Investigation of chromium removal efficacy from tannery effluent by synthesized chitosan from crab shell

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Abstract

The efficiency of chromium removal from tannery effluents using prepared crab shell chitosan was studied. Adsorption of Cr by chitosan was investigated at various contact times, pH values, adsorbent dosages, and temperatures. The amount of Cr adsorbed under different conditions was evaluated using atomic adsorption spectroscopy (AAS). Subsequently, the changes in the physicochemical parameters were also examined. It was found that the total dissolved solids (TDS), electrical conductivity (EC), and turbidity of the tannery effluent decreased significantly after treatment with crab shell chitosan. No significant changes were found after different soaking times; in most cases, the best adsorption was achieved within the first hour of treatment. On the other hand, the total organic carbon (TOC) and pH increased significantly after treatment with chitosan, possibly owing to dissolution of organic compounds from the adsorbent materials. The concentration of Cr was significantly reduced after treatment with chitosan under different treatment conditions. However, the highest amount of Cr was adsorbed within the first hour of contact. After studying different treatment conditions, it was found that maximum Cr removal from the tannery effluent was achieved at pH 3 (60 °C) using an adsorbent dose of 5 g/100 mL.

Thematic Scheme to be inserted here

1. Introduction

The tanning industry has been considered a major pollution source, and tannery wastewater is subsequently a potential environmental concern. Tannery wastewater characteristically contains a complex mixture of both organic and inorganic dissolved and suspended solids with high oxygen demand and potentially toxic metal salt residues [1, 2]. Chlorinated phenols and chromium have been found to be closely associated with tannery waste [3, 4]. Pollution by Cr is of considerable concern, as the metal has found widespread use in electroplating, metal finishing, leather tanning, nuclear power plants, and the textile industry [5]. Cr occurs in two relatively stable valence states in aqueous solution, i.e., in the forms of Cr (III) and Cr (VI), which have quite different effects on biological systems. Cr (III) is considered an essential micronutrient for humans, playing a role in the maintenance of normal glucose, cholesterol, and fatty acid metabolism [6]. In contrast, Cr (VI) is highly toxic, as it can diffuse as CrO_4^{2-} or $HCrO_4^-$ through cell membranes [7]. Its acute toxic effects include immediate cardiovascular shock, with later effects on the kidneys, liver, and blood-forming organs [8, 9], and it can damage nerves, the liver, and bones and block the functional groups of essential enzymes [10–13]. Hexavalent chromium is toxic and mutagenic to most organisms and is known to cause cancer; it also causes lung carcinoma in human beings [14]. Exposure to metals like chromium increases the risk of dermatitis, ulcers, nasal septum perforation, and lung cancer [15].

The conversion of raw leather to finished leather involves different processes, including disinfecting, soaking, fleshing, dehairing, bathing, tanning, and finishing. The various chemicals used for leather processing are the main sources of chemical pollutants [16]. The Hazaribagh tanneries in Bangladesh follow the practice of chrome tanning, which is used by 80% of tanneries in South Asian and African countries. In traditional chrome tanning practices, only 50–60% of the chromium applied is adsorbed by the leather and the rest is discharged as waste [17]. Most of the industries in the Hazaribagh area do not recover chromium for reuse. Once deposited in the soil, chromium may be virtually permanent [18]. It enters the food chain through consumption of plant material. A high concentration of Cr has been found to be harmful to vegetation. As the chromium concentration in plants increases, several biological parameters are adversely affected. Ultimately, there is loss of vegetation, and land sometimes becomes barren [19].

Heavy metals produce undesirable effects, even if they are present in trace quantities. Traditional treatment methods such as chemical precipitation as metal hydroxides, electrodeposition, ion exchange, chemical oxidation or reduction, filtration, electrochemical treatment, application of membrane technology, and evaporation recovery have been applied for metal removal from industrial wastewater [20, 21]. However, these processes have considerable disadvantages including incomplete metal removal, requirement of expensive equipment and monitoring systems, high reagent or energy requirements, or generation of toxic sludge or other waste products that require disposal [22–24]. Sorption, however, seems to be a good alternative. New research has shown effective sorption of heavy metals using agricultural products and by-products, such as Oat biomass, saw dust, rice husk, raw rice bran, Sugarcane bagasse, fly ash, Coconut shell etc. [25].

The use of adsorbents containing natural polymers has received great attention, particularly polysaccharides such as chitin and chitosan [26, 27]. Chitosan is a biodegradable, biocompatible, non-toxic biopolymer reported to be an efficient heavy metal scavenger owing to the presence of amino groups [28]. Biosorption is considered an effective method for heavy metal removal as it is cost effective and environmentally friendly.

