

Original Research Article

Effective Removal of Chromium(VI) Ions from Tannery Effluent Using Chitosan-Alumina Composite

ABSTRACT

A chitosan-alumina composite was prepared by coating chitosan, a glucosamine biopolymer, on activated alumina to remove chromium (VI) ion from tannery effluent. Chitosan was prepared from by demineralization and deproteinization of indigenous shrimp shell collected from Khulna, Bangladesh. and was characterized using FTIR, X-Ray Diffraction (XRD) & Scanning Electron Microscopy (SEM). The composite was prepared by simple solution-evaporation method and was characterized using XRD & SEM. Batch isothermal equilibrium experiments were conducted to evaluate the biosorbent for the removal of hexavalent chromium (VI) from stock solution as well as effluent obtained from tanneries in Hazaribagh area. The optimum pH, dose, and contact time on adsorption was also investigated. Removal of Cr was found to be dependent on pH and maximum adsorption was observed at pH 2.0. The optimum dose and contact time for Cr treatment was 25 g/L and 240 minutes respectively. Experimental equilibrium data were fitted to Freundlich adsorption. The concentration of Cr was determined by Atomic Absorption Spectroscopy (AAS). The chromium (VI) removal efficiency of the prepared chitosan-alumina composite was 90.17% and for tannery effluent the chromium removal efficiency was found as 87.88% under the optimum conditions. Efficiency of chromium (VI) ions removal in terms of adsorption capacity was found to be in the order of chitosan-alumina composite>chitosan>alumina.

Keywords: Chitosan-alumina composite; X-Ray Diffraction (XRD); Chromium (VI); Scanning Electron Microscopy (SEM); Sorption; Tannery effluent treatment; Chitosan.

1. INTRODUCTION

Heavy metal contamination has been a critical problem mainly because these tend to persist and accumulate in the environment. Chromium is used in various industrial processes and this heavy metal contamination exists in aqueous wastes of many industries such as tanneries, metal plating, textile industries, mining operations, radiator manufacturing, smelting, alloy industries and storage batteries industries etc. [1]. Chromium exists in nature as stable hexavalent and trivalent forms. The hexavalent form of chromium is more toxic than trivalent chromium and is often present in wastewater as chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$). The persistant nature of Cr(VI) responsible for accumulation in the food chain and with time Cr(VI) accumulation reach harmful levels in living beings resulting in serious health hazards such as irritation in lungs and stomach, cancer in digestive tract, low growth rates in plants and death of animals. Therefore, serious and immediate attention requires for the removal of Cr(VI) from wastewater prior to its discharge into natural water systems, adjoining landmasses and sewer systems [2]. Considering its toxicity and carcinogenic nature, the maximum levels permitted for trivalent chromium in wastewater is 5 mg/L and for hexavalent chromium as 0.05 mg/L [3].

Chitosan and its composites as bio-adsorbent materials have been used efficiently to remove heavy metals from aqueous bodies, due to its low cost of preparation, availability and the highest sorption capacity for several metal ions [4]. Chitosan (2-acetamido-2-deoxy- β -D-glucose (Nacetylglucosamine) is a partially deacetylated polymer of chitin and is usually prepared from chitin by deacetylation. Chitin (2-acetamido-2-deoxy- β -D-glucose-(N acetylglucan) is the main structural component of molluscs, insects, crustaceans, fungi, algae and marine invertebrates like crabs and shrimps [4,5,6].

Alumina itself is a good adsorbent for heavy metal removal and chitosan alumina composite showed promising features [7]. However cost of preparation and raw materials is an issue in earlier researches. In Bangladesh a huge amount of shrimps are cultivated every year which produces a very good amount of shrimp shells, hence utilizing shrimp shells for making chitosan is cost effective. Chitosan preparation were followed with the literature [8] but in changed reaction conditions as source and type of shrimp shell were different from literature and hence prepared chitosan was characterized along with prepared composites. For more precise determination and finding optimum conditions of Cr(VI) ions, Atomic Absorption Spectroscopy (AAS) was used instead of UV-Vis spectrometer. A large number of tanneries are now exists in this country which pass hazardous Cr(VI) ion through its effluents. Many of these effluents go to the rivers and canals without any treatment which produces serious environmental problems. The present research is carried out to prepare a Chitosan biosorbent using our indigenous shrimp shell to study for the first time, the removal of Cr(VI) ion from tannery waste effluents.

