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Removal of chromium from aqueous solution using chitosan: An experimental study

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In this work, the effectiveness of using chitosan for the treatment of chromium from aqueous solution was studied. Parameters that influence the adsorption process such as adsorbent dose, contact time and pH are studied in batch experiments. It was found that 40 mg dose, contact time of 180 min and pH of 3 are the optimum conditions for the removal of chromium from aqueous solution. The experimental equilibrium adsorption data fitted well to the Langmuir isotherm model, which indicates that adsorption of chromium on the surface of chitosan is monolayer coverage of the adsorbate on the outer surface of the adsorbent under these experimental conditions. The adsorption kinetics followed the pseudo-second-order kinetic model which suggests that the adsorption process is chemisorption and the rate-determining step is probably surface adsorption. This adsorbent was successfully used for the treatment of different operational sectional tannery effluents and it was found that about 83.58 and 90.27% of chromium were removed from chrome tanning and re-tanning, respectively. At the same time other physicochemical properties such as turbidity, conductivity, BOD, COD and TDS were significantly reduced.

Keywords: Chitosan, isotherm, kinetics, adsorption.

INTRODUCTION

Tannery industry represents one of the most important economic sectors in many countries and according to 2003 data leather industry produces 18 billion square feet of leather per year whose estimated value is about $40 billion [1]. During the conversion of rawhide to leather several mechanical and chemical operations are required involving many chemicals like acid, alkali, oil grease, chloride, metalorganic dyes, natural and synthetic tanning agents, salts and many toxic metals [2]. In Bangladesh there are more than 220 tannery industries, about 90% of them are engaged in chrome tanning operation [3]. In chrome tanning operation excess amount of chromium is used, 60-70% of chromium is bonded to rawhide and skin, the remaining chromium salts are directly disposed into the environment without any treatment [4]. The toxicity, mobility, and bioavailability of Cr depend fundamentally on its chemical forms, e.g., hexavalent chromium is highly mobile in soil and water systems and toxic on biological systems whereas trace amounts of trivalent chromium is essential for living organisms and less mobile in water and soil systems [5]. However, in aqueous phase trivalent chromium is considered as a serious threat for the environment because it could be oxidized to Cr(VI) in the presence of oxidizers like manganese dioxide [2]. Several experiments suggest that Cr (III) can be accumulated into wheat, rice grains, soybean, sunflower [5, 6]. So if these tannery effluents are directly disposed into a river or a domestic sewage system, they will contaminate surrounding channels, agricultural fields, irrigation fields, surface water and finally will be introduced into the food chain [7, 8].

Over the past few decades, several physical, chemical, and biological methods have been applied for the removal of toxic metals from wastewater. Several methodologies have been used in removing chromium from wastewater. Chemical coagulation can be used to remove substances producing turbidity in water, consisting of clay minerals and proteinous matter but cannot effectively reduce toxic metals [9, 10]. On the other side, membrane methods such as reverse osmosis, nanofiltration, ultrafiltration, and microfiltration can be used to treat wastewater but these methods possess several disadvantages, e.g., incomplete metal removal, expensive equipment setup and monitoring systems required [11-13]. Natural adsorbents have been highly recommended by the researchers to remove heavy metals as these adsorbents can effectively and economically remove toxic metals from wastewater without or with very little modification of the adsorbent. Moreover, natural adsorbents are biodegradable so that after treatment they have no adverse effect on the environment. Several adsorbents have been used in the past like maple sawdust [14], pine species [15], soya coke [16], green algae [17], tea waste [18], plum tree bark [19]. All of these materials show excellent sorbent properties and this

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is the main reason to carry out the present study. In this experiment, chitosan (adsorbent) from prawn shells was used in a batch study to find out the optimum conditions for the removal of chromium. Equilibrium adsorption data (dose effect) were modeled using Langmuir and Freundlich isotherm models while pseudo-first-order and pseudo-second-order models (time effect) were used to study the adsorption kinetics. The adsorbent (chitosan) was successfully used under the optimum conditions for the treatment of different operational sections of a tannery effluent.

