

## **Chromium (VI) Ions Removal from Tannery Effluent using Chitosan-Microcrystalline Cellulose Composite as Adsorbent**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.*

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### **ABSTRACT**

The bio-adsorbent chitosan-microcrystalline was synthesized from waste materials of shrimp processing industries, and waste cotton rags of garments industries for removal of chromium (VI) ion from tannery effluent. The chitosan was extracted from shrimp shell through the deproteinization, demineralization and deacetylation steps and microcrystalline cellulose was extracted from waste cotton rags by acid hydrolysis. The composite was prepared by simple solution evaporation method. The functional groups, responsible for adsorption and the chemical interaction in the composite formation were evidenced from FTIR results. The observed SEM results indicate that the prepared composite has a rough and porous surface. Batch adsorption

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experiments were conducted and removal of Cr(VI) was found to be reliant on pH and maximum adsorption was observed at pH 5.0. For 2 ppm Cr(VI) stock solution, the optimum dose and contact time treatment was 2 g/L and 240 minutes respectively and the maximum removal efficiency of chromium was found 93%. Tannery effluent was treated with optimum conditions required for maximum removal of Cr(VI). Langmuir isotherm and Freundlich isotherm model were plotted against the adsorption data and found that Langmuir Isotherm was well fitted with  $R^2$  value of 0.997.

**Keywords:** Chitosan-microcrystalline cellulose composite; chromium (VI); Scanning Electron Microscopy (SEM); sorption; tannery effluent treatment; chitosan.

## 1. INTRODUCTION

In recent years, water pollution by heavy metals has posed one of the most severe environmental problems. In many industries such as tanneries, plating facilities, mining operations heavy metals such as Chromium(Cr), Lead(Pb), Mercury(Hg) etc. found as waste [1]. Tanning Industry is considered to be a major source of water pollution and tannery wastewater in particular, is a potential environmental concern because of high concentration of Cr ion. Over 95% of all leather manufactured in tannery industry is chrome tanned and the tanning process requires huge amount of chromium powder and liquor [2,3]. The tannery industries at Hazaribagh, Dhaka, Bangladesh are one of the major polluting industries. Waste water containing a significance quantity of Cr from the tannery industries is discharged as effluent. Chromium enters the air, water, and soil mostly in the Cr(III) and Cr(VI) forms. Cr(III) is an essential nutrient for human body but the hexavalent form Cr(VI) is of particular concern because of its greater toxicity [4].

There are many conventional methods for removing Cr(VI) from industrial effluents but adsorption has become one of the alternative treatments for wastewater treatment due to its high removal efficiency without the production of harmful secondary wastes. The application of biopolymers such as chitosan is one of the emerging adsorption methods for the removal of Cr(VI) ions, even at low concentrations with better performance [5-7].

Chitosan is a type of natural polyaminosaccharide, synthesized from the deacetylation of chitin, which is a polysaccharide consisting predominantly of unbranched chains of (1→4)-2-acetoamido-2-deoxy-d-glucose. Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and

hydroxyl groups, which can serve as the active sites [8].

Microcrystalline cellulose (MCC) is acid hydrolysis product of cellulose. Cellulose is a polydisperse linear polymer consisting of 1, 4 glycosidic linked d-glucose units. The polymer contains three reactive hydroxyl groups which are responsible for the adsorption properties. MCC can develop hydrogen bonds, not only between themselves, but also with the host polymer matrix, creating a porous network [9].

Chitosan based composites are already showing promising features for the treatment of Cr(VI) ions in tannery effluent for e.g. chitosan-charcoal composite [10], chitosan-alumina composite [11], iron doped chitosan coated activated alumina [12]. In optimum conditions above 85% Cr(VI) removal efficiency were achieved in these studies. These results indicate a new search of chitosan-based composite is inevitable. Hence, in this study chitosan- microcrystalline cellulose composite is made to investigate Cr(VI) adsorption efficiency in tannery effluent for the first time. Considering low cost of raw materials and preparation this composite is ideally suited for adsorption studies, as main source of chitosan and MCC are shrimp shells and waste cotton rags respectively. Chitosan preparations were followed with changed reaction conditions than literature mentioned [13,14]. MCC reinforces the composite and makes it porous for better adsorption. Chitosan, MCC and composite were characterized using FTIR spectroscopy and SEM images were taken to study morphology. Batch adsorption experiments were done at different pH, contact time and composite dose using Atomic Absorption Spectroscopy (AAS) instead of UV-Vis spectrometer for precise measurements and maximum Cr(VI) adsorption efficiency was recorded in optimum condition. Finally tannery effluent containing Cr(VI) was treated with chitosan-microcrystalline cellulose composite.

## **2. EXPERIMENTAL**

### **2.1 Materials**

The materials used for this study mainly include raw shrimp shell from Khulna, Bangladesh and waste cotton rags were collected from local garments. All chemicals (NaOH, HCl, NaOCl & H<sub>2</sub>SO<sub>4</sub>) were used reagent grade and purchased from Sigma-Aldrich laborchemikalien. Distilled and deionized water was prepared employing a SIMEX distiller and a deionizer Barnstead (model no-7118, USA).

### **2.2 Preparation of Chitosan**

Chitosan was found mainly by the deacetylation of chitin. The following sequences were maintained during the extraction of chitosan.

