



Crosslinked chitosan/polyvinyl alcohol blend beads for removal and recovery of Cd(II) from wastewater

Mahendra Kumar, Bijay P. Tripathi, Vinod K. Shahi*

Electro-Membrane Processes Division, Central Salt & Marine Chemicals Research Institute, Council of Scientific & Industrial Research (CSIR), G.B. Marg, Bhavnagar 364002, Gujarat, India

ARTICLE INFO

Article history:

Received 30 January 2009

Received in revised form 12 June 2009

Accepted 23 July 2009

Available online 4 August 2009

Keywords:

Adsorption

Cd(II) ion

Langmuir and Freundlich isotherms

Chitosan/PVA beads

Crosslinking

ABSTRACT

Crosslinked chitosan/poly(vinyl alcohol) (PVA) beads were prepared by suspension of chitosan–PVA aqueous solution in a mixture of toluene and chlorobenzene. Some quantity of the water was distilled out as an azeotrope along with toluene–chlorobenzene and the droplets were chemically crosslinked by adding glutaraldehyde. The prepared crosslinked beads were characterized by FTIR, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The developed beads were used as an adsorbent for the adsorption of Cd(II) from wastewater. Effect of time, temperature, pH, adsorbent dose and adsorbate concentration on the adsorption of Cd(II) were investigated in batch process and pseudo-first and pseudo-second-order kinetic models were also evaluated. The equilibrium adsorption obeyed Langmuir and Freundlich isotherms as well as the thermodynamic parameters such as ΔG° , ΔH° and ΔS° were calculated. From thermodynamic data, it was found that the adsorption process was endothermic and spontaneous. The maximum adsorption of Cd(II) ions was found to be 73.75% at pH 6 and indicated that developed material could be effectively utilized for the removal of Cd(II) ions from wastewater.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Toxicities of water sources due to the discharge of industrial effluents, is a world-wide environmental problem. Industrial wastewater often contains considerable amount of heavy metal ions and organic pollutants, which would endanger to public health and the environment. Heavy metals are generally introduced into the environment through natural phenomena and human activities [1]. The contamination of the existing water resources is increasing day by day with industrialization. The disposal of wastewater containing heavy metal ions is always a challenging task for environmentalists [2]. Effective removal of heavy metal ions from aqueous solution is important for the protection of environment and public health [3,4]. Cadmium (Cd(II)) is a toxic heavy metal, normally found in industrial wastewater, especially from metal plating industries, Cd–Ni batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys. Cd(II) adversely effects human health because of serious damage to kidney, renal disturbances and bones lesions. It also causes high blood pressure, skeletal deformity and muscular cramps [5].

The World Health Organization (WHO) has recommended a maximum permissible limit (0.005 mg l^{-1}) for cadmium in drink-

ing water. Various methods have been used for the removal of heavy metal ions and organic pollutants from industrial wastewater such as precipitation, electrochemical reduction, ion exchange, membrane filtration, and reverse osmosis [6–12]. However, these methods have several disadvantages such as unpredictable metal ion removal, high reagent requirements, generation of toxic sludge, large liquid surface and long desorption time. Furthermore, these processes are economically non-feasible especially in developing countries. The sorption process has been found to be economically appealing for the removal of heavy metal ions from wastewater. The numerous chitosan based beads have already been explored as adsorbent for the removal of cadmium ions from aqueous solutions [13–15]. Thus, to develop natural, renewable, and low-cost adsorbent alternatives to synthetic polymer for the removal of heavy metal ions especially Cd(II) ions from wastewater is highly interested for human life.

Chitosan is derived from N-deacetylation of chitin, the major component of the shells of crustacean organisms and the second most abundant naturally occurring biopolymer next to cellulose. Chitin and chitosan have biological and chemical properties such as non-toxicity, biocompatibility, high chemical reactivity, chirality, chelation and adsorption properties [16–21]. The presence of amine groups makes a chitosan unique among biopolymers, for example, its cationic behavior in acidic solutions and its affinity for heavy metal ions [17–19]. Ion exchangers or adsorbents can be made on a large scale and low cost from chitosan. The

* Corresponding author. Tel.: +91 278 2569445; fax: +91 278 2567562/2566970.
E-mail addresses: vkshahi@csmcrici.org, vinodshahi1@yahoo.com (V.K. Shahi).

chitosan based exchangers or adsorbents have been found potential applications in wastewater treatments to remove heavy metal ions [4,17,22–26] and dye removal [27,28].

Chitosan beads have also been used in sorption columns. The use of chitosan beads as an adsorbent are also provides the potential applications for the regeneration after adsorption and reuse of the beads in subsequent adsorption operations. The production of chitosan hydrogel beads involves the dissolution of chitosan in acetic acid solution followed by a precipitation process for injecting the chitosan solution in droplets form into a dilute sodium hydroxide solution [13]. However, the hydrogel beads have the disadvantage due to the poor chemical resistance and mechanical strength. This disadvantage significantly reduces the recycle life of the chitosan beads. To improve these properties, crosslinking of chitosan beads with glutaraldehyde, epichlorohydrin or ethylene glycol glycidyl ether have been carried out [2,15]. In particular, chitosan/PVA blends beads with good mechanical and chemical properties, were extensively studied due to their biomedical applications [29,30]. In addition, these crosslinking processes have been performed by the reaction of the amino functional groups of chitosan with these crosslinkers. As a consequence, the chemical property of the amino functional groups has changed upon crosslinking.

In the present study, we prepared crosslinked chitosan/PVA beads with low water contents and unchanged amino functional groups, which used as an adsorbent for the removal and recovery of cadmium from wastewater. We have explored the adsorption properties of biodegradable material, which can be utilized for the removal of Cd(II) ions from wastewater.

2. Experimental

2.1. Chemicals and reagents

Chitosan (deacetylation 100%; and MW $2.0 \times 10^5 \text{ g mol}^{-1}$) was obtained from Sigma–Aldrich Chemicals and used as received. Poly(vinyl alcohol) (PVA, MW: 125,000, degree of polymerization: 1700, degree of hydrolysis: 88%), Tween-80, acetone, methanol, $\text{Cd}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, glutaraldehyde solution (30%), toluene, chlorobenzene, acetic acid, etc. of AR grade were procured from S.D. fine Chemicals, Mumbai, India and were used without any further purification.