MATERIALS AND METHODS

Materials

Prawn shells and raw clay for modification were collected from local prawn hatcheries in Satkhira, Bangladesh and Bijoypur, Netrokona, Bangladesh. Sodium hydroxide and potassium dichromate were obtained from LOBA Chemie (India). Hydrochloric acid, acetic acid, sulphuric acid were obtained from Merck, Darmstadt, Germany. All materials were of analytical grade or higher. Chemicals were used as obtained without further purification.

Preparation of chitosan from waste prawn shells

Chitosan was extracted from waste prawn shells according to Taslim *et al.* [20]. First, prawn shells were thoroughly washed with tap water and then boiled in water for 2 h at 60°C temperature. After washing the shells were dried and crushed in a milling machine. Crushed shells were then de-proteinized with 4% (w/w) NaOH in 1:16 ratio (w/w) at 70-90°C for 3 h. Water-insoluble proteins were removed in this stage after neutralization. Dried samples of de-proteinized shells were demineralized with 3N HCl at a ratio of 1:16 (w/w) on stirring for 3 h at 70°C. This demineralization yields chitin. The dried chitin was de-acetylated by heating at 80-100°C with 50% NaOH (w/w) solution at a ratio of 1:20 (w/w) for 4 h. After washing and neutralization chitosan was obtained.

Characterization of chitosan

Fourier transform infrared (FTIR) spectrometry (FT-IR 8400S spectrophotometer Shimadzu Corporation, Japan) was used to analyze the functional groups of chitosan in the diffuse reflectance mode at a resolution of 4 cm^{-1} in KBr pellets. To determine thermal properties of chitosan TGA and DSC analysis were performed [21]. TGA was conducted in a TGA-50H SHIMADZU thermogravimetric analyzer, Japan from room temperature (30°C) to 600°C at a heating rate of 10°C /min in nitrogen atmosphere with a flow rate of 10 ml/min on alumina cells. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC7. DSC curves of each film were obtained from the second heating run at a rate of 10°C/min, after the first run of heating up to 190°C and cooling to 25°C at the same rate of 10°C/min, in nitrogen atmosphere, in order to estimate the glass transition temperature [22].

Batch adsorption study

Batch experiments were carried out to evaluate the influence of pH, contact time and adsorbent dose on the removal of chromium from solution. For pH optimization experiments were carried out by adding 40 mg of adsorbents in 100 ml of chromium solution (40 ppm) at a temperature of 30°C on a rotary shaker at 120 rpm for 120 min. The initial pH of the Cr(IV) solution was adjusted to different pH values (2.50, 3.50, 4.00, 4.50, 5.00 and 5.50) by dilute hydrochloric acid and sodium hydroxide using a pH meter (DELTA-320). For determination of the effect of contact time on adsorption, assessments were done with 40 mg of adsorbents in 100 ml of chromium solution (40 ppm) at a temperature of 30°C on a rotary shaker at 120 rpm. The samples were withdrawn from the shaker at predetermined time intervals (30, 60, 90, 120, 150, 180, 210 and 240 min). For dose optimization, 100 ml of 40 ppm stock solution of Cr was taken in a 250 mL conical flask at the optimum pH. Different doses (20, 40, 60, 80, 100, 120, 140, 160 and 180 mg of adsorbent) were added in each of the solutions and agitated at 30°C in a reciprocating shaker at a fixed speed of 120 rpm for 12 min. After adsorption, adsorbents were separated from the solution by centrifugation at 5000 rpm for 10 min. All experiments were replicated and the average results were used in data analysis. The amount of chromium adsorbed per unit adsorbent powder was calculated according to the following equations:

$$\%\mathrm{Removal} = \frac{C_o - C_c}{C_o} \times 100 \qquad (1)$$

$$Q_{max} = \frac{C_o - C_e}{M} \times V \qquad (2)$$

Here, Q_{max} is the adsorption capacity of metal ion adsorbed per gram of adsorbent, C_o and C_e are the initial and final concentration, respectively, M is the mass of the adsorbent (g) and v is the volume of chromium solution taken for the adsorption study (L).