A lot of work has been done in the removal of Cr ions from aqueous solution using chitosan and various modified chitosan [27, 29-37]. Most of the work focused on the removal of Cr using synthetic solutions but not actual water systems. Although the effluent from real industries has a heterogeneous mixture of numerous chemicals with complex interactions between them, there are very few studies regarding these complex water systems. Thus, in this study, the effectiveness of decontamination of tannery wastewater using synthesized chitosan from crab shells was investigated.

2. Materials and Methods

2.1. Materials

Crab shells were collected from a local market. Dihydrogen phosphate salt and potassium hydrogen phthalate salt were purchased from Sigma Aldrich (India). Distilled water and Milli-Q water were employed throughout this work and all other reagents such as acetic acid, hydrochloric acid, and sodium hydroxide were of analytical reagent grade.

2.2. Methods

2.2.1. Preparation of chitosan from crab shells

Chitosan was prepared according to the method of Yen et al. (2008) [38] with some modification. The collected crab shells were washed thoroughly with distilled water. At the preconditioning stage, the crab shells were soaked in a 0.05 M acetic acid solution for 24 h. Then, the shells were washed thoroughly with distilled water and dried to remove excess water. Then, the dried shells were demineralized using 0.68 M HCl (1:10 w/v) at ambient temperature (approximately 30 °C) for 6 h. The residue was washed with distilled water until a pH in the 6.5–7.5 range was obtained and then the residue was dried again. Afterwards, the demineralized shells were deproteinized using a 0.62 M NaOH solution (1:10 w/v) at ambient temperature (approximately 30 °C) for 16 h. Then, the residue was washed thoroughly with distilled water until a pH in the 6.5–7.5 range was obtained. The chitin obtained through the above process was deacetylated with 40% NaOH (1:10 w/v) for 1 h at 120 °C. After deacetylation, the chitosan was washed thoroughly with water and then with distilled water until a pH in the range of 6.5–7.5 was obtained. The chitosan was dried, ground, and screened for later use as an adsorbent.

2.2.2. FTIR analysis of synthesized chitosan

Fourier transform infrared (FTIR) spectroscopy measurement was performed using an FTIR analyzer (IRPrestige-21, Shimadzu, Japan) to determine the presence of functional groups in the synthesized crab shell chitosan at room temperature. The chitosan was dried thoroughly in an oven at 50 °C and KBr was used to prepare pellets. Two grams of KBr were placed in a mortar and the sample was added (about 1–2%), mixed, and ground into a fine powder. Two stainless steel disks were taken. A piece of precut cardboard was placed on top of one disk that had been stored in a desiccator, and the cut-out hole was filled with the finely ground mixture of chitosan and KBr. The second stainless steel disk was placed on top and the "sandwich" was transferred to the pistil of a hydraulic press. The sample pellet was pressed with a pressure of 20000 psi, to prepare a pellet of chitosan-KBr mixture. Then, this film was removed from the hydraulic press, and had become homogeneous and transparent in appearance. When it was ready for FTIR analysis, the analysis was performed in the 4000–400 cm^{-1} range.

2.2.3. Sample collection

The wastewater samples were collected from Eco-Tan Leathers tannery at Hazaribagh, Dhaka, Bangladesh. The samples were collected from the chrome tanning unit of the industrial unit in clean dry plastic containers; each of them contained 20 L of effluent. Prior to sampling, the containers were washed with a 1 M HNO_3 solution and rinsed thoroughly with distilled water. The containers were also rinsed with sample water before the collection of the water samples. After the collection of wastewater, the pH and dissolved oxygen (DO) were measured in situ. Then, the containers were sealed tightly and preserved for later experiments.

2.2.4. Measurement of physicochemical parameters

The measured physicochemical parameters of the tannery wastewater samples were pH, total dissolved solids (TDS), turbidity, biochemical oxygen demand (BOD), DO, electrical conductivity (EC), salinity, and chemical oxygen demand (COD). The pH and TDS were measured using a pH meter (HM-30P pH Meter) and TDS meter (Hanna, HI 8734), respectively. EC, salinity, DO, and turbidity were measured using an EC meter (CM- 31P), salinity meter (Hanna, HI 8734), DO meter (Jenway, 970 DO2 Meter, U.K.), and turbidity meter (Hanna, HI 93703), respectively. BOD and COD were measured using the five-day BOD test and closed reflux colorimetric method, respectively. All instruments were calibrated or verified in accordance with the manufacturers' instructions prior to use in the field. If the instrument readings were not within 10% of the calibration standards, then the unit was recalibrated. The probe or the electrode of the instrument was rinsed thoroughly with distilled water and wiped using tissue paper. The probe was placed in the water sample to be measured and the instrument reading was allowed to stabilize. The final reading was recorded.