2.2. Preparation of crosslinked chitosan/PVA beads

Chitosan/PVA beads were prepared in two steps using the beads preparation followed by chemical crosslinking. The beads were prepared by dissolving the known amount of deacetylated chitosan powder into the deionized water containing 2% (w/w) acetic acid. The PVA solution (12.5%, w/w) was prepared by dissolving in distilled water. PVA and chitosan solution were mixed in 2:1 (w/w) ratio by stirring and resulted to a homogeneous solution. The pH of the blend solution was adjusted approximately 2 by adding dilute HCl. The resulting chitosan/PVA solution (100 ml) was suspended in 100 ml of toluene–chlorobenzene (1:3, v/v) containing 1.5 g Tween-80 in a three-neck round-bottom flask and stirred continuously at 150 rpm. Then system temperature was raised gradually up to 90 °C to distil out some part of water as an azeotrope with aromatic hydrocarbons to reduce the water content of the suspension droplets. The resulting mixture was cooled to room temperature (30 °C) and 50% glutaraldehyde solution in water was added to the flask to make a 2% (w/w) of total solution, and stirred continuously for 8 h at room temperature to crosslink the water soluble suspended beads. The resulting beads were filtered off, and washed several times with acetone followed by water. Since the beads were

prepared in acidic condition, it was neutralized by 0.1 M NaOH and further washed with water.

2.3. Adsorbate solution

Stock solution of cadmium (II) of 1000 ppm concentration was prepared by using $\text{Cd}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in double distilled water.

2.4. FTIR, XRD, and SEM studies

The Fourier transform infrared (FTIR) spectra of unloaded and loaded beads were recorded with spectrum GX series 49387 by KBr pellet method. Wide angle X-ray Diffractogram (WXR) of prepared beads was obtained using Philips Xpert X-ray diffractometer with $\text{Cu K}\alpha$ (1.54056) radiation. For scanning electron microscopy (SEM), gold sputter coatings were carried out on the desired bead samples at pressure ranging in between 0.1 and 1 Pa. Images were obtained at 10^{-3} to 10^{-2} Pa with EHT 15.00 kV with 300 V collector bias using Leo microscope SEMs.

2.5. Water content of chitosan/PVA beads

Swelling of chitosan/PVA beads was tested in terms of their water content. A known amount of dried crosslinked beads was suspended in deionized water and kept under agitation for 24 h in ambient conditions. Weight of wet beads was obtained and the percent water content was calculated by using the following equation:

$$\text{water content (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

where W_{wet} and W_{dry} are the weight of the wet and dry beads, respectively. Measuring error for water content value was 0.01%.

2.6. Adsorption studies

Batch process was carried out for adsorption studies. A 0.5 g of dry beads was placed in a conical flask with glass stopper having 50 ml Cd(II) solution of different concentrations and the mixture was shaken in a shaker incubator at 100 rpm for the predetermined time interval. The concentration of remained Cd(II) in filtrate solution was determined by EDTA titration method and thus the adsorbed amount of Cd(II) was calculated [31]. Measuring error for concentration was 0.1 mg/l. The amount of adsorption of Cd(II) by chitosan/PVA beads was determined by using the following equation [32]:

$$q = \frac{C_i - C_f}{1000 \times W} \times V \quad (2)$$

where q is the amount of Cd(II) adsorbed, C_i and C_f are the initial and final concentration (mg/ml) of Cd(II) before and after the adsorption in solution. V is the volume of experimental solution and W is the weight (g) of chitosan/PVA beads.

Adsorption studies were carried out by varying the adsorbate concentration (10–200 mg/l), adsorption time (0.5–12 h), amount of adsorbent (0.1–1.0 g) and temperature (30, 40 and 50 °C). A series of experiments were carried out by taking a fixed amount of adsorbate under varying the pH of initial solution from 2 to 10 at room temperature (30 °C). Adsorption isotherms were also studied by varying the initial Cd(II) concentration from 25 to 100 mg l^{-1} for a fixed amount of adsorbent (0.5 g). Each experiment was repeated three times and average results were reported.

2.7. Desorption studies

Batch process was also used for the desorption studies. Desired amount of adsorbent for adsorption of Cd(II) was taken in a conical

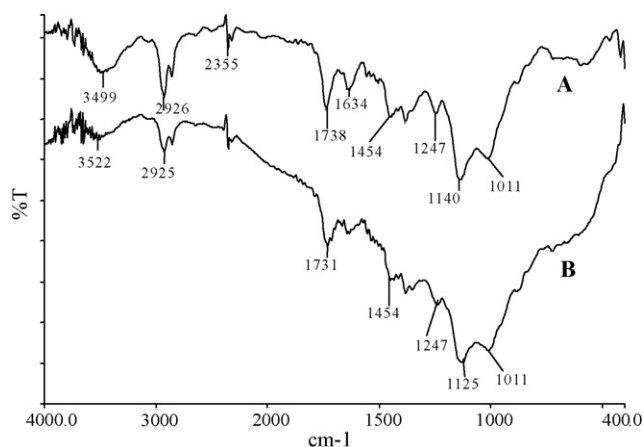


Fig. 1. FTIR spectra of (A) crosslinked chitosan/PVA beads and (B) crosslinked chitosan/PVA beads after adsorption of Cd(II).

flask for a fixed time (8 h), then treated with 50 ml of each 0.1 M HCl, 0.1 M HNO₃, 0.1 M NaCl, and 0.01 M EDTA solution. The amount of Cd(II) desorbed was then determined by back EDTA titration [31].

3. Results and discussion

3.1. Preparation and physical characterization of chitosan/PVA beads

The chitosan/PVA beads were prepared by a solution suspension method. The mixed solution was suspended in chlorobenzene–toluene mixture containing, Tween-80 as surfactant. The water present in solution made an azeotrope with the organic solvents and was removed partially by distillation. Glutaraldehyde was used for crosslinking, while –NH₂ groups of chitosan were converted in to salt during the crosslinking by using HCl, for its protection.

