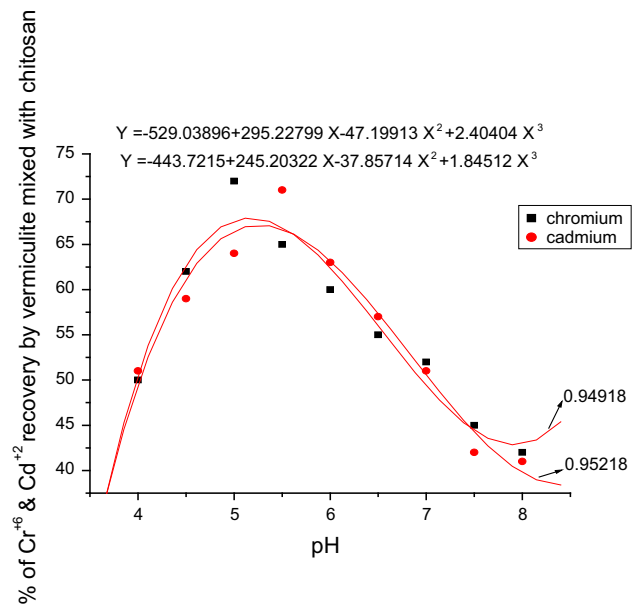


Fig. 4 Percentage of Cr(VI) and Cd(II) recovery by chitosan mixed with vermiculite at different pH

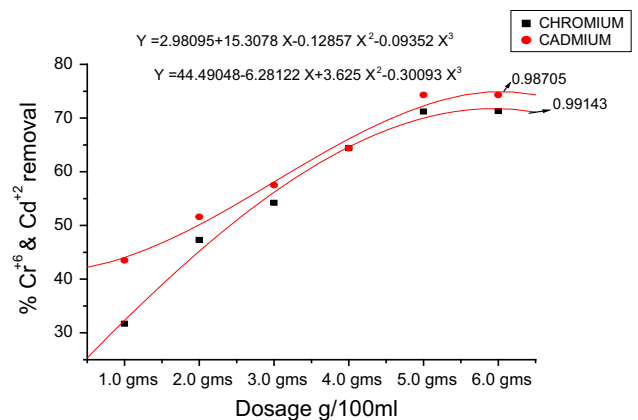


Fig. 5 Percentage removal of chromium and cadmium using chitosan mixed with vermiculite at different adsorbent dosage

the solid to liquid ratio for chitosan biopolymers increases the number of active sites available for adsorption.

Effect of contact time

It has been observed that at a constant concentration of metal ions and fixed amount of adsorbent, the adsorption efficiency increases with increase in the contact time up to a certain level. Figure 5 shows that the adsorption rate first increased rapidly, but after reaching the optimum time value, the removal efficiency slightly decreased with an increase in the contact time. The effect may be due to the saturation of adsorption sites with metal ions on the solid particle. The initial optimum contact time for Cr(VI) was