#### **2.2.1 Deproteinization of shrimp shells**

Finely powdered shrimp shells were deproteinized with 5% NaOH solution at a solid to solvent ratio of 1:5 (w/v). The solution was continuously stirred for 1 hour at 90°C. Then the solution was filtered and washed with distilled water. The residue was then oven dried which is called chitin.

#### **2.2.2 Demineralization**

Demineralization was carried out in a dilute HCl solution. Solid fractions obtained after deproteinization were treated with 2 M HCl in 1:5 (w/v) ratio for 6 hours at 90°C under constant stirring. It was then allowed to stand for 1 hour to separate the residue from filtrate. The residue was washed to neutrality with distilled water and then dried in oven for 8 hours at 75°C.

#### **2.2.3 Deacetylation of chitin to chitosan**

The demineralized chitin was added into 50% NaOH solution in the ratio of 1:10 (w/v) and heated using a magnetic hot plate. The temperature was maintained at 85°C for 60 minutes. After heating, filtration was carried out and the residue was washed with deionized water. The product found is known as chitosan which was dried in oven at 70°C for 6 hours.

### **2.3 Preparation of Microcrystalline Cellulose (MCC) from Waste Cotton Rags:**

Cotton is the richest source of  $\alpha$ -cellulose. The extraction of  $\alpha$ - cellulose from cotton is a very easy and simple two step process.

#### **2.3.1 Isolation of $\alpha$ -cellulose**

Dried cotton rags were cut into small pieces and chemically digested with 2% (w/v) sodium hydroxide for 5 hours at 80°C. It was bleached with 250 1:1 aqueous dilution of sodium hypochlorite for 15 minutes at 80°C. The material was then washed sufficiently with water and treated with 250 mL of 17.5% (w/v) sodium hydroxide at 80°C for 1 hour. The resulting  $\alpha$ -cellulose was washed thoroughly with distilled water [15].

#### **2.3.2 Production of microcrystalline cellulose (MCC)**

About 30 g  $\alpha$ -cellulose was placed in a conical flask and hydrolyzed with 1 M sulfuric acid in a ratio of 1:10 (w/v) at a boiling temperature of 105°C for 15 minutes. The hot acid mixture was poured into 1.5 L of cold tap water which was followed by vigorous stirring with a spatula and allowed to stand overnight. The MCC obtained by this process was centrifuged, washed with water until neutral, centrifuged and dried in a hot air oven at a temperature of 100°C for 60 minutes [16].

### **2.4 Preparation of Chitosan- MCC Composite**

Around 0.5 g chitosan was dissolved in 1% acetic acid. Then the solution was stirred for 3 hours. A gel like solution was formed during stirring. Approximately 2 g MCC powder was added into the gel like solution. The mixture was stirred for 3 hours. This stirring makes the uniform dispersion of cellulose powder into the acidic solution. After continuous stirring the solution was poured into petri dish and vacuum drying was done. The dry film was immersed into 2 M NaOH solution and then dried at 56°C for 5 hours.

### **2.5 Characterization of the Chitosan- MCC Composite**

Structural and morphological characterization of chitosan biopolymers were carried out by FTIR spectroscopy and Scanning Electronic Microscopy (SEM) respectively. The Degree of deacetylation (DA) was determined and calculated by titrimetric method and infrared spectroscopy [17].

In titrimetric method, dried chitosan (0.2 g) was first dissolved in 20 cm<sup>3</sup> 0.1 M hydrochloric acid

and then in 25 cm<sup>3</sup> deionized water (DI). After 30 minutes of continuous stirring, next portion of deionized water (25 cm<sup>3</sup>) was added and stirring was continued for another 30 minutes. When chitosan was totally dissolved, the solution was titrated with 0.1 mol-dm<sup>-3</sup> sodium hydroxide solution using automatic burette (0.01 cm<sup>3</sup> 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<sup>-3</sup> 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. From experiment, volume of required 0.1 mol-dm<sup>-3</sup> sodium hydroxide solution found is  $V_2 - V_1 = 10.06$  mL. So the calculated degree of deacetylation of prepared chitosan is 84.28%.

Degree of deacetylation measurement by infrared spectroscopy is based on absorbance ratios of various spectral bands [17]. The ratio of absorbance of amide-I at 1655 cm<sup>-1</sup> to that of hydroxyl group at 3450 cm<sup>-1</sup> in chitosan depends upon the degree of deacetylation in the chitosan. The lower the absorption of amide-I group, the higher is the degree of deacetylation. The formula used for DD calculation is below:

$$DD [\%] = \frac{A_{1655}}{A_{3450}} \times 115 \quad [17]$$

By using the Lambert- Beer's law of absorbance, the absorbance at 1655 cm<sup>-1</sup> and 3450 cm<sup>-1</sup> were calculated as  $A_{1655} = 0.120$  and  $A_{3450} = 0.187$  respectively.

Degree of deacetylation of chitosan calculated from infrared spectroscopy= 73.39%

## 2.6 Preparation of Chromium (VI) Stock Solution

To prepare 1000 ppm chromium solution, 0.287 g solid pure potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) was dissolved in 1L de-ionized water. The prepared solution was kept as stock solution and solution of various concentrations was made by diluting this stock solution. Further dilution resulted 0.5

ppm, 1.0 ppm and 1.5 ppm Cr(VI) stock solution for the process treatment.