Preparation of chitosan/PVA beads, its crosslinking, and structure were assessed by FTIR spectra, presented in Fig. 1. The spectrum was recorded before and after adsorption of Cd(II) ions for the crosslinked chitosan/PVA beads to study the effect of adsorption. The stretching frequency at 1150–1130 cm⁻¹ indicates the formation of acetal ring by crosslinking. The strong broad band at 3300–3500 cm⁻¹ is the characteristic of the N–H and –OH stretching vibration. The significant decrease in transmittance in this band after adsorption of cadmium indicated that the bonding of metals with NH₂ group was occurred [4]. Thus the nitrogen atom of chitosan moiety acted as main adsorption site for Cd(II) adsorption on the crosslinked chitosan/PVA beads. Also, the FTIR spectra showed that the N–H bending vibrations at 1644 and 1562 cm⁻¹ shifted to 1634 and 1553 cm⁻¹ after the adsorption of Cd(II), which suggested that the interactions between Cd(II) and –NH₂ groups. Since Cd(II) can act as Lewis acid and –NH₂ is a Lewis base, therefore coordination is possible by electron transfer.

WXR D pattern of the crosslinked chitosan/PVA beads is shown in Fig. 2, which showed amorphous nature of crosslinked chitosan/PVA beads [32]. SEM images of the dried crosslinked chitosan/PVA beads before and after Cd(II) adsorption are also shown in Fig. 3. The SEM images indicate that the surface was quite rough and dense in nature, thus provide maximum surface area for the adsorption of Cd(II).

3.2. Swelling study

The water content of the polymeric beads is directly related to its swelling characteristics. Generally, the beads used for adsorption

column, should possess lower swelling. The chitosan/PVA beads are water loving in nature and thus soluble in water without crosslinking. However, after suitable crosslinking they become complete water insoluble material. Water loving nature of beads aroused due to considerable hydrogen bonding with hydrophilic groups. Because of crosslinking, the swelling behavior of chitosan/PVA beads was also reduced to 40.3% (w/w). Thus, the crosslinking is necessary to enhance the chemical stability of beads in acidic medium.

3.3. Effect of pH

Fig. 4 represents the effect of pH (between 2.0 and 10.0), for the adsorption of Cd(II) on chitosan/PVA beads. Adsorption of Cd(II) with 50 mg l⁻¹ initial concentration at pH 2 was observed about 44%, which further increased up to 73.75% at pH 6.0 and attained a maximum value. In acidic medium (pH < 7) due to high H⁺ concentration, active sites of the adsorbent were protonated and leads to the prevention of metal ions adsorption [2]. However, with the increase in pH, deprotonation of chitosan amino groups take place and hence the adsorption of Cd(II) increased. The solubility of metals decreases with the increase in pH, and precipitated as hydroxides on the surface of adsorbent. At a constant concentration, the adsorption capacity increased with pH of the solution and attained limiting value beyond pH 6.0. The precipitation of Cd(II) as hydroxide was found to occur in basic solution, therefore all adsorption studies were carried out in low acidic medium at pH 6.0.

3.4. Effect of concentration of Cd(II)

Crosslinked chitosan/PVA beads were an effective adsorbent over a wide range of adsorbate (Cd(II)) concentration at pH 6.0. At lower Cd(II) concentration, chitosan/PVA beads showed close to 97% adsorption, which reduced slowly with the increase in initial Cd(II) concentration (Fig. 5). At 50 mg l⁻¹ Cd(II) concentration, 75% adsorption was observed, which reduced steeply with further increase in Cd(II) concentration up to 200 mg l⁻¹. These data can be used effectively for the maximum utilization of adsorbent for the removal of Cd(II) concentration from the wastewater. High adsorption (close to 97%) of Cd(II) by chitosan/PVA beads indicates that its potential application for the removal of Cd(II) from wastewater. Furthermore, one has to optimize the dose of adsorbent depending on the concentration of adsorbate for the removal of toxicity up to maximum extent and complete utilization of adsorbent.

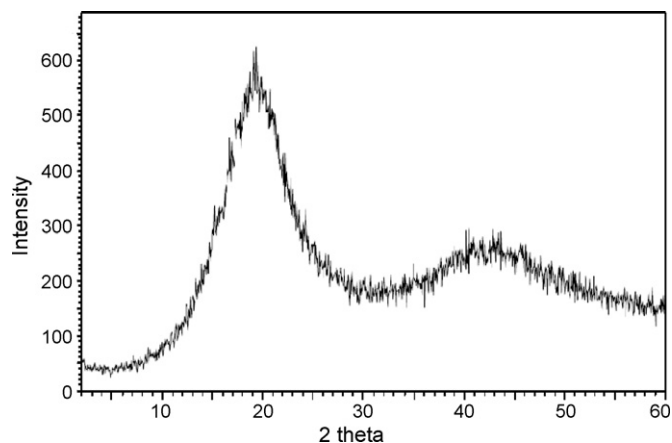


Fig. 2. WXR D pattern of the crosslinked chitosan/PVA beads.

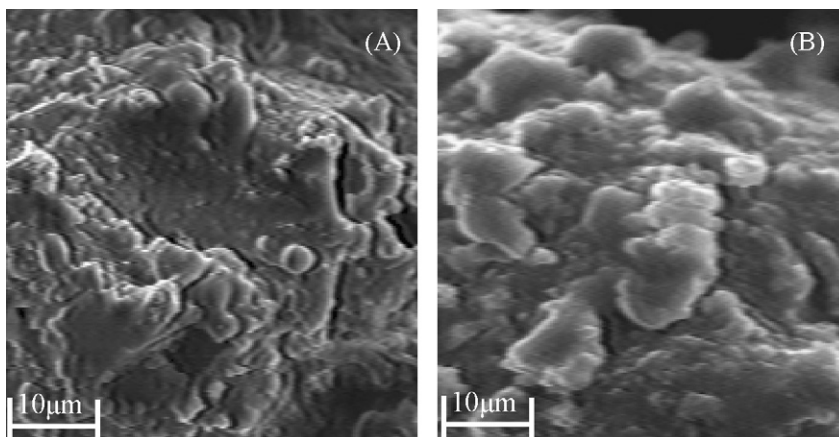


Fig. 3. SEM images of (A) crosslinked chitosan/PVA beads and (B) crosslinked chitosan/PVA beads after Cd(II) adsorption.