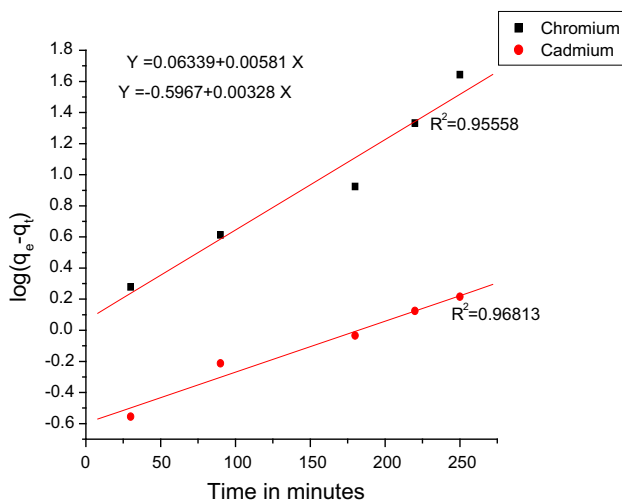


Fig. 6 Plot of $\ln(q_e/q_e - q)$ versus time in chromium and cadmium

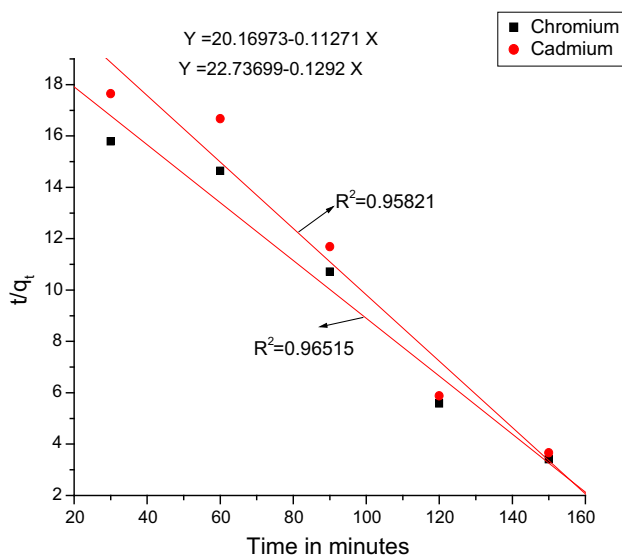


Fig. 7 Plot of t/q versus time in chromium and cadmium

300 min with 59.2 % adsorption and 300 min for Cd(II) with 71.5 % adsorption. The slight decrease in adsorption after the optimum contact time may be due to the breakage of newly formed weak adsorption bonds due to the constant shaking.

Kinetics of adsorption

Pseudo first and second order kinetics of adsorption

The sorption data of Cr(VI) and Cd(II) uptake by chitosan:vermiculite adsorbent was fitted using Lagergren pseudo first and second order model and these are given in

Figs. 6 and 7. The linearized form of the first order Lagergren equation is given as Eq. 1.

$$\log(q_e - q_t) = \log q_e - \frac{K_{1,ads}}{2.303} t \quad (1)$$

The pseudo-second-order Eq. 2

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

where q_e is the mass of metal adsorbed at equilibrium (mg g^{-1}), q_t the mass of metal at time (min), k_1 , ads the pseudo first order reaction rate of adsorption (per min), k_2 , ads the pseudo second order rate constant of adsorption $\text{mg g}^{-1} \text{min}^{-1}$. A comparison between the two kinetic models suggested is presented in Table 1. These facts suggest that the obtained Cr(VI) and Cd(II) adsorption onto chitosan mixed vermiculite kinetic data followed the pseudo second order kinetic model which describes the biosorption as the rate limiting step (Hanif et al. 2007).

Adsorption isotherm models

Effect of adsorbent mass

Adsorption to a maximum of 5 g/100 ml (using 50 ppm metal solution) for Cr(VI) and 5 g/100 ml (10 ppm metal solution) for Cd(II). By increasing the quantity of adsorbent beyond the optimal mass, there is no significant change in the removal efficiency. 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. The optimum adsorbent mass is 5 g/100 ml for both metals with 71.3 % removal of Cr(VI) and 74.3 % removal of Cd(II).

Adsorption isotherms

Langmuir adsorption isotherms The Langmuir is used to describe the experimental adsorption isotherm. The Langmuir isotherm equation may be formulated as

$$\frac{C_{eq}}{C_{ads}} = \left(\frac{1}{Qb} \right) + \left(\frac{C_{eq}}{Q} \right) \quad (3)$$

where non linearity is indicated in Figs. 8 and 9. From this it is not possible to correlate to the isotherm with the experimental data and it is clear that the experimental data is not following Langmuir isotherm. Another essential dimensionless equilibrium constant of Langmuir isotherm is R_L which is applied in many operations and is expressed as:

$$R_L = \frac{1}{1 + bC_i} \quad (4)$$

Table 1 Comparison between Lagergren pseudo first and second order kinetic of adsorption

Metal ion	Pseudo first order kinetic model			Experimental value q_e (mg g ⁻¹)	Pseudo second order kinetic model		
	q_e (mg g ⁻¹)	k_1 (min ⁻¹)	R^2		q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
Cr(VI)	1071.86	0.001962	0.9555	124	360.73	0.005037	0.9582
Cd(II)	563.09	0.003804	0.96813	132	169.72	0.005231	0.9651