The BOD was measured using the five-day BOD test. In order to obtain BOD_5, the DO concentrations in a sample must be measured before and after the incubation period and appropriately adjusted by the corresponding sample dilution factor. This analysis was performed using 300 mL incubation bottles in which buffered dilution water was dosed with sample water and stored for five days in an incubator at 20 °C to prevent DO production via photosynthesis [39]. The BOD_5 was calculated as follows:

$$BOD_5 = \frac{(D_0 - D_5)}{P} \quad \text{.......................................(1)}$$

Where, D_o is the dissolved oxygen (DO) of the diluted solution after preparation (mg/l), D_5 is the DO of the diluted solution after 5 day incubation (mg/l) and P is the decimal dilution factor.

2.2.5. Batch adsorption using crab shell chitosan

The adsorption of chromium ions by chitosan was examined at different contact times (1, 2, 5, 6, 12, and 24 h). Five grams of chitosan were soaked in 100 mL of tannery wastewater. Then, the mixture was stirred continuously using a shaking incubator for 1–24 h at room temperature. After incubation for different times, the chitosan was separated from the wastewater by filtering. Then, the physicochemical parameters were measured. Furthermore, adsorption of Cr by chitosan was examined at different adsorbent dosages (1, 1.5, 2, 3, 4, and 5 g), pH values ranging from 3 to 8, and temperatures (30, 40, 50, and 60 °C).

2.2.6. AAS analysis

Atomic adsorption spectroscopy (AAS) is one of the most popular analytical techniques used for the determination of metals and metalloids in solution. Five standard solutions of chromium of different concentrations (1, 2, 3, 4, and 5 ppm) were prepared as reference solutions. After filtering the chitosan from the wastewater, 0.05 mL of concentrated HNO_3 was added to each filtrate. The filtrates and raw samples were analyzed using flame AAS (AA-700, Shimadzu, Japan) to determine the amount of chromium adsorbed by chitosan.

2.2.7. TOC analysis

For TOC analysis, TOC vials and microfiber filter papers were combusted in a digital muffle furnace (MF-03, made in Korea) at 450 °C. Then, the filtrates and raw samples were filtered using glass microfiber filter paper (Whatman Schleicher & Schuell Glass Microfibre filters, England) using a filter unit and analyzed to determine the TOC using a potassium hydrogen phthalate solution as the standard solution in the TOC analyzer (TOC-L CNP, Shimadzu). The standard solution was prepared by dissolving 0.21 g of potassium hydrogen phthalate in 1000 mL of Milli-Q water.

3. Results

3.1. Physicochemical parameters of tannery effluent

The physicochemical parameters of the tannery effluent, such as BOD, color, chromium concentration, DO, EC, odor, pH, salinity, TDS, TOC, turbidity, and COD, were measured. Most of the values of these parameters were above the acceptable limits. The pH was 4.56, whereas the acceptable range is 6.5–9 [40]. The chromium concentration was 1345 mg/L, which is very much toxic for living beings, and the acceptable value is only 2 mg/L. The TDS and EC were alarming because the acceptable value for TDS is only 2100 mg/L. The tannery effluent was odorous and bluish, which will affect photosynthesis in water bodies. The physicochemical parameters are shown in Table 1.

Table 1 to be inserted here

3.2. FTIR analysis of chitosan

The FTIR spectrum of the synthesized chitosan showed many peaks (Fig. 1). Among them, a characteristic peak at 3305.99 cm^{-1} due to the N-H symmetric stretching vibration indicates the presence of amino ($-NH_2$) groups. The peak at 1645.28 cm^{-1} due to N-H bending also indicates 1°amines. The peaks at 3643.53 and 3444.8728 cm^{-1} are attributed to O-H stretching for an alcohol or phenol. The peak at 1070.49 cm^{-1} indicates C-N stretching for aliphatic amines. Therefore, the FTIR spectrum suggests that chitosan was prepared successfully [41].

Figure 1 to be inserted here

3.3. Changes in physicochemical parameters of the tannery effluent after adsorption by chitosan

From the result of physico-chemical properties of tannery effluent after adsorption with synthesized chitosan (Fig 2), it was found that the each parameter (pH, TOC, EC and TDS) was changed significantly ($p < 0.05$) from their respective initial content. In the batch adsorption the pH, adsorbent dose and temperature were 4.56, 5g/100ml, and 30˚C respectively. The pH (Fig 2a) of the effluent increased to an acceptable limit (8.13-8.72). There was a significant difference between the initial value and the value after treatment for different soaking time (1-24 hr) at 5% level of significance. However, there is no significant change observed within the applied soaking time (1-24 hrs).