3.5. Effect of contact time

The effect of contact time on the adsorption of Cd(II) at 50 mg l^{-1} initial concentration is shown in Fig. 6. Initially, rate of adsorption was faster up to 7 h and maximum removal of Cd(II) occurred. Time

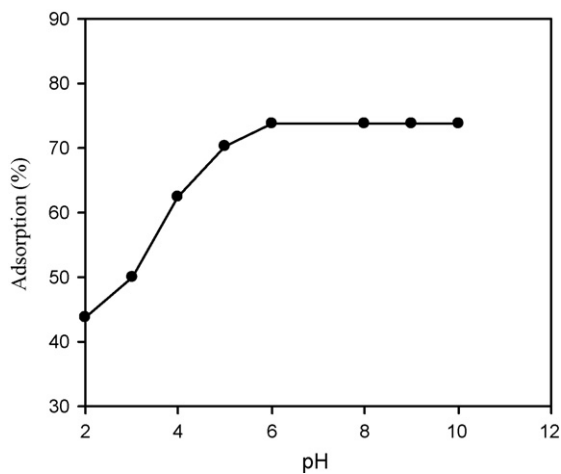


Fig. 4. Effect of pH for Cd(II) (50 mg l^{-1}) adsorption on crosslinked chitosan/PVA beads.

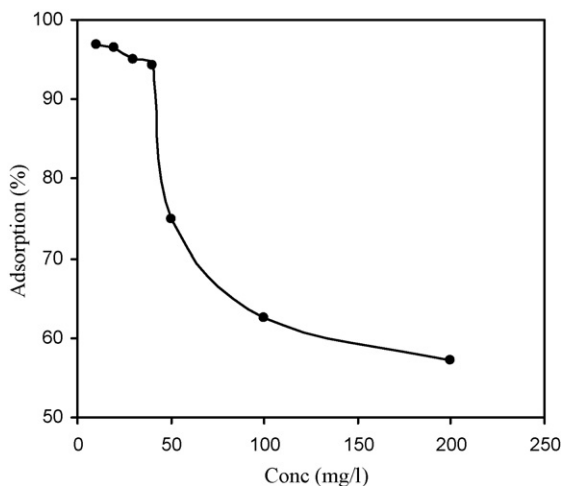


Fig. 5. Effect of initial Cd(II) concentration on its adsorption (%) by crosslinked chitosan/PVA beads at pH 6.

for equilibrium was observed around 8 h, and beyond this time no change in adsorption was occurred. Thus, the equilibrium time was maintained 8 h in subsequent adsorption studies. In the beginning fast adsorption, may be explained due to the availability of more number of adsorption sites [33,34]. After initial adsorption of adsorbate, the available sites in the adsorbent reduced and thus rate of adsorption further decreased [4], which attained a limiting value at equilibrium. Rate of adsorption is of great significance for developing the adsorbent-based water technology [35]. Thus, the ability of developed beads to adsorb maximum amount of Cd(II) within 4 h indicates their suitability as an effective adsorbent.

3.6. Effect of adsorbent dose

The adsorption density (adsorption capacity) and percentage adsorption of Cd(II) on crosslinked chitosan/PVA beads are presented in Fig. 7 as function of amount of adsorbent. Experiments were carried at 50 mg l^{-1} initial Cd(II) concentration, with varied adsorbent dose from 0.1 to 1.0 g at constant temperature (30°C). Adsorption (%) increased from 27.5 to 78.4% while adsorption density decreased from 39.43 to 13.97 mg g^{-1} with the increase in adsorbent dose. The reduction in adsorption density may be due to the fact that some of the adsorption sites remain unsaturated when adsorbent dose is increased. On the other hand large amount of Cd(II) was adsorbed as the number of available adsorption sites are

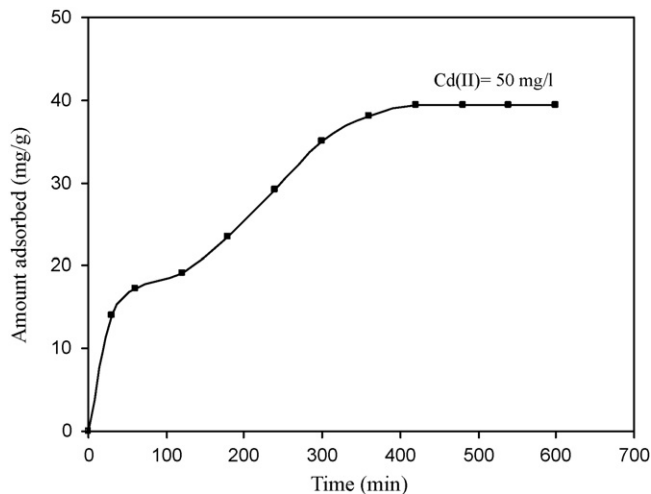


Fig. 6. Effect of time on the adsorption of Cd(II) (50 mg l^{-1}) on crosslinked chitosan/PVA beads at pH 6.

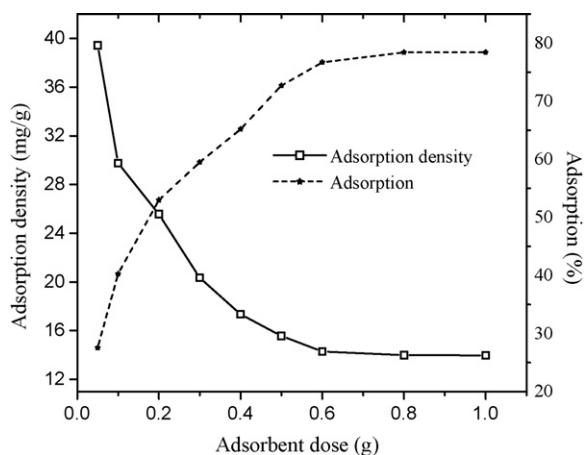


Fig. 7. Effect of adsorbent dose for Cd(II) (50 mg l^{-1}) adsorption on crosslinked chitosan/PVA beads at pH 6.

increased, resulting in the over all increase in the removal efficiency [36].