2. EXPERIMENTAL

2.1 Materials

Indigenous shrimp shells were collected from Bagherhat, Khulna, Bangladesh. All chemicals (NaOH, HCL) used were industrial grade and were purchased from local market. Distilled and deionized water was prepared employing a SIMEX distiller and a deionizer Barnstead (model no-7118, USA). Alumina was purchased from Sigma-Aldrich labor chemikalien.

2.2 Preparation of Chitosan

Chitosan preparation consists of three consecutive processes. At first Shrimp shells were demineralized with 5% HCl for 24 hours with a solid to solvent ratio of 1:6. After 24 hours, those were rinsed with distilled water, dried and then deproteinized by keeping in 6% NaOH solution at 60-70° C for 48 hours at a solid to solvent ratio of 1:10 (w/v). The residue was then collected and washed to get the product chitin. Chitin contains acetyl groups which were removed by using 80% NaOH solution with a solid to solvent ratio of 1:10 (w/v). The reaction was carried out at 70° C for first 2 hours, then at room temperature for 72 hours. Chitosan was washed to neutrality in running tap water and finally rinsed with distilled water. It was then filtered and dried in an electric oven at 60° C. About 25 g of chitosan was slowly added to 500 mL of 10 wt% oxalic acid solution with stirring. A viscous gel was formed, which was then heated to 40-50 °C to facilitate the mixing. Approximately 250 mL of the chitosan gel was diluted two fold with distilled water and heated to 40-50 °C.

2.3 Preparation of Chitosan–Alumina Composite

About 250 g of the oxalic acid treated alumina was slowly added to the diluted gel and stirred for about 36 hours. Alumina was oxalic acid treated in order to remove trace impurities and oxalic acid can act as binding site for chitosan. The contents were allowed to settle, and the clear liquid was filtered and dried in the oven at 55°C under vacuum for 24 h. The coating process was repeated once to increase loading of chitosan on the alumina. Treatment with aqueous NaOH neutralized excess oxalic acid in the composite biosorbent. The mixture was then filtered, washed with deionized water and then dried in an oven under vacuum at 55 °C for about 48 hours. The chitosan-alumina composite was then characterized by X-ray diffraction (XRD) method and Scanning Electronic Microscopy (SEM).

2.4 Characterization of the Chitosan and Prepared Composite

Characterization of chitosan biopolymers was carried out by IR spectroscopy, X-ray diffraction (XRD), and Scanning Electronic Microscopy (SEM). The Degree of deacetylation (DA) was determined and calculated by titrimetric method [9]. Dried chitosan (0.2 g) was dissolved in 20 cm³ 0.1 M hydrochloric acid and 25 cm³ deionized water (DI). After 30 minutes of continuous stirring, next portion of deionized water (25 cm³) was added and stirring was continued for another 30 minutes. When chitosan was completely dissolved the solution was titrated with 0.1 mol·dm⁻³ sodium hydroxide solution using automatic burette (0.01 cm³ accuracy). Degree of deacetylation (DA) of chitosan was calculated using formula:

$$DA [\%] = 2.03 \left(\frac{(V_2 - V_1)}{m + 0.0042 (V_2 - V_1)} \right)$$

where: m – weight of sample, V_1 , V_2 – volumes of 0.1 mol·dm⁻³ sodium hydroxide solution corresponding to the deflection points measured from titration, 2.03 – coefficient resulting from the molecular weight of chitin monomer unit, 0.0042 – coefficient resulting from the difference between molecular weights of chitin and chitosan monomer units.