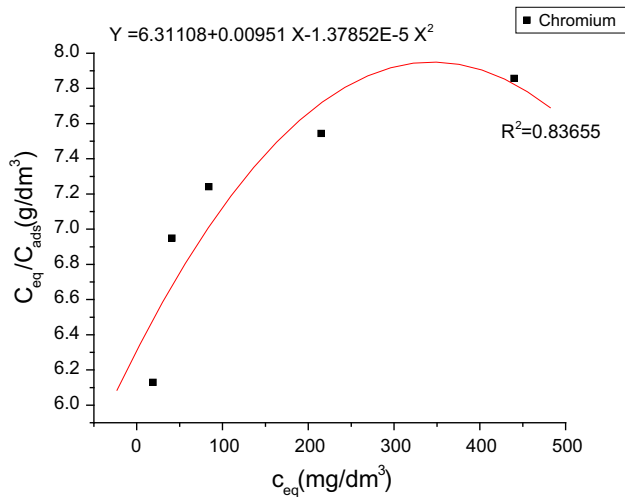


Fig. 8 Langmuir isotherm plot for chromium

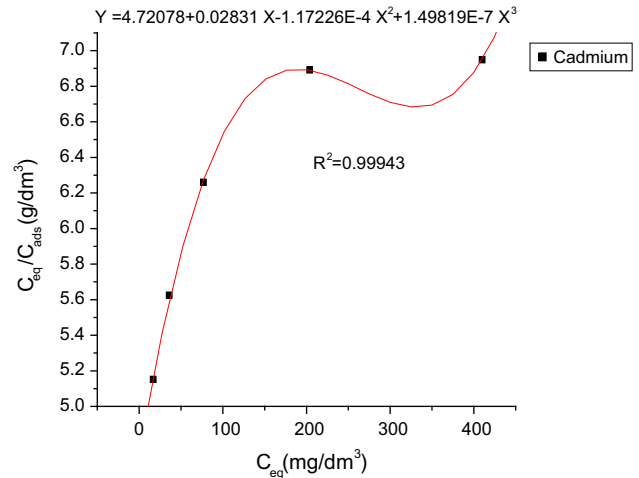


Fig. 9 Langmuir isotherm plot for cadmium

where, C_i the initial concentration is the analyst in the solution. If $R_L > 1$, then it is considered unfavourable. $R = 1$ corresponds to linear and $0 < R < 1$ is favourable (Table 2).

Freundlich adsorption isotherms The Freundlich model is used in essential of adsorption concentration of the adsorbate on the adsorbent surface (Freundlich 1926) and expressed as:

$$C_{ads} = K C_{eq}^{1/n} \tag{5}$$

The linearized (Figs. 10, 11) form of this equation is expressed as

$$\log C_{ads} = \frac{1}{n} \log C_{eq} + \log K \tag{6}$$

whereas, $1/n$ is Freundlich characteristic constant related to energy, and K is the maximum adsorption capacity. Both n and K are temperature dependant. 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 the slope and intercept. At the regions of moderate coverage Freundlich isotherm is similar to the Langmuir isotherm. Values of $1/n$ indicate the steepness or flatness of the slopes. $1/n$ close to 1

Table 2 Adsorption isotherm constant, C_{max} and correlation coefficients

Metal ions	Langmuir constants			
	KL (dm ³ g ⁻¹)	b (dm ³ mg ⁻¹)	C_{max} (mg g ⁻¹)	R^2
Cr(VI)	6.642	0.003139	2115.96	0.8365
Cd(II)	5.571	0.004061	1371.83	0.9994

indicates the steep slope and high adsorption capacity and equilibrium concentrations which diminishes at low equilibrium concentrations. On the other hand $1/n \ll 1$ indicates a flat slope and adsorption capacity is slightly reduced at low equilibrium concentration (Faust and Aly 1987).

Adsorption isotherms results Langmuir and Freundlich The adsorption isotherm is fundamental in describing the interactive behaviour between solutes and adsorbent (Chiou and Li 2003; Ofomoja and Ho 2006). According to Ofomaja and Ho (2006), the isotherm yields certain constant values, which expresses the surface properties and affinity of the adsorbent. It also plays an important role in the design of an adsorption system.