3.7. Adsorption mechanisms

In the developed crosslinked chitosan/PVA beads, it was expected that nitrogen atom of amino groups in chitosan and the oxygen atom of the hydroxyl groups in both chitosan and PVA acted as adsorption sites for Cd(II). Both nitrogen and oxygen atom possess lone pair of electrons, can bind a positively charged ion through the electron pair sharing. The easy release of lone pair from nitrogen atom makes it the main binding site and forms stable metal complex. With the above consideration, the following chemical reactions are proposed to account the mechanism of Cd(II) adsorption and desorption:

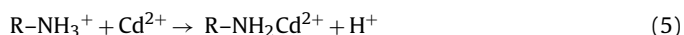


Table 1

Pseudo-first- and second-order kinetics constants, correlation coefficients (R^2) for adsorption of Cd(II) on crosslinked chitosan/PVA beads at pH 6.0.

Concentration (mg l^{-1})	Pseudo-first-order kinetics		Pseudo-second-order kinetics			
	K_1 (min^{-1})	R^2	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg g^{-1})	h (mg g^{-1})	R^2
25	0.00622	0.987	0.000124	27.71	0.0949	0.997
50	0.00576	0.997	0.000116	31.54	0.1157	0.998
100	0.00484	0.994	0.000062	50.51	0.1512	0.995

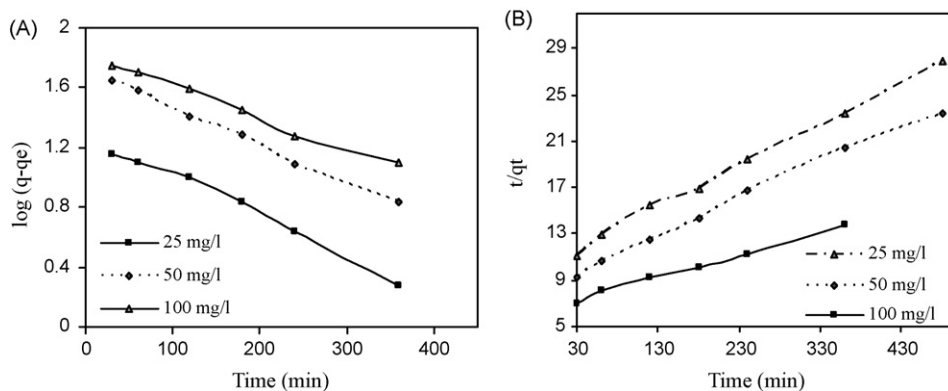


Fig. 8. (A) Pseudo-first-order, and (B) second-order plots for Cd(II) adsorption on crosslinked chitosan/PVA beads at different concentrations: adsorbent dose: (0.5 g) at pH 6.

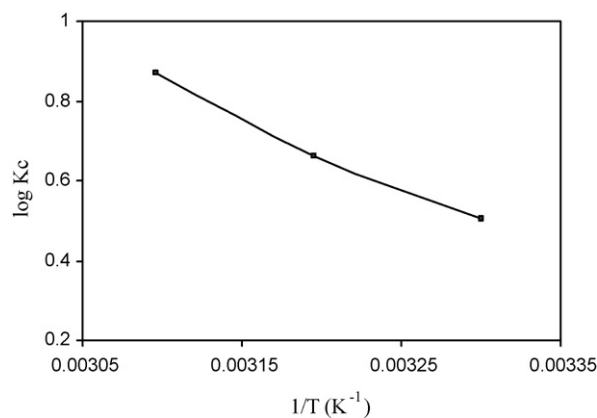
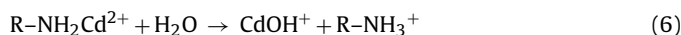


Fig. 9. Plot of $\log K_c$ vs. $1/T$. Adsorbent dose: 0.5 g, pH 6, and initial Cd(II) concentration: 50 mg l^{-1} .



where R represents all other components except $-\text{NH}_2$ in crosslinked chitosan/PVA beads.

The equilibrium of the reaction (Eq. (3)) was established by pH of the initial solution. The adsorption was started according to Eq. (4) with the presence of cadmium ions. However, the binding of Cd^{2+} to a nitrogen atom expected to be stronger in comparison to the binding of H^+ to nitrogen atom (i.e., protonation of the amino group), because of the electrostatic interaction between the lone pair of electrons on nitrogen and the divalent cadmium ion (Cd^{2+}) would be stronger in comparison to the monovalent proton (H^+). This difference in the binding force drives the reaction according to Eq. (5) and a competitive adsorption of Cd^{2+} over H^+ takes place. Such adsorption process can also be termed as an ion exchange mechanism [33]. However, the reaction in Eq. (5) may be slower than the reaction in Eq. (4), because of smaller attraction between N in R-NH_3^+ and Cd^{2+} ion in comparison with attraction between N in R-NH_2 and Cd^{2+} ion. In addition, $\text{R-NH}_2\text{Cd}^{2+}$ complex was subjected to the reaction in Eq. (6), due to the greater binding attraction of Cd^{2+} with $-\text{OH}$ group from water than with the nitrogen of the amino group in chitosan.

3.8. Adsorption kinetics

The rate constants were calculated by using pseudo-first- and second-order kinetic models [2]. The first-order expression is given as:

$$\log(q_e - q) = \log q_e - \frac{K_1}{2.303t} \quad (7)$$

where q_e is the amount of Cd(II) adsorbed per unit weight of adsorbent at equilibrium or adsorption capacity (mg g^{-1}), and q the amount of Cd(II) adsorbed per unit weight of adsorbent at any given time t . K_1 is the first-order rate constant. The values of K_1 were calculated from the slope of the linear plot of $\log(q_e - q)$ versus t at different concentrations (Fig. 8(A)). The values of correlation coefficient (R^2) and rate constants at various concentrations of Cd(II) are given in Table 1.