Isothermal studies

The equilibrium isotherms were experimented in order to get a better insight into the adsorption mechanism. There are many theories relating to adsorption equilibrium. Three isotherm equations were tested in the present research, namely Langmuir and Freundlich.

Langmuir isotherm model is commonly used to describe the relationship between the equilibrium concentration of the adsorbate and the amount adsorbed on the surface of the adsorbent. The surface interaction of chromium with the composite adsorbent can be represented as

$$C + S \rightleftharpoons CS$$

where, C and S represent the chromium and the composite surface, respectively, and CS refers to the chromium adsorbed on the adsorbent. This isotherm model was utilized to calculate the maximum adsorption capacity which was obtained by fitting the experimental data to Langmuir isotherm model by assuming that a monolayer is formed at maximum adsorption [23, 24]. The linearized form of Langmuir equation can be expressed as:

$$\frac{1}{q_e} = \frac{1}{K_L q_o} . \frac{1}{C_e} + \frac{1}{q_o} \qquad (3)$$

where, C_e is the equilibrium concentration of the metal ion in mg L^{-1}, q_e is the amount of Cr(VI) adsorbed at equilibrium in mg g^{-1}, q_o is the maximum adsorption capacity in mg g^{-1}, and K_L is a constant (L mg^{-1}) related to the energy of adsorption. The maximum adsorption capacity, q_o and the constant K_L are obtained from the slope and intercept of the plot of $1/q_e$ against $1/C_e$.

The Freundlich isotherm [25] is a useful model to study the adsorption for dilute solutions. The adsorption on inequivalent adsorption sites is well described by this empirical isotherm. The Freundlich equation takes into account the logarithmic decrease in the energy of adsorption with increasing surface coverage and this is attributed to the surface heterogeneity [25, 26]. The linearized form of this isotherm can be expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

where, C_e is the equilibrium concentration of the Cr(VI) ion in mg L^{-1}, q_e is the amount of Cr(VI) adsorbed at equilibrium in mg g^{-1}, and K_F and n are the Freundlich constants which indicate the adsorption capacity and the adsorption intensity, respectively. The values of K_F and n were obtained from the slope and intercept of the logarithmic plot of q_e *vs* C_e.

Kinetics of adsorption

The kinetic parameters were evaluated using the well-known first-order and pseudo-second-order models [27]. Equations for these models can be described as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

where, q_e and q_t refer to the amount of Cr adsorbed at equilibrium and time t with the first- and second-order rate constants k_1 and k_2, respectively. The slope and intercept obtained from the plots of log (q_e- q_t) and t/q_t against t give the respective kinetic parameters. a is the initial adsorption rate (mg (g min) $^{-1}$), and the parameter 1/b (mg g^{-1}) is related to the number of sites available for adsorption.

RESULTS AND DISCUSSION

Characteristics of composites

FTIR spectroscopic analysis. FTIR spectra of chitosan showed several bands in the region 4000-500 cm^{-1}, as seen in Fig. 1. The peak at 3450 cm^{-1} is due to –OH stretching. The C–H stretching (symmetric and asymmetric) vibrations of the polymer backbone are demonstrated through strong peaks at 2900 cm^{-1} and 2850 cm^{-1}. A sharp peak at 1600 cm^{-1} corresponds to aromatic carbon (C=C stretching). Peaks at 1375 cm^{-1}, 1130 cm^{-1} and 1080 cm^{-1} are observed due to asymmetrical C-H bonding of the CH_2 group; C_3-O stretching and C_6-O stretching overlapped with C=O stretch vibration, respectively. The transmittance bands at 1580 cm^{-1} are due to N–H bonding vibration of chitosan, the peak at 1430 cm^{-1} is due to -C-O stretching of the primary alcoholic group in chitosan. Similar FTIR peaks were also observed in previous studies for chitosan [28, 29].