## 2.7 Preparation of Tannery Effluent for Adsorption Study by Digestion

Major source of Cr(VI) contamination is tannery effluent which is released directly into river water. Tannery waste water sample was collected from tannery in local area. As the tannery effluent contains a great amount of suspended solid which may create difficulty during atomic absorption spectroscopy (AAS) measurement. So before treatment it is necessary to digest the sample. About 30 mL effluent was taken in a beaker and 15 mL of conc. HNO<sub>3</sub> was added. Then the solution was heated on a hot plate at 60-75°C to reduce its quantity to half, 7.5 mL of HClO<sub>4</sub> was added to solution and the solution was heated until all the acids were removed. Then the sample was diluted with water to get the required volume and finally the sample was ready for analysis. Initially the concentration of digested sample was evaluated by AAS and used as stock solution of tannery effluent which was diluted to 1.00, 2.00 and 3.00 ppm solution. Effluents physico-chemical characteristics are presented in Table 1. The tannery waste water samples were treated with the composite materials at optimized conditions (pH 5.0, contact time 240 minutes, dose 2 g/L).

**Table 1. Physico-chemical characteristics of tannery effluent**

Characteristics	Values
Color	Bluish
pH	02.56
Odor	Pungent
Conductivity, ms/cm	43.90
Dissolve oxygen(DO), mg/l	06.40
Total dissolve solid(TDS), mg/l	22.00
Salinity,%	28.30
Cr(VI) (after 10 times dilution), ppm	26.45

## 2.8 Procedure for Batch Adsorption Studies

Adsorption studies were carried out in batch mode to investigate the effects of different parameters such as pH, dosage and varying contact time. Cr(VI) solution was initially adjusted at pH 7.00 by adding 0.1M HCl or 0.1M NaOH while keeping the temperature constant at 25°C. The solution containing adsorbate and adsorbent

was agitated at predetermined time intervals, decanted and filtered. The filtered solution was subjected to determine its Cr(VI) content using AAS (SHIMADZU AA-7000). The different experimental conditions were shown in Table 2.

To compare the Cr(VI) removal capacity of chitosan and prepared composite, known amount (2 g/L) of chitosan and composite were added to 1,2,4 ppm of Cr(VI) solution in different conical flasks. The percentage of Cr(VI) adsorption was calculated using the relation:

$$A (\%) = \frac{C_o - C_e}{C_e} \times 100$$

Where  $C_o$  and  $C_e$  were the initial and final concentration of Cr(VI) ions in identical unit.

### 3. RESULTS AND DISCUSSION

#### 3.1 FT-IR Analysis

##### 3.1.1 FT-IR analysis of the prepared chitosan

The FT-IR spectra of prepared chitosan showed important absorption bands to identify the characteristic functional groups which were recorded in the middle infrared (4000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$ ). The infrared spectra for chitosan biopolymers are shown in Fig. 1. The stretching vibrations of -OH bond of the prepared chitosan was found at 3478.68  $\text{cm}^{-1}$  and that for C-H were observed at 2924.13  $\text{cm}^{-1}$ . The absorption peaks at 1656.88  $\text{cm}^{-1}$ , 1571.05  $\text{cm}^{-1}$ , 1422.53  $\text{cm}^{-1}$ , 1378.16  $\text{cm}^{-1}$  were associated with the presence of the C=O stretching of the amide I band, bending vibrations of the N-H (N-acetylated residues, amide II band), C-H bending, OH bending respectively. The peak at 1157.31  $\text{cm}^{-1}$  was assigned for anti-symmetric stretching of (C-O-C) bridge, 1075.33  $\text{cm}^{-1}$  and 1025.18  $\text{cm}^{-1}$  were anticipated to the skeletal vibration involving C-O stretching.

##### 3.1.2 FT-IR analysis of the MCC

The FT-IR spectrum of Microcrystalline Cellulose is shown in the Fig. 2. For MCC the band at 3438.17  $\text{cm}^{-1}$  was attributed to the O-H stretching vibration of hydroxyl group in the cellulose. The band at 2910.63  $\text{cm}^{-1}$  corresponds to C-H stretching vibration of -CH<sub>2</sub>- groups. The band at 1640.49  $\text{cm}^{-1}$  was assigned for C=O in the aldehyde on the terminal anhydroglucose unit. The peak at 1436.99  $\text{cm}^{-1}$  was due to CH<sub>2</sub>

blending. Band found at 1366.59  $\text{cm}^{-1}$  was associated with C-O stretching vibration of CH<sub>2</sub>-OH groups. Also a band observed at 1051.22  $\text{cm}^{-1}$  was for -C-O-C- in the cellulose molecule [18-20].

##### 3.1.3 FT-IR analysis of chitosan-MCC composite

The FTIR spectrum of the chitosan-MCC film in Fig. 03 showed that, the broad peak for-OH and -NH groups were shifted from 3438.17  $\text{cm}^{-1}$  to 3631.96  $\text{cm}^{-1}$ . This shift indicated that interaction between amine groups in chitosan and OH groups in cellulose occurred. The sharp peak of -OH at 3631.96  $\text{cm}^{-1}$  indicated the availability of free -OH group of MCC. The carbonyl band of the composite was shifted to a lower frequency, from 1656.88  $\text{cm}^{-1}$  to 1654.92  $\text{cm}^{-1}$ . This FTIR spectrum showed that the composite may be prepared by the interaction of -NH group of chitosan and -OH group of MCC.