The kinetic rate equation for pseudo-second-order is given as:

$$\frac{t}{q} = \frac{1}{h} + \frac{1}{q_e} t \quad (8)$$

where $h = K_2 q_e^2$ and K_2 is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). The values of h were calculated from the intercept of the linear plots of t/q versus t at different Cd(II) initial concentrations as presented in Fig. 8(B). The values of K_2 , h and R^2 are also presented in Table 1. These data showed that adsorption process of Cd(II), on chitosan/PVA beads followed second-order kinetics under studied concentration range ($25\text{--}100 \text{ mg l}^{-1}$), rather than pseudo-first-order kinetics [36]. The experimentally calculated values of q_e at various concentration of Cd(II) were in good agreement with theoretical calculated values. Furthermore, the values of correlation coefficients (R^2) for pseudo-first-order kinetic model were slightly lower than the pseudo-second-order kinetic model, indicate that pseudo-second-order kinetic model is better obeyed in compare with the pseudo-first-order kinetic model.

3.9. Effect of temperature

The adsorption process was also assessed at different temperatures between 30 and 50 °C. Thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated by using the following equation [37]:

$$K_c = \frac{C_{Ac}}{C_e} \quad (9)$$

where K_c is the equilibrium constant, C_{Ac} and C_e are equilibrium concentrations (mg l^{-1}) of Cd(II) on the beads and in the solution, respectively.

$$\Delta G^\circ = -2.303 RT \log K_c \quad (10)$$

Table 2

Thermodynamic parameters and correlation coefficients (R^2) at different temperatures for the adsorption of Cd(II) on crosslinked chitosan/PVA beads at pH 6.0.

Temperature (°C)	ΔS° ($\text{kJ K}^{-1} \text{mol}^{-1}$)	ΔH° (kJ mol^{-1})	ΔG° (kJ mol^{-1})	R^2
30	0.105	29.02	-2.81	–
40	0.123	34.41	-4.09	0.992
50	0.142	40.32	-5.38	–

where T is the absolute temperature (K) and R is the universal gas constant.

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (11)$$

The values of ΔH° and ΔS° were calculated from the slope and intercept of Von't Hoff plot of $\log K_c$ versus $1/T$ as presented in Fig. 9 and their values are recorded in Table 2. Values presented in Table 2 revealed that ΔH° and ΔS° were increased with temperature, while ΔG° decreased. Thus the Cd(II) adsorption on crosslinked chitosan/PVA beads is endothermic in nature [38]. It was also found that the adsorption of Cd(II) on crosslinked chitosan/PVA beads is spontaneous and spontaneity increased with the temperature. Positive value of ΔS° suggests randomness at the solid-solution interface during adsorption [39].

3.10. Adsorption isotherms

The adsorption isotherm model describes the interaction of adsorbate with adsorbents and its wide-ranging knowledge is essential for the most effective use of the adsorbent. Thus, it is essential to correlate the equilibrium data by either theoretical or empirical models for designing a perfect operating adsorption system for industrial effluents. In the present study, the equilibrium data were derived from the linear form of Freundlich (Eq. (12)) and Langmuir (Eq. (13)) model of adsorption isotherm [22]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (12)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (13)$$

where C_e is the remaining Cd(II) ion concentration (mg l^{-1}) in solution, q_e the Cd(II) ion concentration (mg g^{-1}) in the adsorbent, K_F the Freundlich constant and $1/n$ is the heterogeneity factor, while a_L and K_L are the Langmuir constants.

Freundlich isotherm describes the heterogeneous system and reversible adsorption and not restricted to the monolayer formation [40,41]. This model predicts that the Cd(II) ion concentration in the adsorbent increased with the increase in its initial concentration in solution. On the other hand in, Langmuir model, it is

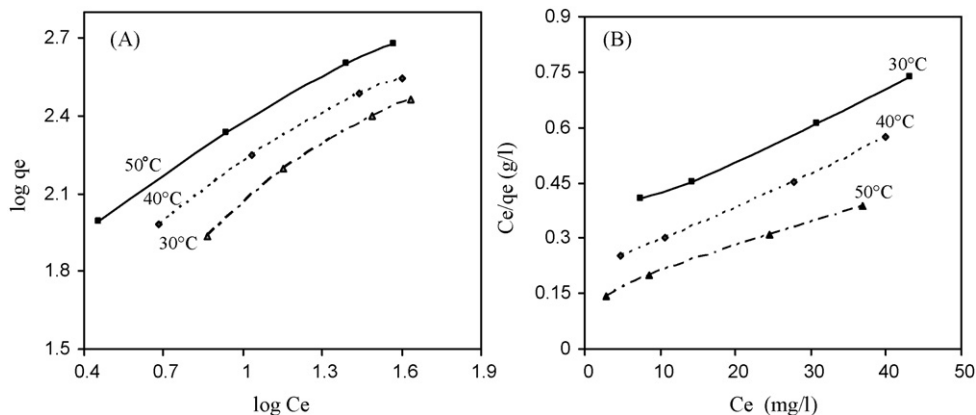


Fig. 10. (A) Freundlich plot and (B) Langmuir plot, for Cd(II) adsorption on crosslinked chitosan/PVA beads at equilibrium under different experimental conditions.

Table 3
Freundlich and Langmuir constants and correlation coefficients (R^2) for the Cd(II) adsorption on crosslinked chitosan/PVA beads at pH 6.0.

