

REMOVAL OF CHROMIUM FROM TANNERY EFFLUENT USING CHITOSAN-CHARCOAL COMPOSITE

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Abstract

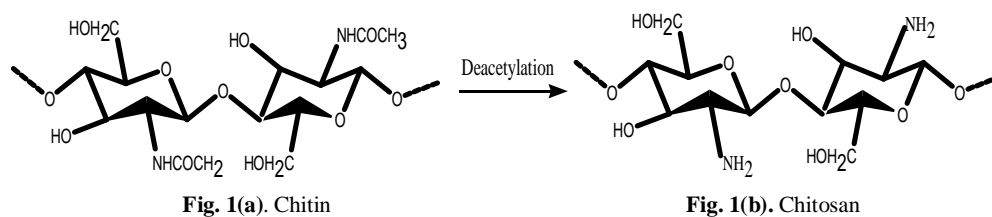
Chitosan-charcoal composite was applied as a media to treat tannery effluent. The composite was prepared by a simple solution-evaporation method and the morphology of the prepared composite was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Adsorption of chromium (Cr) was investigated by varying the contact time between adsorbate (Cr) and composite, pH of solution and dose of composite. The concentration of Cr was determined by atomic absorption spectroscopy (AAS). Removal of Cr was found to be dependent on pH and maximum adsorption was observed at pH 4.0. The optimum dose and contact time for Cr treatment was 40 g/L and 250 minutes respectively. The results showed that prepared composite can be used efficiently for the treatment of tannery wastewater containing chromium.

Introduction

At least 20 metals are classified as toxic and half of these are present in the environment in sufficient quantities that pose risks to human health¹. Chromium and its compounds are toxic, which are being mixed with natural water from a variety of industrial effluents. The major sources are from textile dyeing, leather tanning, electroplating and metal finishing industries, as well as from oxidative dyeing and water cooling towers which cause severe environmental and public health problems². It leads to liver damage, pulmonary congestion, oedma and causes skin irritation as well as results in ulcer formation³. The concentration of Cr in industrial wastewater was found in the range of 0.5 mg/L to 270000 mg/L⁴. The tolerance limit for the discharge of Cr (VI) into inland surface water is 0.1mg/L and in potable water it is 0.05 mg/L⁵. Chromium exists in the environment in two oxidation states i.e. Cr(VI) and Cr(III). Cr(III) is a nutrient species used for control of glucose and lipid metabolism in membranes, while Cr(VI) is highly carcinogenic and mutagenic due to its high oxidative character^{6,7,8}. Owing to these contradicting characteristics, chromium contamination is a hot topic in modern analytical chemistry⁹. Chitosan (2-amino-2-deoxy- - D-glucopyranose) (Fig.1.(b).) is a deacetylated derivative of chitin (2-acetamino-2-deoxy- -Dglucopyranose)¹⁰ (Fig.1.(a).). Due to its polycationic nature, chitosan is used as flocculating agent and acts as chelating agent and heavy metal trapper¹¹.

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Chitosan chelates five to six times the amounts of metals than chitin. This is attributed to the free amino groups exposed in chitosan because of deacetylation of chitin¹². Natural biopolymers are industrially attractive because of their capability of lowering transition metal-ion concentration to parts per billion. Natural products that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly¹³. The bio-adsorbent material chitosan is slightly soluble at low pH and poses problems for developing commercial applications. It is also soft and has a tendency to agglomerate or form a gel in aqueous solutions.



In addition, the active binding sites of chitosan are not readily available for adsorption. Transport of the metal contaminants to the binding sites plays a very important role in process design. Therefore, it is necessary to provide physical support and increase the accessibility of the metal binding sites for process applications. The aim of this study was to develop a biocomposite of chitosan coated on charcoal for the removal of Cr from industrial effluents.

Experimental

Materials and Methods

Raw Materials

Shrimp shell was collected from Khulna, Bangladesh. The shell was scraped free of loose tissue, washed with cold water and dried in the sun for 2 days. Then the shell was grounded to powder. Dried ground shell was placed in opaque plastic bottles and stored at an ambient temperature for use. Activated charcoal was purchased from Merck, India and tannery wastewater was collected from Hazaribag tannery industrial area, Dhaka, Bangladesh.

Preparation of chitosan and chitosan gel

Chitosan (DD=72%) was obtained from shrimp shell and characterized as reported earlier¹⁰. About 50 g of chitosan was slowly added to 1000 mL of 10 wt% oxalic acid with constant stirring. The mixture was heated to 40-50°C to facilitate mixing. At room temperature, the chitosan-oxalic acid mixture formed a whitish viscous gel¹⁴.

Preparation of chitosan-charcoal composite

About 250 g of the charcoal was slowly added to the chitosan gel and stirred continuously. The mixture was then dried slowly at 55-60°C to get the product. The gel coated charcoal was then washed with deionized water and dried. The chitosan-charcoal composite was then characterized by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM).