2.5 Preparation of Chromium (VI) Stock Solution

Solid pure Potassium dichromate (K₂Cr₂O₇) was used as the source of chromium (Cr) stock solution. K₂Cr₂O₇ (2.828g) was weighed in an analytical balance, dissolved in de-ionized water and was diluted upto 1000 ml in a volumetric flask to prepare a 1000 ppm Cr stock solution. Further dilution gave 20 ppm and 10 ppm Cr stock solution for the process treatment.

2.6 Procedure for Batch Adsorption Studies

Batch mode adsorption studies were carried out to investigate the effect of different parameters such as adsorbent concentration (5-30mg/l), pH (1-6), and varying contact time (30-240 minute). The solution containing adsorbate and adsorbent was taken in a 250 ml capacity conical flask and agitated at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper (Whatman No-40). To compare the Cr removal capacity of chitosan, alumina and prepared composite, known amount (20 g/L) of chitosan, alumina and composite were added to 20 ppm of Cr solution in

three different conical flasks. The metal solution was initially adjusted at pH 7.00 by adding 0.1M HCl or 0.1M NaOH. Temperature was kept constant at 25°C and the contact time of standard chromium solution and adsorbent was 4 hours.

The filtered solution was subjected to determine its Cr(VI) content AAS (SHIMADZU AA-7000). The removal efficiency, E(%) of Cr(VI) was calculated using the relation:

$$E(\%) = \frac{C_i - C_f}{C_i} \times 100$$

Where C_i and C_f were the initial and final concentration of Cr(VI) ions in identical unit.

2.7 Treatment of Tannery Waste Water by Prepared Composite

Tannery waste water sample was collected from tannery industrial area (Hazaribagh) and were analyzed in the laboratory and its physico-chemical characteristics is presented in table 1. The tannery waste water samples were treated with the composite materials at optimized conditions (pH, contact time & dose) which were determined by the process treatment of stock solution. All samples were digested by 5ml of conc. HNO_3 prior to analysis by AAS.

Table 1. Physico-chemical characteristics of tannery effluent

pH	Conductivity millisiemens/cm	TSS* (mg/L)	TDS** (mg/L)	Heavy metal ion concentration (mg/L)			
				Cr	Mn	Zn	Pb
6.51	11.33	5008	5964	9.28	1.99	1.82	BDL***

* TSS -Total suspended solid, **TDS -Total dissolved solid, ***BDL- Beyond detection limit,

3. RESULTS AND DISCUSSION

3.1 FT-IR Analysis of the Prepared Chitosan

FTIR spectra were recorded in the middle infrared (4000 cm^{-1} to 400 cm^{-1}) with a resolution of 4 cm^{-1} in the absorbance mode for 8 to 128 scans at room temperature. The infrared spectra for chitosan biopolymers are shown in Fig. 01. The prepared chitosan was confirmed by comparing the positions of the characteristic peaks and their intensities, which are nearly the same as those reported by other researchers [10, 11]. The wide band found at 3427 cm^{-1} attributed to OH stretching vibrations of water and hydroxyls, and NH stretching vibrations of free amino groups and the band at 2924 cm^{-1} attributed to the $-\text{CH}_3$ groups. Bands identified at 1560 cm^{-1} and 1404 cm^{-1} are typical of the N-H group bending vibration and vibrations of the primary alcoholic groups $-\text{OH}$ group respectively. The band at 1070 cm^{-1} could be attributed to the stretching of hydroxyl groups of $\text{C}_3\text{-OH}$, and the band at 1022 cm^{-1} could correspond to the stretching of hydroxyl groups of $\text{C}_6\text{-OH}$. The band at 873 cm^{-1} corresponds to the characteristic skeletal vibration of β -anomers [11]. A weak intensity peaks rises at 3649 cm^{-1} showing non hydrogen bonded hydroxyl groups.