Thermogravimetric analysis. The thermal stability of chitosan was checked by thermogravimetric analysis (TGA) and results are shown in Figure 2. Thermal decomposition of chitosan exhibits three different stages, within the ranges of 50-200°C, 200-350°C and 350-650°C. In the first stage, 16% mass loss was associated with the evaporation of water from the surface of the chitosan film. In the second stage, a sudden drop of the weight loss with temperature was observed, due to decomposition of organic and other volatile matters present in the samples [22]. After 350°C only 34% of the mass remained. Further, in the third stage from 350-650°C, a significant mass loss of chitosan was observed. After 650°C only 1% residue was found which was attributed to the presence of minerals.

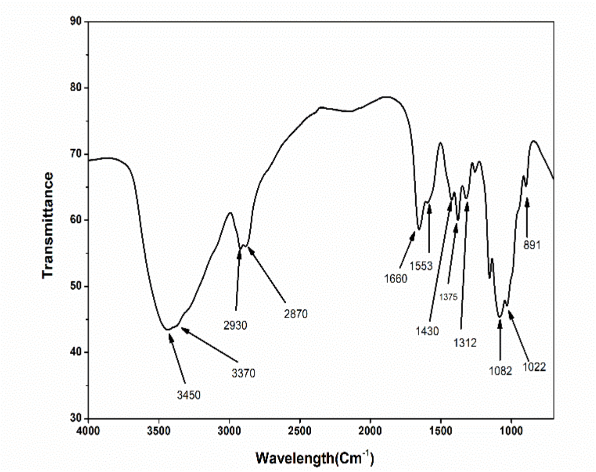

Figure 1. FTIR spectrum of the chitosan film

Differential scanning calorimetry. The DSC thermogram of chitosan within the temperature range of 50 to 400°C at a heating rate of 10°C/min is shown in Figure 3. One endothermic and one exothermic peak were observed. The endothermic peak at 81°C was due to a loss of moisture content in the sample. A sharp exothermic peak at 278°C was observed which is due to the decomposition of the higher content of amine groups.

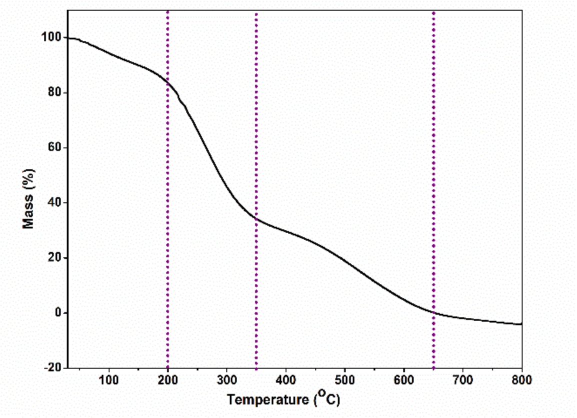

Figure 2. TGA curve of chitosan.

Batch studies

Effect of pH on Cr (VI) adsorption. The optimization of pH is an important factor in the adsorption study. Hexavalent chromium can exist in various forms such as $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$ depending on pH and concentration of the aqueous phase. In the pH range 2.5-4.5, Cr(VI) exists in solution primarily as bichromate ($HCrO_4^-$) anion, whereas the dichromate ($Cr_2O_7^{2-}$) anion predominates at lower pH values and higher concentrations [30]. The favorable pH for the adsorption of Cr(VI) was observed in weakly acidic medium (2.5-4.5).