Temperature (°C)	Freundlich constants				Langmuir constants			
	K_F	$1/n$	n	R^2	a_L	K_L	Q_0 (mg g ⁻¹)	R^2
30	23.06	0.690	1.45	0.983	0.029	3.10	106.4	0.997
40	38.38	0.615	1.63	0.987	0.044	4.87	109.8	0.999
50	53.60	0.617	1.62	0.995	0.053	7.58	142.9	0.996

assumed that intermolecular forces decrease rapidly with distance and thus lead to the coverage of adsorbent by monolayer of adsorbate [41]. Furthermore, it is assumed that once an adsorbate species occupy the available sites of the adsorbent, no further adsorption takes place at that site [4]. Theoretically, adsorbent has finite number of sites and after occupation of sites by adsorbate, no further adsorption is possible. By plots of experimental data into linearized form of Freundlich isotherm (Fig. 10(A)), obtained various constants and R^2 are presented in Table 3. Data showed the deviation from linearity (under total concentration range is taken into the consideration). This may be due to either: (i) the presence of different groups such as amino, hydroxyl, acetyl in the crosslinked chitosan/PVA beads producing irregular energy distribution in the adsorbent, or (ii) by a purely physical adsorption [2,4,41]. However, Langmuir isotherm model correlated well ($R^2 = 0.999$) as compared to Freundlich isotherm ($R^2 = 0.995$) only, when one line was used to represent the entire range of experimental data as shown in Fig. 10(B). The values of Langmuir constants and (R^2) are derived from the linear curves of Langmuir isotherm and the values are reported in Table 3. It is concluded that the values of a_L increased with temperature, which indicated the strong binding of Cd(II) ion with $-NH_2$ group [4]. It was also found that the monolayer saturation capacity (Q_0) values increased with temperature [41]. Our experimental findings are also well correlated with the saturation capacities, predicted by Langmuir equation at different temperatures.

The essential feature of Langmuir isotherm model can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L) given by relation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (14)$$

where K_L is the Langmuir constant and C_0 is the initial Cd(II) ion concentration (mg l⁻¹). The values of R_L is in between 0.586 and 0.164 (Table 4) for 25–100 mg l⁻¹ the initial Cd(II) concentration, which indicates the favorable adsorption [21].

3.11. Desorption study

Desorption studies helps to reveal the nature of adsorption process and to recover the Cd(II) ions from crosslinked chitosan/PVA beads. Desorption studies were carried out by using HCl, HNO₃, NaCl and EDTA solution. Desorption occurred only with the EDTA solution. About 62.4% desorption of Cd(II) was obtained crosslinked chitosan/PVA beads.

Table 4
 R_L values for the adsorption of Cd(II) onto crosslinked chitosan/PVA beads at various temperatures.

Temperature (°C)	R_L values at different concentration of Cd(II) in solution			
	25 (mg l ⁻¹)	50 (mg l ⁻¹)	75 (mg l ⁻¹)	100 (mg l ⁻¹)
30	0.586	0.417	0.327	0.268
40	0.487	0.321	0.241	0.192
50	0.441	0.282	0.208	0.164

4. Conclusion

Crosslinked chitosan/PVA beads with low water content were prepared by suspension of aqueous solution of chitosan/PVA in toluene–chlorobenzene medium using glutaraldehyde as crosslinking agent in acidic conditions. The developed beads were well characterized by FTIR, SEM and WXRD to assess the structure. Swelling study reveals quite low degree of swelling of prepared beads due to water loving nature of beads and considerable hydrogen bonding with hydrophilic groups. It was also observed that crosslinking of chitosan/PVA beads reduced the swelling behavior by 40.3% (w/w), and enhanced the chemical stability of beads in acidic medium. The kinetic data show that pseudo-second-order kinetic model followed better in compare with pseudo-first-order kinetic model, because of previous one model provides better correlation with the experimental data at different initial concentrations of adsorbate. The Langmuir and Freundlich isotherms, both indicate the favorable adsorption of Cd(II) on the beads. The recovery of Cd(II) ions was achieved by desorption in 0.01 M EDTA solution, and found to be 62.4%. While desorption was not achieved by HCl, HNO₃ and NaCl, which indicate that adsorption occurred mainly via complexation. Above research findings clearly indicate that the developed chitosan/PVA material based beads can be efficiently utilized to recover Cd(II) ions from wastewater and effluents up to high purity. Furthermore, chitosan is a low-cost material and utilization of modified chitosan is novel and challenging, as it is inexpensive, nonhazardous, and environmentally benign.

Acknowledgements

Authors are extremely thankful to the BNRS, DAE, Govt. of India, for providing financial assistance by sanctioning project no. 2007/35/35/BRNS/102. We also acknowledge the services of Analytical Science Division, CSMCRI, Bhavnagar for instrumental support.

References

- [1] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances, *Water Res.* 37 (2003) 1619–1627.
- [2] W.S.W. Ngah, C.S. Endud, R. Mayanar, Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads, *React. Funct. Polym.* 50 (2002) 181–190.
- [3] V.K. Gupta, Equilibrium uptake sorption, dynamics process, development, column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag, a low-cost adsorbent, *Ind. Eng. Chem. Res.* 37 (1998) 192–202.
- [4] L. Jin, R. Bai, Mechanisms of lead adsorption on chitosan/PVA hydrogel beads, *Langmuir* 18 (2002) 9765–9770.
- [5] F. Banat, S.A. Asheh, L. Makhadmeh, Kinetics and equilibrium study of cadmium ion sorption onto date pits—an agricultural waste, *Adsorpt. Sci. Technol.* 21 (2003) 245–260.
- [6] M. Rao, A.V. Parwate, A.G. Bhogle, Removal of Cr⁶⁺ and Ni²⁺ from aqueous solution using bagasse and fly ash, *Waste Manage.* 22 (2002) 821–830.
- [7] N.V. Narayanan, M. Ganesan, Use of adsorption using granular activated carbon (GAC) for the enhancement of removal of chromium from synthetic wastewater by electrocoagulation, *J. Hazard. Mater.* 161 (2009) 575–580.
- [8] R. Kiefer, A.I. Kalinitchev, W.H. Ho, Column performance of ion exchange resins with aminophosphonate functional groups for elimination of heavy metals, *React. Funct. Polym.* 67 (2007) 1421–1432.
- [9] H. Bessbousse, T. Rhlalou, J.-F. Verchere, L. Lebrun, Sorption and filtration of Hg(II) ions from aqueous solutions with a membrane containing