X-ray diffraction (XRD)

XRD patterns of composite were recorded on Philips PWO4 Xpert pro X-ray diffractometer. The X-ray source was Cu K α with a voltage of 40 kV and a current of 30 mA. The measurement was in the scanning range of 5–70 at a scanning speed of 50 s⁻¹.

Scanning Electron Microscope (SEM)

A HITACHI S-3400N, Japan (BSE) scanning electron microscope (VP-SEM) was used to examine the microstructure of chitosan and composite without any coating to the sample surface and the image was taken at an accelerated voltage of 15.0kV.

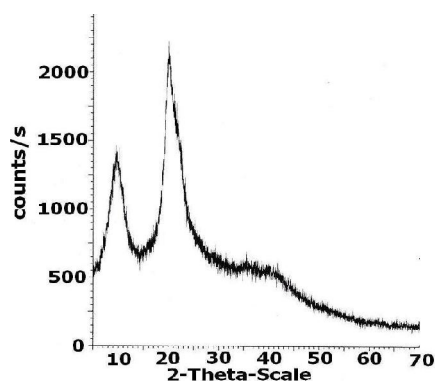


Fig. 2(a). XRD of Chitosan

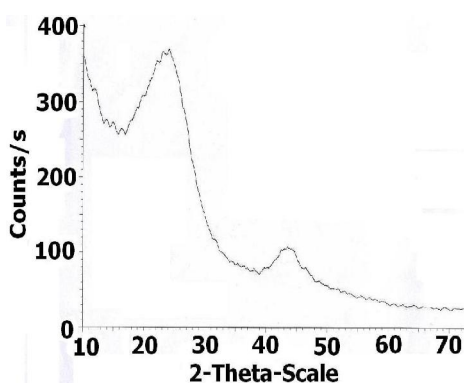


Fig. 2(b). XRD of Composite

Preparation of chromium (Cr) stock solution

Potassium dichromate (K₂Cr₂O₇) (Merck, Germany) was used as the source of Cr (VI) in the solution. 0.707g of K₂Cr₂O₇ was dissolved in de-ionized water and was diluted to 500mL in a volumetric flask to prepare 500 ppm Cr stock solution. Then the solution was further diluted for treatment.

Preparation of standard chromium (Cr) solution

0.2, 0.5, 1.0, 2.0, 3.0, and 4.0 ppm standard solutions of Cr were prepared for calibration by appropriate dilution of a 1000 ppm of chromium (stand scharlau, spain) solution. Quality control standards, duplicate samples and blanks were analyzed with samples from

effluents to ensure the quality of analysis. Air acetylene flame was used during analysis of Cr by FAAS. For estimation of Cr atomic absorption spectrophotometer (AA-240FS Varian, Australia) was used.

Comparison of Cr removal capacity of charcoal, chitosan and prepared composite

To compare the Cr removal capacity of charcoal, chitosan and the composite, known amount (20 g/L) of chitosan, activate charcoal and composite were added to 10 ppm of Cr solution in three different polyethylene tubes. The metal solution was initially adjusted at pH 4.00 by adding 0.1M HCl or 0.1M NaOH. The tubes were shaken well and centrifuged (Digisystem Laboratory Inc.). The contact time of standard chromium solution and adsorbent was 4 hours.

Treatment of tannery waste water by prepared composite

Two samples were collected from Hazaribagh tannery industrial area and were analyzed in the laboratory. The physico-chemical characteristics of the samples are shown in Table 1. The samples were treated with the composite materials prepared in this research at optimized condition (pH, contact time & dose) determined by previous experiments.

Table 1. Physico-chemical characteristics of tannery effluent

pH	Conductivity (mS/cm)	DO	TSS	TDS	Cr	Pb	Mn	Zn	Cd	Ni
		Unit: mg/L								
4.67	3.94	5.28	252	3158	9.98	7.00	0.14	0.43	BDL	BDL
7.97	7.64	0.18	1168	5080	39.8	7.50	0.43	0.30	BDL	BDL

Removal efficiency (E) of adsorbent on chromium

The influences of several operational parameters such as dose of adsorbent, initial pH of Cr solution and contact time were investigated. The result we expressed as the removal efficiency (E) of the adsorbent on Cr, which is defined as

$$E (\%) = [(C_0 - C_1) / C_0] \times 100$$

Where C_0 and C_1 are the initial and equilibrium concentration of Cr solution (mg/L), respectively. The Cr concentration was determined by atomic absorption spectrophotometer according to Standard Methods¹⁵.

Results and Discussion

This research focused on to develop a suitable adsorbent for treatment of chromium contaminated industrial wastewater. To prepare the chitosan-charcoal composite, the used

chitosan was obtained from the shrimp shell by using standard method¹⁰. A composite bio-adsorbent was prepared by coating chitosan onto charcoal as reported in the literature¹⁴.