#### 3.2 Scanning Electron Microscopy (SEM) Analysis of Prepared Materials

The SEM micrographs were fashioned at a scanning electron microscopy (model JSM-6490) with accelerating voltage of 20KV, to explore the morphology and surface structure of the adsorbents with required magnification at room temperature.

##### 3.2.1 SEM analysis of chitosan

Under the electron microscopic examination with X5000 magnification Fig. 4(c), chitosan illustrated non homogenous and non smooth facade with straps and shrinkage [21]. It is also revealed that the diameter of the chitosan particle is 5  $\mu\text{m}$  and that the surface of chitosan is closely packed with wrinkle effect which might trap Cr(VI) ions in solution. These surface features of prepared chitosan agreed with the literature [21,22].

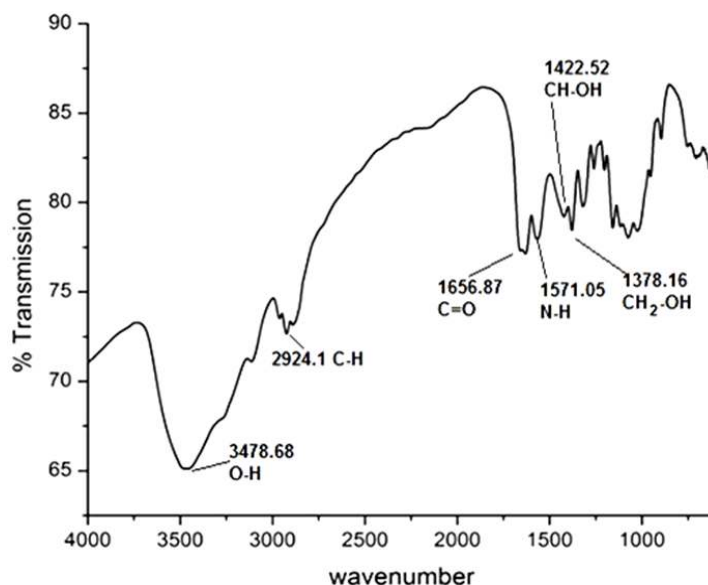
##### 3.2.2 SEM analysis of MMC

The morphology of MCC powder after acid hydrolysis was studied through SEM and closer examination of this micrograph revealed that the sizes of MCC fibers are inconsistent. Because of acid hydrolysis a big fraction of amorphous areas were entirely destroyed and cellulose crystallites in the needle form was formed. Portions with agglomerated micro fibrils could also be observed in Fig. 4(b) with magnification of

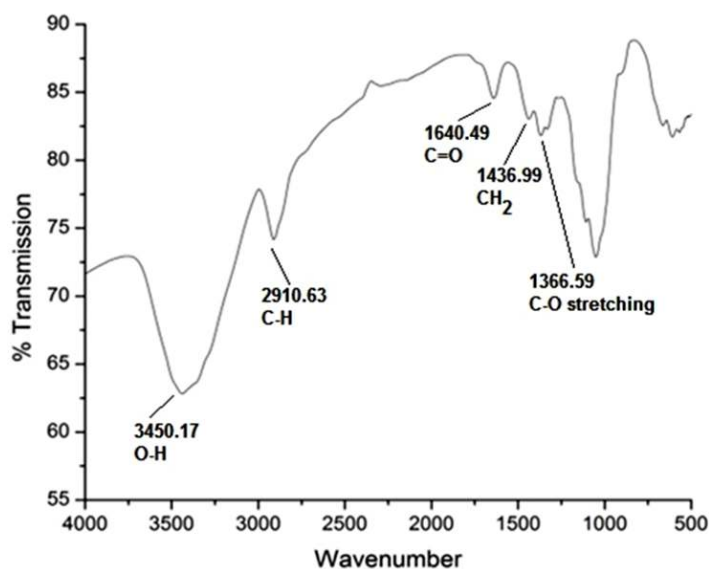
X2000. The MCC fibers also exposed the rod like fractured surface which also showed good structure appearance and ribbon shaped with agreement with literature [23].

**Table 2. Experimental conditions for Cr(VI) removal**

Experimental conditions	pH	Time (Minutes)	Initial Conc. (ppm)	Dosage (g/L)
Effect of pH	2.0-6.0	60	2	2
Effect of contact time	5.0	60-300	2	2
Effect of adsorbent dose	5.0	240	2	0.25-5.0
Effect of initial concentration	5.0	240	1-4	2



**Fig. 1. FT-IR spectrum of the prepared chitosan**



**Fig. 2. FT-IR spectrum of the prepared MCC**

### 3.2.3 SEM analysis of chitosan-MMC composite

In Fig. 4(c) with X2000 magnification of composite, the rough and porous surface was observed because of the interaction of MCC with chitosan. Because of irregular void surfaces of composite, increase in the contact area were resulted which improved Cr(VI) adsorption capacity. For in-situ applications, the efficiency of the sorbent increased by decreasing the particle size. Composite particles diameters found from SEM are between 1  $\mu\text{m}$  to 3  $\mu\text{m}$  which is significantly small particle. Hence chitosan-MCC composite showed enhanced adsorption capacity.