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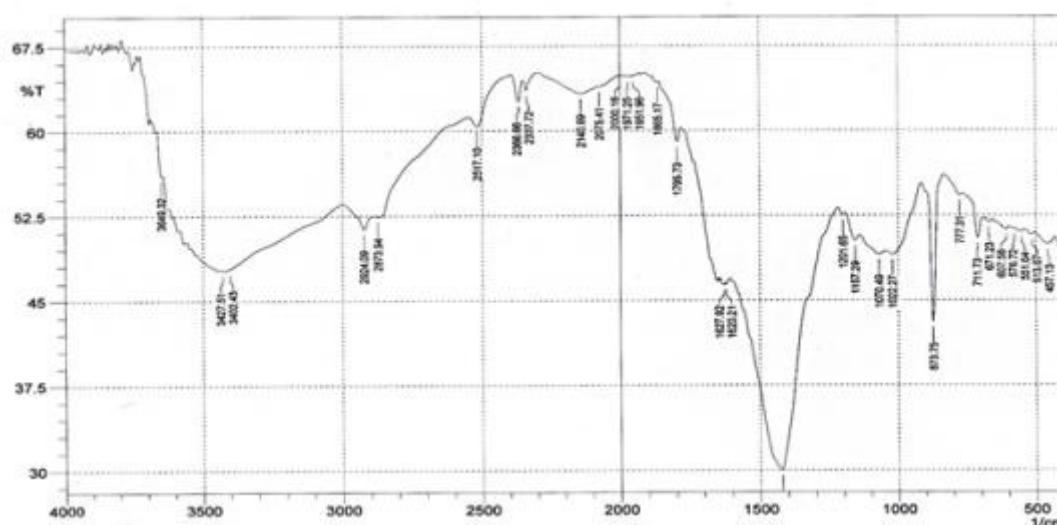


Fig. 01. FT-IR spectrum of the prepared chitosan

3.2 X-Ray Diffraction of Prepared Chitosan & Composite Material

XRD analysis is used to determine the percentage of crystallinity present in the material and whether the physical nature of the polymer could change with respect to temperature. XRD patterns of both chitosan and composite were recorded on Bruker, D8 advance diffractometer. Fig. 02 shows XRD pattern of chitosan which exhibits a strong characteristic peak at about $2\theta = 20.02^\circ$ which is similar to XRD of pure Chitosan [12]. Else there is a sharp peak at $2\theta = 29.36^\circ$ and the existence of 2θ peaks at approximately 36° , 39.3° , 43.1° , 47.4° , 48.4° corresponding to the amorphous nature of the prepared chitosan, which is good for heavy metal adsorption [13]. It is generally known that the structure of chitosan is strongly dependent on its processing treatment, such as dissolving, precipitation, and drying, as well as its origin and characteristics, such as degree of deacetylation and molecular weight.

Composite material's XRD peak differs from the materials from which the composite is made off usually shifting of XRD peak indicates significant intercalation in the hybrid structure or formation of composite material [14, 15]. Fig. 02 shows the XRD patterns of chitosan-alumina biopolymers used in this study. In case of composites the XRD peaks have shifted at $2\theta = 18.6^\circ$ from 20.02° , from 29.36° to 28.9° , from 36° to 35.1° , from 39.3° to 37.7° , from 43.1° to 43.3° , from 47.4° to 45.5° respectively indicating the chitosan-alumina physical bond formation.