The parameter indicates the effect of separation factor on isotherm shape according to Table 3. The values of R_L

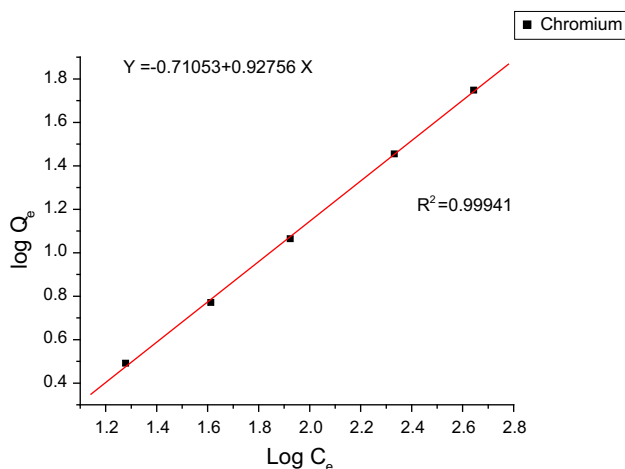


Fig. 10 Freundlich isotherm plot for chromium

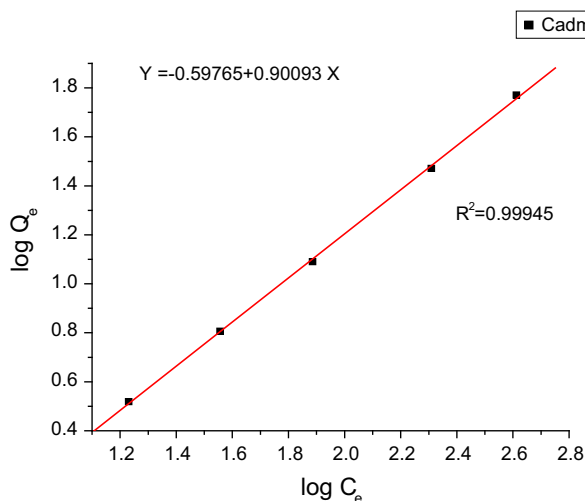


Fig. 11 Freundlich isotherm plot for cadmium

Table 3 Adsorption isotherm constant Freundlich

Metal ions	Freundlich constants		R^2
	K	n	
Cr(VI)	0.1948	1.0780	0.9994
Cd(II)	0.2526	1.1100	0.9994

calculated for different initial metal ion concentration are given in Table 4. If the R_L values are in the range of $0 < R_L < 1$, it indicates that the adsorption of Cr(IV) and Cd(II) onto chitosan beads are favourable. Thus, chitosan beads are favourable adsorbents. The mechanism of ion

Table 4 R_L values based on Langmuir adsorption

Metal ions	Initial concentration C_0 (mg dm^{-3})	Final concentration C_f (mg dm^{-3})	R_L values
Cr(VI) ion	1000	440	0.4200
	500	215	0.5970
	200	84	0.7913
	100	41	0.8860
Cd(II) ion	50	19	0.9437
	1000	410	0.3752
	500	204	0.5469
	200	77	0.7618

adsorption on porous adsorbents may involve three steps: (1) diffusion of the ions to the external surface of adsorbent; (2) diffusion of ions into the pores of adsorbents; (3) adsorption of the ions on the internal surface of adsorbent.

Conclusion

Chitosan mixed with vermiculite has been successfully used as the adsorbent for the removal of Cr(VI) and Cd(II) from wastewater. Cadmium recovery is slightly higher at all times than chromium. The maximum adsorption for Cr(VI) has been obtained at pH 5.0 and for Cd(II) at pH 5.5. The percentage of adsorption of chromium and cadmium increases steadily with solid to liquid ratio of 1–3 % whereas at 4–6 saturation is attained. The adsorption of Cr(VI) and Cd(II) is found to be 59.2 and 71.5 % respectively with the contact time of 300 min. Kinetic data of adsorption studies indicate that adsorption follows pseudo second order model and bio adsorption is found to have rate limiting step. The optimum adsorption mass is 5 g/100 ml for both metals with 71.3 % removal of Cr(VI) and 74.3 % removal of Cd(II). The cross linker being glutaraldehyde enhances the thermal and chemical stability. Further, cross linking increases intra molecular hydrogen bonding enabling greater adsorption. The feasibility of using chitosan with vermiculite added with glutaraldehyde in the ratio 3:1 is established and this composition yields greater capacity for adsorption

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