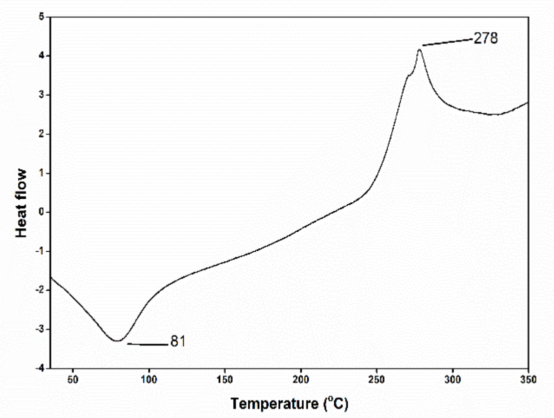

Figure 3. DSC curve of chitosan.

According to Pearson’s classification [31], chromium is categorized as a hard acid and chitosan is classified as a hard base. This can be used to explain the variety of complexation reactions. As they are both strong, good interaction between the positively charged protonated amine group of chitosan and the negatively charged bichromate anion can be expected. In acidic medium surface hydroxyl groups of clay can also be protonated and this could serve as electrostatic interaction with bichromate anion either. With the increase in pH, adsorption decreased which could be attributed to the deprotonation of the surface hydroxyl groups [32]. From Figure 5 it can be seen that the optimum pH for chitosan is 3.0 (85.45 mg/g); below and above this pH, adsorption capacity was significantly reduced.

Effect of dose on Cr (VI) adsorption. The adsorption of chromium by chitosan was studied at various adsorbent quantities (20, 40, 60, 80, 100, 120, 140, 160 and 180 mg/100 ml solution) in the test solution keeping chromium concentration 40 ppm at a temperature of 30°C and pH 3 for optimum contact time of 180 min. After 180 min the percentage of adsorbed chromium was calculated. It was found that increasing the dose of adsorbent increased the percentage of chromium removed from the solution which can be attributed to increased adsorbent surface area and availability of a larger number of adsorption sites (Figure 4). However, after 140 mg adsorbent dose chromium removal from the solution was not significant. The adsorption capacity decreased with increase in adsorbent dose. This is due to the low dose, all adsorption sites are exposed and adsorption on the surface is saturated faster, that results in higher adsorption capacity. But at higher adsorption dose, the availability of higher energy sites decreases with a larger fraction of lower sites occupied as well as adsorption surface area may be overlapped or aggregated at higher dose and less active sites available to chromium [33], produce lower adsorption capacity [34-36]. From Figure 4 it is evident that the optimum dose is 40 to 60 mg. In this range chromium removal percentage and capacity were in optimum condition.

Effect of time on Cr (VI) adsorption. Contact time is an important parameter of adsorption which also reflects adsorption kinetics of an adsorbent for a solution with given concentration and pH values. The batch studies were carried out at 30°C with initial concentration of Cr (VI) of 40 ppm in 100 ml of solution, pH 3 using 40 mg composites at various contact time periods. Figure 5 shows the effect of contact time on the adsorption capacity of the composites for Cr (VI). The results show that adsorption capacity of Cr (VI) increases with increasing contact time from 30 to 240 min and after 180 min the capacity remains constant and attains equilibrium, which indicates that 180 min of contact time is enough for the maximum removal of Cr (VI) ions from aqueous solution under these experimental conditions. Equilibrium adsorption achieved may be due to the accumulation of Cr (VI) ions on the vacant sites and causes limited mass transfer of the adsorbate from the bulk liquid to the external surface of adsorbent [37].

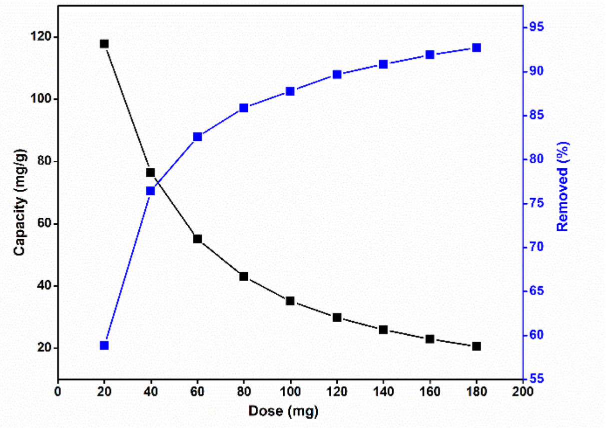

Figure 4. Effect of sorbent dose on chromium adsorption.