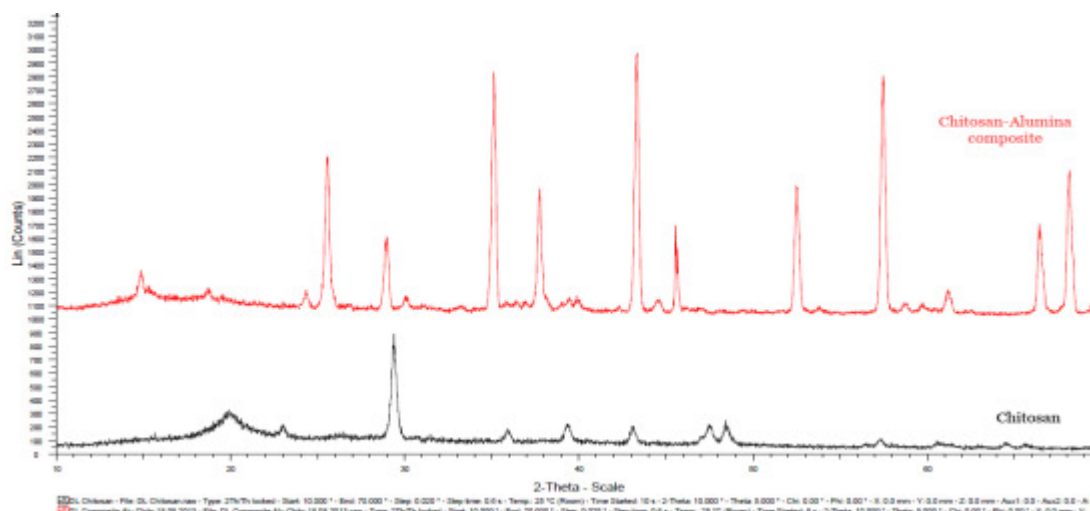


Fig. 02. XRD pattern of the prepared chitosan & chitosan–alumina composite

3.3 SEM of Prepared Chitosan, Alumina & Composite Material

The SEM micrographs were produced at a scanning electron microscopy; model HITACHI F-34001N, to examine the morphology and surface structure of the adsorbents at the required magnification at room temperature which are shown in Fig. 03.

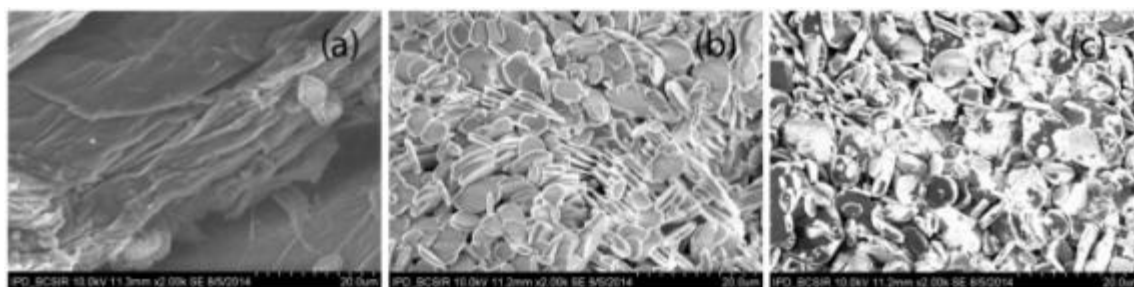


Fig. 03. Scanning Electronic Microscopy (SEM) micrographs of (a) chitosan, (b) alumina and (c) chitosan-alumina composite upon 2000x magnification

The micrograph of chitosan in Fig. 03(a) shows non homogenous and non smooth surface with strips and shrinkage. The structure also indicates that the powerful adsorption capacity of Cr(VI) may rise from such structure and composition. On the other hand the micrograph of alumina in Fig. 03(b) composed of hexagonal crystal shaped disks. Coating chitosan on alumina modified the surface morphology of alumina matrix showing in Fig. 03(c) which is significantly irregular, rough, tiny interspaced structures, resulting increase in the contact area and improve metal ion adsorption capacity making it useful for water treatment.

3.4 Effect of pH on Chromium (VI) Adsorption

The pH affects the solubility of chromium ion to a great extent. The pH of the aqueous solution is the controlling factor in the adsorption process; hence it become necessary to determine at what pH, max adsorption will takes place. To examine the effect of pH on the Cr removal efficiency, the pH was varied from 1.0 to 6.0. As shown in Fig. 04 the uptake of free ionic Cr depends on pH, where optimal metal removal efficiency occurs at pH 2.0 and then declining at higher pH. Removal efficiency increased from 83.71% to 87.15% over pH range from 1.0 to 2.0, then the efficiency decreased to 81.73% at pH 6.0 and higher pH condition. The effect of pH on the adsorption of Cr (VI) on the biosorbent is shown in Figure 6. Adsorption is greater at low pH and decreases with increasing pH. At low pH (below 4), the amine group on chitosan is protonated to varying degree leading to the formation of NH_3^+ group. The NH_3^+ group on the chitosan is responsible for Cr (VI) adsorption. Chromium (VI) forms stable anions, such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , CrO_4^{2-} , and HCr_2O_7^- , and the relative abundance of a particular complex depends on the concentration of the chromium ion and the pH of the solution. With the increase of pH from 3 to 6, the degree of protonation of the adsorbent functional group decreases gradually and hence removal of Cr (VI) decreases. X-ray photoelectron spectroscopy spectrum by Tiemann and Dambies [16, 17] reveals that chitosan biomass after contact with chromium (VI) at pH around 5, about 55% of chromium (VI) gets reduced to chromium (III). During Preparation of Chitosan coated alumina adsorbent, oxalic acid treatment helps to increase the availability of active binding sites on the chitosan for adsorption of Cr (VI) at low pH conditions.