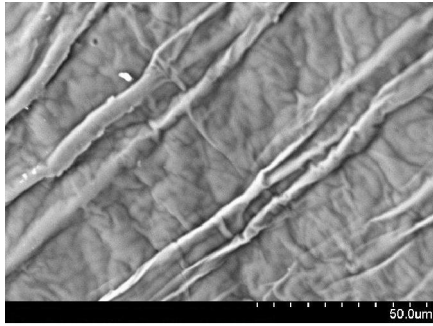


Fig. 3 (a).SEM image of Chitosan

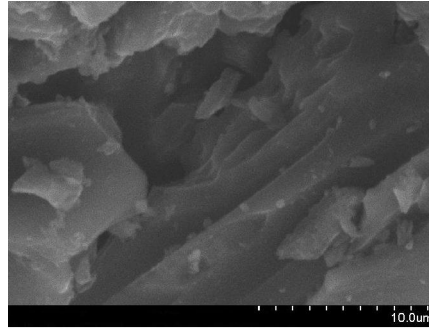


Fig. 3 (b).SEM image of composite

Characterization of chitosan-charcoal composite

The structure of chitosan-charcoal composite was characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD) methods. Fig.2. showed the XRD patterns of chitosan and composite respectively. The XRD pattern in Fig.2(a). showed diffraction peak at $2\theta = 10^\circ$ and 21° which is a typical fingerprints of semi-crystalline chitosan¹⁰. The diffraction peak at $2\theta = 21^\circ$ of chitosan was shifted to about $2\theta = 25^\circ$ of chitosan-charcoal composite (Fig.2.(b)) which is an indication of the interaction between chitosan and charcoal. The morphology of chitosan-charcoal composite biopolymer was studied by Scanning Electron microscope (SEM). It is observed (Fig.3.) that chitosan-charcoal composite biopolymers has non homogenous, non smooth surface with some porous straps and shrinkage and fibril structures whereas chitosan shows non homogenous and non smooth surface with strips and shrinkage¹⁰.

Cr removal capacity of charcoal, chitosan and prepared composite

Fig.4. represents the removal efficiency of chromium by three adsorbents charcoal, chitosan and chitosan-charcoal composite at pH 4.0 with 4 hours contact time. The efficiency of chitosan-charcoal composite was found 98% which is higher than that of chitosan (56.4%) and charcoal (69.2%) due to the fact that chitosan-charcoal composite had non homogenous, non-smooth surface with some porous straps and shrinkage structure which might facilitate such removal efficiency.