### 3.3 Batch Adsorption Experiments

#### 3.3.1 Effect of pH

The pH of the solution affects the surface charge of the adsorbents, so the effect of pH on adsorption of Cr(VI) using composite is a very sensible factor. The hydrogen and hydroxyl ions can be adsorbed quite strongly, and therefore the adsorption of other ions is affected by the pH of the solution [24]. To investigate the effect of pH on the Cr(VI) removal efficiency, pH was varied from 1.0 to 6.0 and to adjust pH, 0.1M HCl and 0.1 M NaOH solutions were employed.

As shown in Fig. 5 (error bar =  $\pm$  SD, n=3) the maximum adsorption was found at pH 5.0 and it

is 86.60%. The concept of increasing Cr(VI) removal efficiency with increasing pH 2.0 to pH 5.0, can be explained on the basis of a decrease in competition between proton and Cr(VI) for same functional groups which resulted in a lower electrostatic repulsion between composite surface and Cr(VI) ions.

At low pH, the amine groups of chitosan reacted with  $\text{H}^+$  and got protonated.



So, at solution chitosan got positively charged while Cr(VI) ion was also positively charged. As a result repulsive forces occurred between Cr(VI) ion and chitosan instead of attraction. So at low pH chromium uptake by composite was reduced. Decrease in adsorption at higher pH (pH 6.0) was due to formation of soluble hydroxyl complexes [25]. Therefore pH of the media should be properly controlled according to the type of metal to be absorbed.

#### 3.3.2 Effect of contact time

Contact time was varied from 60-300 minutes and adsorption increased with increase in time of contact until it reached the equilibrium which is shown in Fig. 6 (error bar =  $\pm$  SD, n=3). pH of solution was kept at 5.0 and temperature was maintained at 25°C.

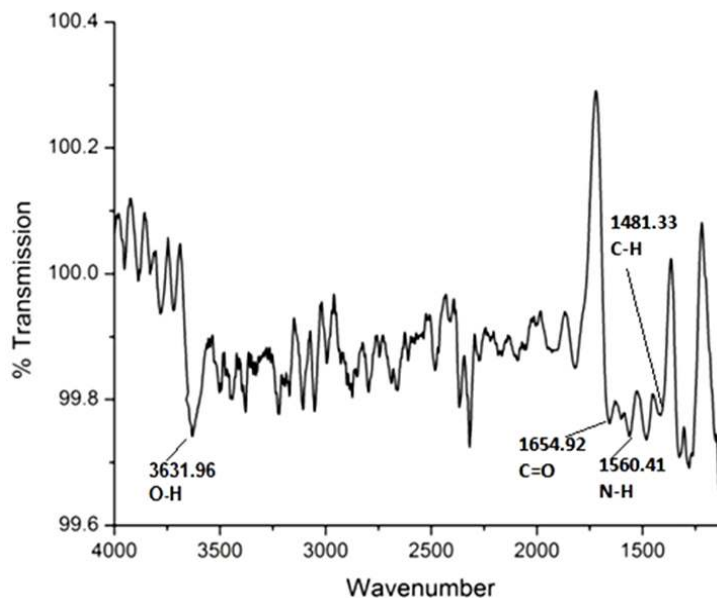
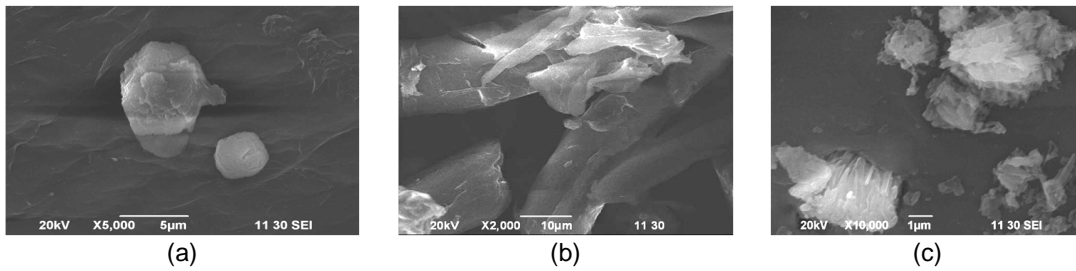
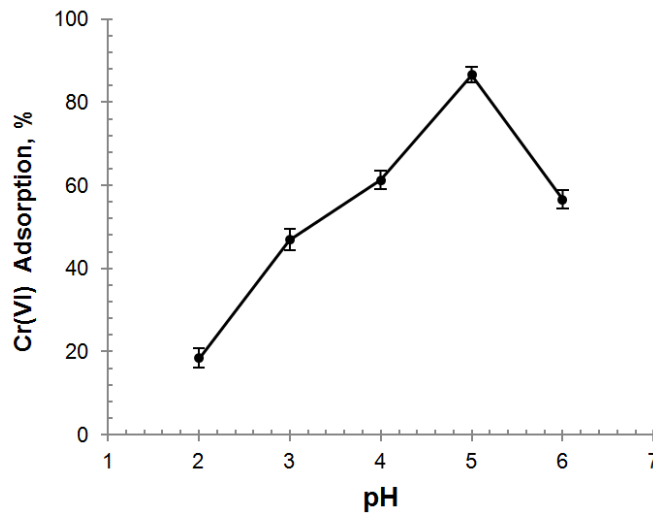