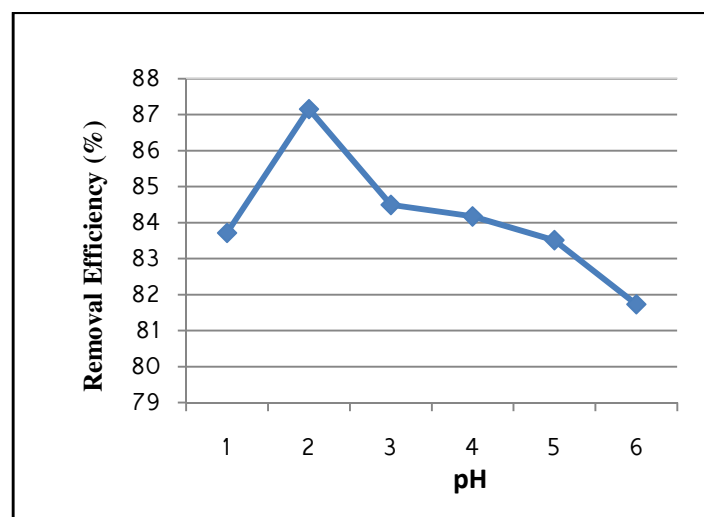


Fig. 04. Effect of pH on the adsorption of Cr (VI)

3.5 Effect of Contact Time on Chromium (VI) Adsorption

Removal efficiency of Cr(VI) ion increases with an increase in contact time before equilibrium is reached. pH of solution was kept optimum, while temperature was kept at 25°C. It can be seen that Cr removal efficiency of composite was increased from 40.8% to 89.09% when contact time was increased from 30 to 240 min. Optimum contact time adsorbent was found to be 240 min. From Fig. 05, it can be seen that, increasing of contact

time more than 240 min also increased the efficiency, but for industrial purpose 240 minute contact time is sufficient for adsorption process.

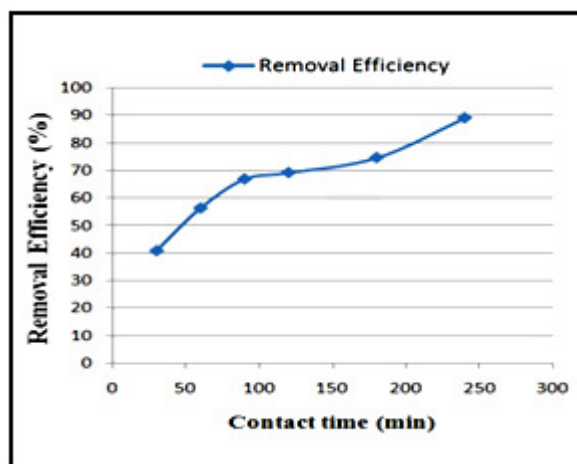


Fig. 05. Effect of contact time on removal efficiency of Cr(VI)

3.6 Effect of Dose on Chromium (VI) Adsorption

The dependence of Cr sorption on dose was studied by varying the amount of adsorbents from 5 to 35 g/L, while keeping other parameters (pH, contact time) constant. Fig. 06 represents the Cr (VI) removal efficiency of the prepared composite.