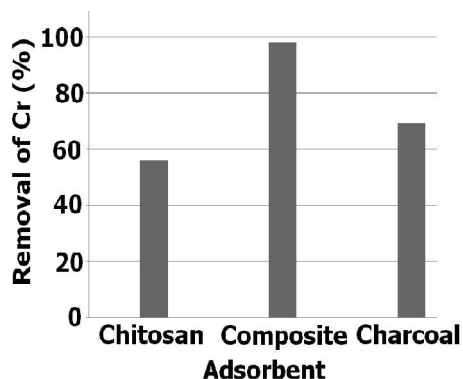


Fig. 4. Comparison of Cr removal efficiency

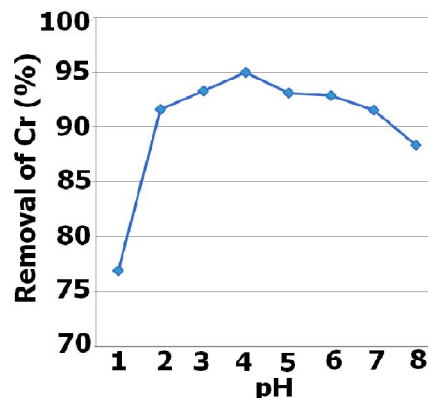


Fig. 5. Effect of pH on the adsorption of Cr on composite

Factors influencing the adsorption of Cr by composite

Effect of pH

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate. To examine the effect of pH on the Cr removal efficiency, the pH of Cr solution was varied from 1.0 to 8.0. As shown in Fig.5. the uptake of free ionic Cr depended on pH, the optimum metal removal efficiency occurred at pH 4.0 and then declined at higher pH. Removal efficiency increased from 77% to 95% upon pH increasing from 1.0 to 4.0. At low pH (below 4), the amine group on chitosan was protonated to varying degree. The NH_3^+ group on the chitosan was responsible for Cr (VI) adsorption. Chromium formed stable anions, such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , CrO_4^{2-} , and HCr_2O_7^- , the fraction of any particular species was dependent upon the chromium concentration and pH¹⁶. During Preparation of Chitosan coated activated charcoal adsorbent, oxalic acid treatment helped to increase the availability of active binding sites on the chitosan for adsorption of Cr at low pH. It was also suggested that during acid treatment, formation of more acidic surface oxides on the carbon surface enhanced its hydrophilic character and hence improved the hydrodynamic flow¹⁷. The combined active binding sites of chitosan coated charcoal showed higher adsorption capacity than chitosan and charcoal separately which is shown in Fig. 4. Hence, the optimum pH was around 4.0 and removal efficiency reduced drastically from pH 4 to 8. At higher pH, the presence of oxygen containing functional groups made the adsorbent surface negatively charged and hence there was repulsive electrostatic interaction between the adsorbent and the anions^{18,19}. At pH greater than 8.5, insoluble chromium hydroxide started to precipitate from the solution.

Effect of dose

The dependence of Cr adsorption on dose was studied by varying the amount of adsorbents from 5 to 45 g/L, by keeping the other parameters (pH, contact time) constant. From the Fig.6. it could be observed that removal efficiency of the adsorbent generally increased with increasing dose. This was expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions. The composite showed no further increase in adsorption after a certain amount of adsorbent was added (40-50 g/L). At 16.6 mg/L concentration of Cr, the maximum Cr removal efficiency was about 95% at the dosage of 40 g/L. The observation suggested that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. Chromium and some other metals such as arsenic, depending on the pH, are known to exist as anions. At low pH (below 5), the amine group on chitosan was protonated to varying degree^{20,21}. The NH_3^+ group on the chitosan was chiefly responsible for interaction with anions and negatively charged surfaces.

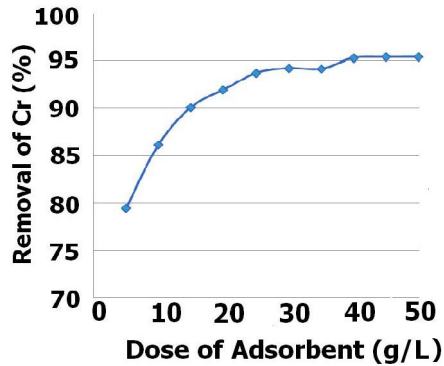


Fig. 6. Effect of dose on the removal efficiency of Cr on composite

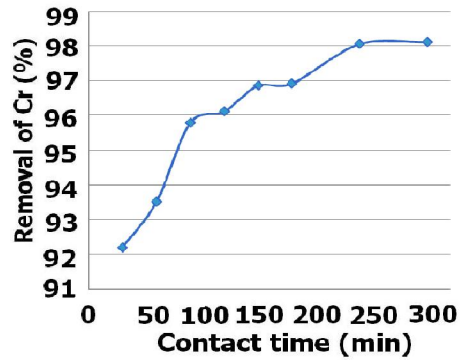


Fig. 7. Effect of contact time on the removal efficiency of Cr on composite

Effect of contact time

The interaction of adsorbent and chromium contained solution was performed at pH 4.0 and adsorbent dose was 20g/L. The contact time for treatment was varied from 30 min to 300min and centrifuging time was 15 min. Fig.7. represents that removal efficiency increases with an increase in contact time before equilibrium is reached.

It can be seen that Cr removal efficiency of composite increased from 92% to 98% when contact time was increased from 30 to 240 min. Optimum contact time for the adsorbent was found to be 240 min.

Treatment of tannery effluent by composite at optimized condition

Two sample of tannery effluents described in Table1 were treated by chitosan-charcoal composite at optimized conditions, pH=4.0, dose=40g/L & contact time=240 min determined by experiments and the removal efficiency was found 90.5% and 91.9% for both of the samples Fig.8. The efficiency for tannery effluent was somehow less than that of standard chromium solution (95-98%). This may be due to the presence of other metals in tannery effluent which competed with Cr to adsorb on chitosan-charcoal composite.

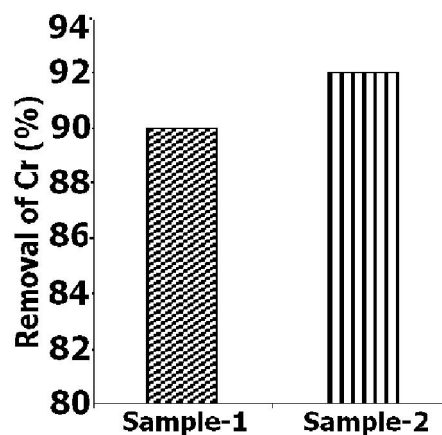


Fig. 8. Removal of Cr from two tannery effluents

Conclusion

A chitosan-charcoal composite was prepared and characterized by SEM and XRD. The composite was used to remove Cr from aqueous solution and an optimum condition was found for maximum removal which was used later for the treatment of tannery effluents. The Cr removal efficiency of the composite was more than 90%.

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