- poly(ethyleneimine) as a complexing polymer, *J. Membr. Sci.* 325 (2008) 997–1006.
- [10] L. Ducoroy, M. Bacquet, B. Martel, M.M.A. Ducoroy, M. Bacquet, B. Martel, M. Morcellet, Removal of heavy metals from aqueous media by cation exchange nonwoven PET coated with β -cyclodextrin-polycarboxylic moieties, *React. Funct. Polym.* 68 (2008) 594–600.
- [11] S. Boussetta, C. Branger, A. Margailan, J.-L. Boudenne, B. Coulomb, Salicylic acid and derivatives anchored on poly(styrene-co-divinylbenzene) resin and membrane via a diazo bridge: synthesis, characterization and application to metal extraction, *React. Funct. Polym.* 68 (2008) 775–786.
- [12] H. Hyung, J.-H. Kim, A mechanistic study on boron rejection by sea water reverse osmosis membranes, *J. Membr. Sci.* 286 (2006) 269–278.
- [13] G.L. Rorrer, T.-Y. Hsien, J.D. Way, Synthesis of porous-magnetic chitosan beads for removal of cadmium ions from waste water, *Ind. Eng. Chem. Res.* 32 (1993) 2170–2178.
- [14] J.R. Evans, W.G. Davids, J.D. MacRae, A. Amirbahman, Kinetics of cadmium uptake by chitosan-based crab shells, *Water Res.* 36 (2002) 3219–3226.
- [15] T.-Y. Hsien, G.L. Rorrer, Heterogeneous cross-linking of chitosan gel beads: kinetics, modeling, and Influence on cadmium ion adsorption capacity, *Ind. Eng. Chem. Res.* 36 (1997) 3631–3638.
- [16] K. Kurita, Controlled functionalization of the polysaccharide chitin, *Prog. Polym. Sci.* 26 (2001) 1921–1971.
- [17] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, *Prog. Polym. Sci.* 30 (2005) 38–70.
- [18] E. Guibal, Heterogeneous catalysis on chitosan-based materials: a review, *Prog. Polym. Sci.* 30 (2005) 71–109.
- [19] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, *Bioresour. Technol.* 97 (2006) 1061–1085.
- [20] E.B. Denkbasi, M. Odabasi, Chitosan microspheres and sponges: preparation and characterization, *J. Appl. Polym. Sci.* 76 (2000) 1637–1643.
- [21] P.A. Felse, T. Panda, Studies on applications of chitin and its derivatives, *Bio-process Eng.* 20 (1999) 505–512.
- [22] T.N.C. Dantas, A.A.D. Neto, M.C.P.A. Moura, E.L.B. Neto, E.P. Telemaco, Chromium adsorption by chitosan impregnated with microemulsion, *Langmuir* 17 (2001) 4256–4260.
- [23] V.M. Boddu, K. Abburi, J.L. Talbott, E.D. Smith, Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent, *Environ. Sci. Technol.* 37 (2003) 4449–4456.
- [24] N. Li, R. Bai, A novel amine-shielded surface cross-linking of chitosan hydrogel beads for enhanced metal adsorption performance, *Ind. Eng. Chem. Res.* 44 (2005) 6692–6700.
- [25] N. Li, R. Bai, C. Liu, Enhanced and selective adsorption of mercury ions on chitosan beads grafted with polyacrylamide via surface-initiated atom transfer radical polymerization, *Langmuir* 21 (2005) 11780–11787.
- [26] C. Gavilan, A.V. Pestov, H.M. Garcia, Y. Yatluk, J. Roussy, E. Guibal, Mercury sorption on a thiocarbamoyl derivative of chitosan, *J. Hazard. Mater.* 165 (2009) 415–426.
- [27] M.S. Chiou, G.S. Chuang, Competitive adsorption of dye metanil yellow and RB15 in acid solutions on chemically cross-linked chitosan beads, *Chemosphere* 62 (2006) 731–740.
- [28] L. Wang, A. Wang, Adsorption properties of congo red from aqueous solution onto N,O-carboxymethyl-chitosan, *Bioresour. Technol.* 99 (2008) 1403–1408.
- [29] M. Miya, R. Iwamoto, S. Mima, FT-IR study of intermolecular interactions in polymer blends, *J. Polym. Sci.* 22 (1984) 1149–1151.
- [30] S. Nakatsuka, A.L. Andrad, Permeability of vitamin B-12 in chitosan membranes. Effect of crosslinking and blending with poly(vinyl alcohol) on permeability, *J. Appl. Polym. Sci.* 44 (1992) 17–22.
- [31] A.I. Vogel, *Quantitative Inorganic Analysis*, 3rd ed., Longmans, London, 1961, p. 324.
- [32] B. Benguella, H. Benaissa, Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies, *Water Res.* 36 (2002) 2463–2474.
- [33] E. Onsoyev, O. Skaugrud, Metal recovery using chitosan, *J. Chem. Technol. Biotechnol.* 49 (1990) 395–404.
- [34] D.N. Bajpai, *Advanced Physical Chemistry*, S. Chand and Company, New Delhi, India, 1998.
- [35] A. Saeed, M. Iqbal, M.W. Waheed, Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk), *J. Hazard. Mater. B* 117 (2005) 65–73.
- [36] N. Sankararamkrishnan, A. Dixit, L. Iyengar, R. Sanghi, Removal of hexavalent chromium using a novel cross linked xanthated chitosan, *Bioresour. Technol.* 97 (2006) 2377–2382.
- [37] N. Sankararamkrishnan, A.K. Sharma, R. Sanghi, Novel chitosan derivative for the removal of cadmium in the presence of cyanide from electroplating wastewater, *J. Hazard. Mater.* 148 (2007) 353–359.
- [38] C. Namasivayam, K. Ranganathan, Removal of Cd(II) from wastewater by adsorption on “waste” Fe(III)/Cr(III) hydroxide, *Water Res.* 29 (1995) 1737–1744.
- [39] W.S.W. Ngah, S.A. Ghani, A. Kamari, Adsorption behaviour of Fe(II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads, *Bioresour. Technol.* 96 (2005) 443–450.
- [40] S. Chatterjee, S. Chatterjee, B.P. Chatterjee, A.K. Guha, Adsorptive removal of Congo red, a carcinogenic textile dye by chitosan hydrobeads: binding mechanism, equilibrium and kinetics, *Colloids Surf. A: Physicochem. Eng. Aspects* 299 (2007) 146–152.
- [41] J.C.Y. Ng, W.H.G. Cheung, Equilibrium studies for the sorption of lead from effluents using chitosan, *Chemosphere* 52 (2003) 1021–1030.