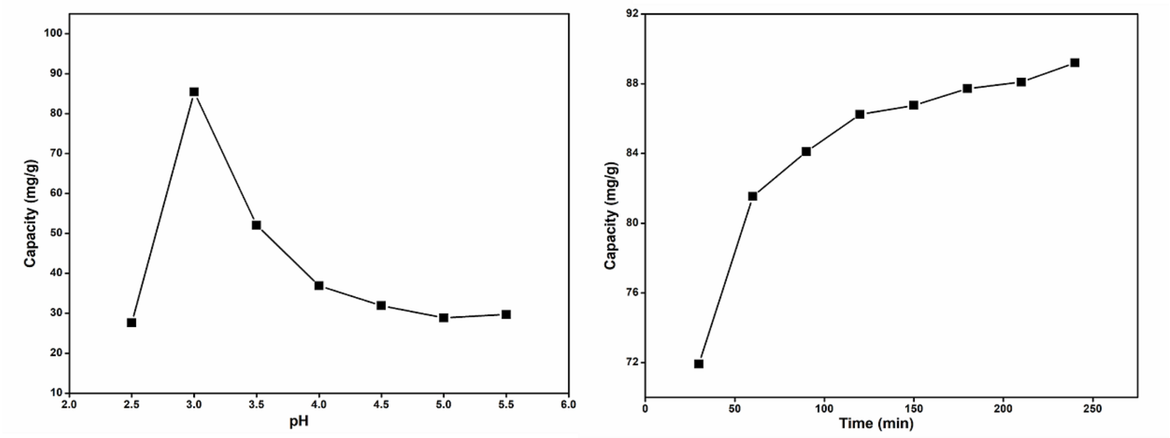

Figure 5. Effect of pH and time on chromium adsorption.

Table 1. Comparison of the isotherm and kinetics constant and calculated and experimental q_e values for chitosan.

Isotherm			Kinetics		
Langmuir			First order		
	K_L	0.082		q_e	20.88
	R^2	0.9970		K_1	0.01474
				R^2	0.9739
Freundlich			Second order		
	n	0.96		q_e	91.74
	K_F	6.87		K_2	0.00133
	R^2	0.9937		R^2	0.9999

Adsorption isotherm modeling

The data obtained from isotherm studies were tested for their applicability to the two models. Table 1 summarizes the values of all adsorption constants and regression coefficients for each of these isotherms, which were then calculated from the best-fit lines. According to Mckay *et al.* for best fit of Freundlich isotherm the n value should be from 1 to 10 [38, 39]. In this study the n value for the adsorbent was 0.96, which is out of the accepted range. The values of the regression coefficients for Langmuir and Freundlich are 0.9970 and 0.9937, respectively, which implies that Langmuir adsorption model is the best fit. This observation implies that monolayer adsorption on homogenous surface may co-exist under the applied experimental conditions.

Adsorption kinetics modeling

The pseudo first-order and pseudo-second-order kinetic models were used to obtain the rate constants and equilibrium adsorption capacity of chitosan. The values of pseudo-first order model constants k_1 and q_e were obtained from the slope and intercept of the plots of log (q_e-q_t) *vs* t while pseudo-first-order model constants, k_2, and q_e were calculated from the slope and intercept of the plots of t/q_e *vs* t. All of these constants and correlation coefficient values are summarized in Table 1. As seen from the table, calculated adsorption capacity and regression coefficient conform that adsorption of chromium onto adsorbent follows a pseudo-second-order kinetic model. The applicability of the pseudo-second-order kinetic model specifies that the adsorption process is chemisorption and the rate-determining step is probably surface adsorption. Similar phenomenon has been experienced for adsorption of chromium on other bio-adsorbents [40-42].