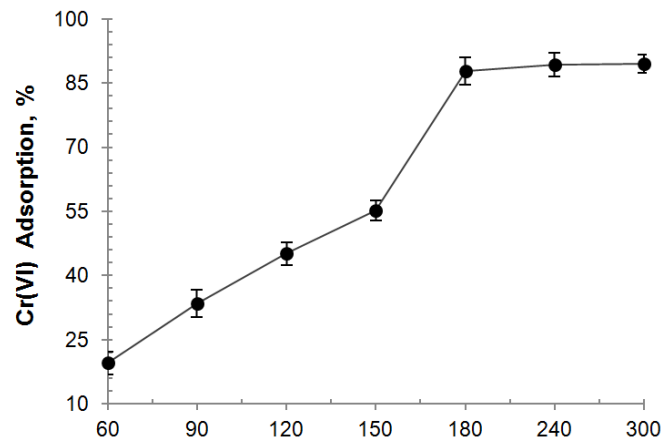
Fig. 3. FT-IR spectrum of the chitosan-MCC composite



**Fig. 4. Scanning Electronic Microscopy (SEM) micrographs of (a) Chitosan, (b) MCC and (c) Chitosan-MCC composite**



**Fig. 5. Effect of pH on the adsorption of Cr(VI)**



**Fig. 6. Effect of contact time on removal efficiency of Cr(VI)**

Initial removal occurred immediately as soon as the metal and composite came into contact and after some extent further increase in contact time did not increase the uptake, due to decrease of the easily available

active sites for the binding of metal ions the equilibrium is reached [26]. After 240 minutes in contact the adsorption was not further proceeding and it remained constant at 300 minutes.



### 3.3.3 Effect of dose

The experiment was carried out by taking various adsorbent concentrations ranging from 0.25 to 5 g/L separately keeping the other variables (pH and contact time) constant. Fig. 7 (error bar = ± SD, n=3) represents the % removal of Cr(VI) of the prepared composite. At 2 ppm Cr(VI) initial concentration, the % removal of Cr(VI) increased with the increase of the adsorbent dosage. The increase in adsorption with the increase in amount of composite dose may be attributed to the fact that more surface area were available for adsorption to occur. The optimum adsorption was found at 2 g/L dose and it is 93.03%. After that with increasing the adsorbent dose the adsorption did not change significantly because there was a chance of aggregation of active sites of adsorbent.

### 3.3.4 Effect of initial concentration

The initial concentration of heavy metal ions is an important parameter in adsorption. Fig. 8 (error bar = ± SD, n=3) shows the effect of initial Cr(VI) concentration ranged from 1-4 ppm and maintaining other conditions as constant. It was observed that the percentage of adsorption efficiency increased from 82.24% to 93% at initial concentration of 1 ppm to 2 ppm respectively. Because of more active Cr(VI) species to active adsorption sites available, % removal efficiency increased. Increase from 2 ppm initial solution resulted decrease in Cr(VI) adsorption, since a definite amount of adsorbent can adsorb a specific amount of Cr(VI) ions and

occupied sites are unavailable for excess Cr(VI) ions.

## 3.4 Equilibrium Model

Adsorption isotherms are mathematical models based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir and Freundlich isotherms.

### 3.4.1 Langmuir isotherm

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions [27]. According to Langmuir theory, the saturated monolayer isotherm can be expressed as:

$$q_e = \frac{q_{max} b C_e}{1 + b C_e}$$

The above equation can be rearranged as following linear form:

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{1}{q_{max}} C_e$$

Where:

$C_e$  = equilibrium concentration ( $\text{mg L}^{-1}$ ),  
 $q_e$  = amount of metal ion adsorbed ( $\text{mg g}^{-1}$ ),  
 $q_{max}$  = maximum adsorption capacity ( $\text{mg g}^{-1}$ )  
 $b$  = sorption equilibrium constant ( $\text{mg L}^{-1}$ ).

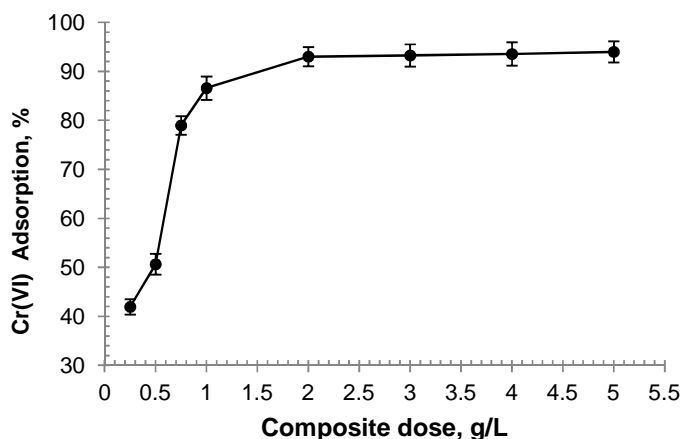
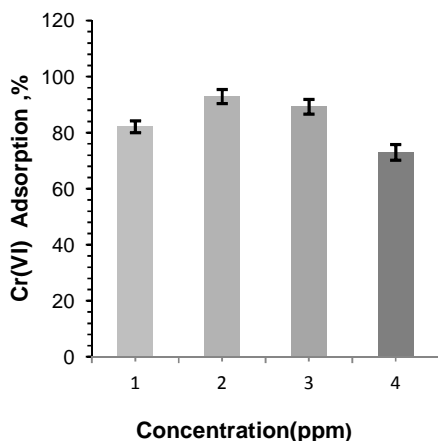


Fig. 7. Effect of Dose on the removal efficiency of Cr(VI)