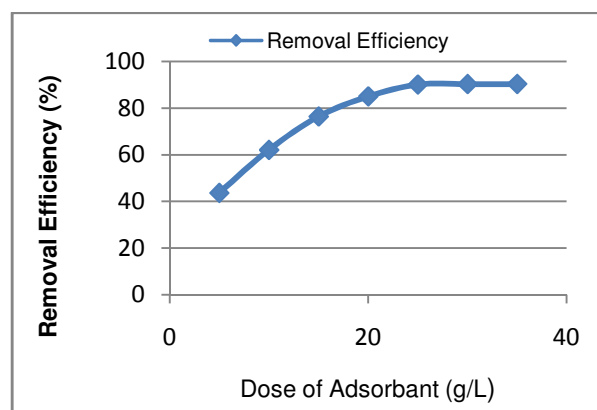


Fig. 06. Effect of Dose on the removal efficiency of Cr (VI)

It is observed that the removal efficiency of the adsorbent was improved with increasing dose. This is expected due to the fact that the higher dose of adsorbents in the solution creates greater availability of exchangeable sites for the ions. The composite shows no further increase in adsorption after a certain amount of adsorbent was added (30-35 g/L). At 9.14 mg/L concentration of Cr (VI), the maximum Cr (VI) removal efficiency was about 90.17% at the dosage of 25 g/L. This suggests 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.

3.7 Effect of Initial Concentration

The initial heavy metal ions concentration is an important parameter in adsorption since a certain amount of adsorbent can absorb a certain amount of heavy metal ions. Fig. 07 shows the effect of initial adsorbate concentration on percentage adsorption efficiency. It is observed that the percentage of adsorption efficiency decreases with the increase of adsorbate concentration. The percentage of adsorption efficiency decreased from 87% to 43.54% at a constant pH (2.0).

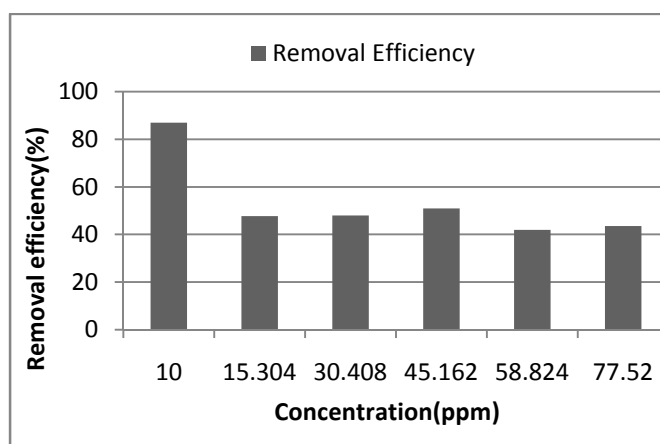


Fig. 07. Effect of initial concentration on the adsorption of Cr(VI)

3.8 Equilibrium Model

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir and Freundlich isotherms. Freundlich equation plot of $\log C_{ads}$ vs. $\log C_{eq}$ from Table 2 yielded a straight line as shown in Fig. 08. The Freundlich equation which is used to describe heterogeneous surface energies are expressed as:

$$C_{ads} = K_F C_{eq}^{1/n}$$

In this study the following linearised form of the Freundlich equation was used.

$$\log C_{ads} = \log K_F + 1/n \log C_{eq}$$

Where:

C_{ads} = amount of Cr adsorbed ($mg \cdot g^{-1}$)

C_{eq} = equilibrium concentration in solution ($mg \cdot ml^{-1}$)

$1/n$ = Freundlich constant ($mg \cdot g^{-1}$)

Table 2: Logarithmic values of C_{eq} and C_{ads} for Freundlich Isotherm

$\log C_{eq}$	$\log C_{ads}$
2.203	2.465
2.500	2.765
2.646	2.963
2.834	2.994
2.942	3.130