Application of chitosan for the treatment of industrial waste water

In this study chitosan was used to determine the usefulness of chitosan for the removal of chromium and some other physicochemical properties of waste water. For that purpose, effluent from different operational sections of tannery industry has been collected and the initial and final properties of waste water after the treatment with chitosan were determined. All of these results are summarized in Table 2 and 3. In this experiment, 0.5 g of chitosan was used to treat 250 ml of waste water at a temperature of 30°C and pH 3 with contact time180 min. After analysis it was found that only chrome tanning and re-tanning waste water contain chromium in high quantities while all other sectional waste waters do not contain any chromium or this level was below detection limit. For that reason, after treatment with chitosan only these two sectional waters were quantified to determine chromium. In this experiment it was found that 83.58 and 90.27 % of chromium was reduced from chrome tanning and re-tanning waste waters, respectively. All other physicochemical parameters such as turbidity (78-84%), conductivity (68-80%), BOD (62-75%), COD (58-75%) and TDS (69-79%) were significantly reduced, which indicates that this adsorbent can be successfully used for the treatment of tannery effluent, as well as domestic waste water.

Table 2. Initial physicochemical parameters of effluents from different chemical operations before treatment

Name of operation	Turbidity (NTU)	Conductivity (µS/cm)	BOD (mg/L)	COD (mg/L)	TDS (mg/L)	Chromium (mg/L)
Soaking	927	87550	2750	6100	45150	
Liming	1020	137150	4953	14120	67000	
De-liming	921	107000	3750	7710	55150	
Bating	879	89500	2900	5150	45550	
Pickling	793	74100	2150	4340	37550	
Chrome tanning	1123	128100	2450	6130	64500	1723.6
Neutralization	927	104100	3010	7150	52550	
Re-tanning	1050	127500	2750	6150	63500	1038
Dyeing	950	102100	5150	13165	51500	
Fat-liquoring	954	94100	6150	17195	47500	

Table 3. Changes of physicochemical parameters of effluents from different chemical operations after treatment

Name of operation	Turbidity (NTU)	Conductivity (µS/cm)	BOD (mg/L)	COD (mg/L)	TDS (mg/L)	Chromium (mg/L)
Soaking	151	27500	950	2250	14200	
Liming	201	37100	1810	4250	18500	
De-liming	187	31010	1410	3170	15200	
Bating	177	27550	755	1910	13500	
Pickling	127	19700	527	1650	11550	
Chrome tanning	224	37900	801	2150	19100	283
Neutralization	191	20100	721	1810	11500	
Re-tanning	227	35150	1027	2450	18150	101
Dyeing	163	19510	1520	3710	10500	
Fat-liquoring	174	23010	1810	4150	11710	

CONCLUSION

The removal of chromium from aqueous solution using chitosan was investigated under different experimental conditions in a batch mode. For that purpose, chitosan was successfully prepared from prawn shells and its formation was confirmed by FTIR, TGA and DSC analysis. In this study, results indicate that adsorbent dose, contact time and pH have a high impact on chromium uptake capacity of bioadsorbents. The adsorption follows the Langmuir model that means monolayer coverage of the adsorbate on the outer surface of the adsorbent. The adsorption kinetics followed the pseudo-second-order kinetic model which suggests that the adsorption process is chemisorption and the rate-determining step is probably surface adsorption. This adsorbent was used for the treatment of waste water and it was found that it can remove more than 80% of the chromium (250 ml, >1700 ppm solution). At the same time other physicochemical parameters such as turbidity, conductivity, BOD, COD and TDS were significantly reduced. This investigation implies that chitosan could be a good alternative to expensive chemicals and methods and hence the waste water treatment process (industrial, as well as domestic waste water) can become very economical.

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