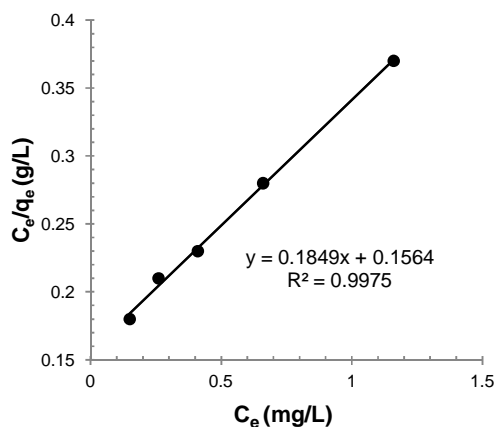


**Fig. 8. Effect of initial concentration on the adsorption of Cr(VI)**

A graph of  $C_e$  versus  $C_e / q_e$  gives the straight line of slope  $1/q_{max}$  and intercept of  $1/bq_{max}$  (Fig.09). It shows the adsorption of Cr(VI) follows Langmuir isotherm model. The values calculated from the intercept and slope of linear dependencies and the correlation coefficient ( $R^2$ ) associated to Langmuir isotherm are summarized Table 3.

**Table 3. Values of Langmuir isotherm constants**

$R^2$	$q_{max} (mg \cdot g^{-1})$	$b (L \cdot mg^{-1})$
0.997	5.434	1.18



**Fig. 9. Langmuir adsorption isotherm**

### 3.4.2 Freundlich isotherm

The Freundlich equation which is used to describe heterogeneous surface energies are expressed as:

$$q_{max} = K_F C_{eq}^{1/n}$$

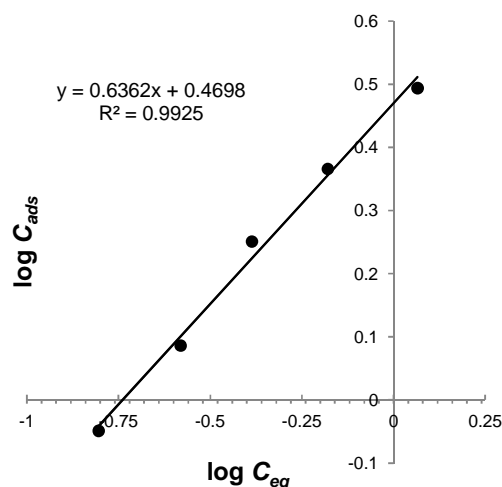
In this study the following linearised form of the Freundlich equation was used.

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

Where:

$C_{ads}$  = amount of Cr(VI) adsorbed ( $mg \cdot g^{-1}$ )  
 $C_{eq}$  = equilibrium concentration in solution ( $mg/L$ )  
 $K_F$  = Freundlich constant ( $mg/g)(L/mg)^{1/n}$  where  $1/n$  is dimensionless

Freundlich equation plot of  $\log C_{ads}$  vs.  $\log C_{eq}$  from yielded a straight line as shown in Fig. 10.



**Fig. 10. Freundlich adsorption Isotherm**

**Table 4. Values of Freundlich isotherm constants**

$R^2$	$k_F (mg \cdot g^{-1})$	$1/n$	$n$
0.992	2.944	0.636	1.57

The Cr(VI) solutions were at low concentrations hence the logarithmic values were found negative. Linear regression value found from Fig. 10 is 0.992, which is very good fit with Freundlich isotherm [28].

The  $R^2$  value indicates the shape of the isotherm. According to literature [29]  $R^2$  values between 0 and 1 indicate favorable adsorption. Also  $R^2$  values equal to 0 indicate irreversible adsorption,  $R^2 = 1$  is linear and  $R^2 > 1$  is unfavorable. As shown in Table 3 and Table 4 according to the correlation coefficients ( $R^2$ ), a suitability order of the two models tested was Langmuir and Freundlich. Thus, the Langmuir model was the most acceptable to explain the adsorption

process of Cr(VI) onto Chitosan-MCC composite surface suggesting a monolayer adsorption process. The maximum adsorption capacity ( $q_{max}$ ) for Cr(VI) from Langmuir model was  $5.434 \text{ mg.g}^{-1}$ . Furthermore, the value of  $1/n$  obtained from Freundlich model was less than 1, which also suggested the favorable adsorption of Cr(VI) onto composite. This is consistent with the result of Langmuir model. Freundlich isotherm constant  $n$  value ranging from 1 to 10 indicates beneficial adsorption [30].

### 3.5 Removal of Cr(VI) from Tannery Waste Water

Tannery effluents described in Table 1 were first digested as presented earlier. Prior treating with chitosan-MCC composite pH of the collected sample was adjusted to 5.0. From tannery stock solution, 20 mL of 2.0 ppm solution was taken and optimum composite dose (2 g/L) was added. Then the mixture was continuously shaken using a shaker for 4 hours at room temperature (25°C). Then the solution was filtered and the filtrate was analyzed using AAS (Shimadzu, AA-7000) to determine amount of Cr(VI) adsorbed by composite.

Final Concentration of Cr(VI) in tannery effluent after treating with composite was 0.205 ppm and the removal efficiency of Cr (VI) from tannery effluent by chitosan-MCC composite was 89.75%. Presence of other metals ions in tannery effluent may reduce the efficiency than that of standard Cr(VI) solution (93.03%).