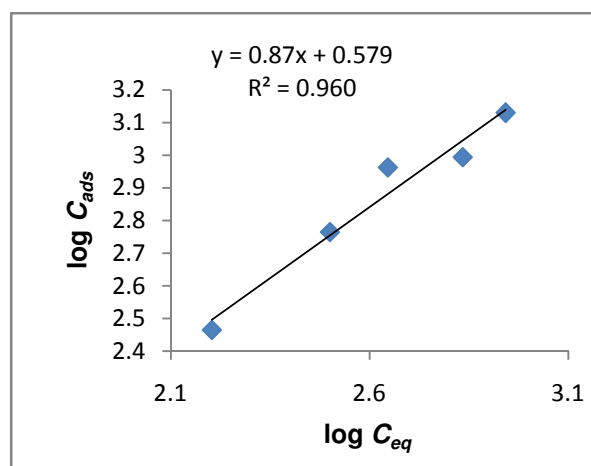


Fig. 08: Freundlich adsorption Isotherm

From Fig. 08 it is evident that the values of $1/n$ and K_F , which are rough measurements of the adsorption intensity and adsorption capacity of the adsorbent, have been determined by the least square fit. The values obtained from Freundlich equation and plot is shown in Table 3.

Table 3: Values of Freundlich Isotherm Constants

$1/n$	n	K_F	R^2
0.870	1.149	3.793	0.960

The chromium solutions were at low concentrations and the surface of the composite material was heterogeneous which is best fit to the Freundlich model [18]. The correlation coefficient, R^2 value found from Fig. 08 is 0.960, which is a measure of quite good fit to Freundlich isotherm model. For fixed values of C_{eq} and n , the larger the value of K_F the larger the amount of Cr adsorbed, C_{ads} . For fixed values of K_F and C_{eq} , the smaller the value of n , the stronger is the adsorption bond [19]. Values of K_F and n obtained from the intercept and slopes of Fig. 08, indicating adsorption system is favorable.

3.9 Comparison of Adsorption of Chromium (VI) by Chitosan, Alumina and Composite

Certain dose of chitosan, alumina and chitosan-alumina composite were applied to 20 mL of 20 ppm chromium solution. pH of the chromium solution was maintained at 7.0. Comparison of adsorption of Chromium (VI) is illustrated in table 4 and it is observed that chitosan-alumina composite has greater adsorption capacity than chitosan and alumina itself. This might be due to the exposure of larger amount of amino groups in the composite. Composite production required 10 times less chitosan, if chitosan alone was used as adsorbent. Hence the composite production is very economical.

Table 4: Chromium removal from stock solution by three adsorbents

Absorbent	Initial Concentration (ppm)	Final Concentration (ppm)	Total Chromium Removed (ppm)	Removal efficiency (%)
Chitosan	20.00	6.854	13.146	65.73
Alumina	20.00	9.422	10.578	52.89
Composite	20.00	3.752	16.248	81.24

3.10 Removal of Chromium from Tannery Waste Water

Sample of tannery effluents described in Table 1 were treated by chitosan-alumina composite. Prior treating with chitosan-alumina composite pH of the collected samples were adjusted to 2.0. Optimum dose 25 g/L and contact time 240 min were applied to treat the effluent. Initial Concentration of Cr (VI) in tannery effluent was 9.28 ppm.

Final Concentration of Cr (VI) in tannery effluent after treating with composite was 1.18 ppm and the removal efficiency of Cr (VI) from tannery effluent by chitosan-alumina composite was 87.88%. The efficiency for tannery effluent is somehow less than that of standard chromium solution (90.17-90.42%). This may be due to the presence of other metals in tannery effluent which competed with chromium to absorb on chitosan-alumina composite.

4. CONCLUSION

The present work aims for the systematic studies of removal of Cr (VI) ions from waste water using chitosan-alumina composite. In this study chitosan was prepared from indigenous sources. As a result of optimization of conditions, Cr (VI) ions were efficiently removed from stock solution as well as from tannery effluent. Determinations of Cr (VI) ions concentration were made by AAS, hence the results obtained are more accurate and the kinetic data fits well with the Freundlich isotherms. However, the effluents are generated by the industries in very large quantities, treatment of which in the batch systems can no longer be applied. Therefore, a suitable operational strategy, adsorption kinetics and investigation of the

356 potential regeneration of material needs to be developed for continuous removal of Cr (VI)
357 ions from the industrial effluents.

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