Another analysis was done to compare chitosan and chitosan-MCC composite as adsorbent on tannery effluent with same treatment condition (pH 5.0, contact time 240 minutes, dose 2 g/L). The results are presented in Table 5.

**Table 5. Cr(VI) removal from tannery effluent by two adsorbents**

Adsorbent	Initial conc. (ppm)	Final conc. (ppm)	Removal efficiency (%)
Chitosan	1.9539	0.4682	76.12
Composite	1.9539	0.2981	89.34

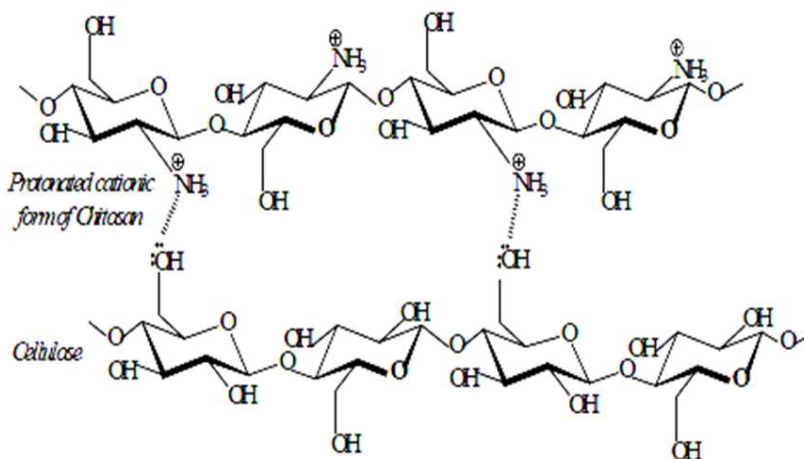
Composite showed the higher removal efficiency than chitosan. It might be due to the exposure of larger amount of amino group and the hydroxyl group of microcrystalline cellulose in the chitosan-MCC composite.

### 3.6 Process Mechanism

#### 3.6.1 Composite formation mechanism

There was an interaction of chitosan and MCC during composite formation. Fig. 11 proposes the interaction in acidic solution:

Chitosan contains amine groups  $-\text{NH}_2$ , which would be in the protonated cationic form ( $-\text{NH}_3^+$ ) in acidic solution, in contact with the nucleophilic surface of cellulose containing  $\text{OH}^-$  groups. It could be interacted via hydrogen bonding and/or ion-dipole interactions forming cross linked biopolymers composites.

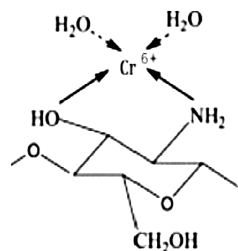


**Fig. 11. Structure of Chitosan-MCC interaction**

### 3.6.1 Cr(VI) adsorption mechanism

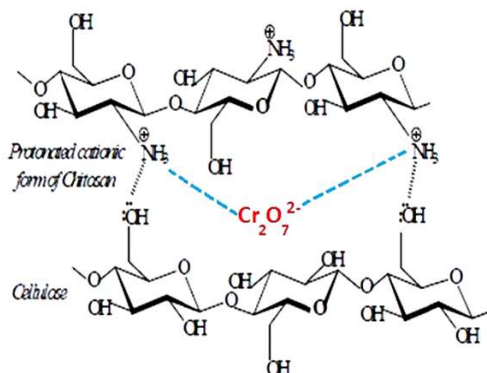
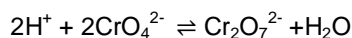
The mechanism of adsorption of Cr(VI) ions by chitosan-MCC composite by  $-NH_2$  group and  $-OH$  group can be explained in two way.

1. The amine group ( $-NH_2$ ) may initiate a coordinate bond with Cr(VI) ion which is shown in Fig. 12. The bond is formed between the free electron pairs of the nitrogen in the amine group and the void orbitals of the metal. The fraction of acetylated units determines the number of free amine groups available for binding [25]. Chitosan used in this study had a higher degree of deacetylation, so in composite large number of amino group exposure may be happened leading to superior adsorption capacity.



**Fig. 12. Coordinate bond with Cr(VI) ion by chitosan-MCC composite**

2. In this mechanism (Fig. 13) Cr(VI) at low pH forms stable anions such as  $Cr_2O_7^{2-}$ , while the composite is in the protonated cationic form ( $-NH_3^+$ ) within acidic solution, leading to the electrostatic attraction between sorbent and sorbate.



**Fig. 13. Entrapment of Cr(VI) ion by chitosan-MCC composite**

### 4. CONCLUSION

It is concluded from our results that, the bio-adsorbent chitosan-microcrystalline cellulose composite is a good adsorbent for removal of chromium (VI) ion from tanning effluent. The optimum pH for the the maximum adsorption was found at pH 5.0 and it is 93% with a composite concentration (2 g/L) and the effective settling rate was 240 minutes. The bio-adsorbent prepared from waste materials (shrimp shell and waste cotton rags) could be a viable adsorbent for removal of Cr(VI) ions from tannery effluent. Experimental results obtained were modeled using Langmuir isotherm and Freundlich isotherm. It is found that Langmuir Isotherm was well fitted with  $R^2$  value of 0.997. The unique properties of chitosan-MCC composite together with availability make it an exciting, promising and environment safely agent for the heavy metal adsorption from wastewater.

### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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