Figure 2 to be inserted here

There was a significant change in the Total Organic Carbon after adsorption with synthesized chitosan from the initial TOC value (1302 mgL^{-1}) and was increased to a certain value (up to 1916 mgL^{-1}). A significant difference was found in TOC value with increasing soaking time for adsorption ($p<0.05$) (Fig 2b). The TDS values after the adsorption with synthesized chitosan showed a significant decrease ($p<0.05$) from the initial value (Fig 3c). TDS decreased from 65500 to 43600mg/L within one hour of adsorption. After one hour the decrease of TDS was not significant with the TDS at one hour of adsorption.

A significant decrease ($p<0.05$) was observed in EC values from the initial value after adsorption with the synthesized chitosan (Fig 2d). EC decreased from105.1 to 92.8 mS/cm within two hours of adsorption time. There was no significant difference in residual EC value at 5, 6, 12 and 24 hour of adsorption, compared with the residual EC value of two hours of adsorption time.

The turbidity is one of the prominent factor determine water quality. The turbidity after adsorption was significantly changed ($p<0.05$) from the initial value (47.73 FTU). Turbidity was almost removed by adsorption with synthesized chitosan within two hours (Fig 3). After two hours the decrease of turbidity was not significant with the turbidity value at two hours of adsorption.

Figure 3 to be inserted here

3.4. Removal of Cr by adsorption onto chitosan

The result of chromium removal by adsorption with crab shell chitosan in different treatment conditions is shown in Figs 4 and 5.In temperature study, adsorption was increased with increasing temperature. The residual chromium concentrations after adsorption with synthesized chitosan at different temperature, are significantly different ($p < 0.05$) from each other. At 60ºC chitosan absorbed best and the concentration of chromium was 0.2089 $mgL^{-1}$and in 30˚C, the Cr concentration was1.20 mg/L (Fig 4a).

In pH variable study, a significant difference ($p < 0.05$) was observed in residual chromium ions concentration in tannery effluent after adsorption with synthesized chitosan (Fig 4b). Adsorption of chromium onto synthesized chitosan was increased with decreasing pH. Adsorption reached its highest point at pH 3, when the chromium concentration was 0.07 mgL^{-1}, and lowest adsorption at pH 8, when the chromium concentration of the solution was 0.995 mgL^{-1}.

Figure 4 to be inserted here

In dose variable experiment, a significant difference ($p<0.05$) was found in chromium concentration after the adsorption with synthesized chitosan of different doses. Adsorption of chromium was increased with increasing adsorbent doses. After using 1 g of chitosan, the chromium concentration of the effluent was 1.17mg/L and using 5 g of adsorbent the chromium concentration was 0.281mg/L(Fig 5a). With increasing adsorption dose, residual chromium concentrations were significantly decreased ($p< 0.05$).

Figure 5 to be inserted here

The initial concentration of chromium in tannery effluent was 1345 mg/L. A significant decrease of chromium concentration was observed after adsorption with 5 g/100ml of synthesized chitosan (Fig 5b). Chromium concentration decreased to 1.17mg/L within one hour of adsorption. So the removal efficiency was 99.9%. After one hour of adsorption the chromium concentration decrease was not statistically significant.

4. Discussion

The tanneries in Bangladesh are the source of severe water pollution. They produce both solid and liquid wastes containing high levels of chromium and discharge continuously into the Buriganga River. The pollution in the aqueous environment affects fish and other organisms, and may ultimately affect human beings via the food chain. It has been known that the meat tissue scraped out of raw hides is used as chicken feed after some treatment. The feed may be contaminated with high levels of chromium, which may enter our bodies through the food chain. Therefore, treatment of tannery effluents is a great concern. The batch adsorption study showed that chitosan can be used as an efficient adsorbent for the treatment of tannery effluents. The levels of some physicochemical parameters became acceptable after using the synthesized crab shell chitosan. After the adsorption process, the pH and turbidity reached acceptable values. The values of some parameters (TDS and EC) changed to a good extent, and TOC was increased dramatically. This situation suggests that other treatment methods are also needed after treating with chitosan.

After adsorption with synthesized chitosan pH increased to nearly 8 and that is an acceptable value for tannery effluent. The Increase of pH probably caused by excess sodium hydroxide remained with chitosan from the preparation stage. But with increasing adsorption time there was no difference in pH value. There was a significant change in the Total Organic Carbon after adsorption onto synthesized chitosan from the initial TOC value and was increased up to 1916 mgL^{-1}.TOC value was increased with adsorption time. It may be because of dissolution of chitosan in the solution with time.

TDS and EC were decreased significantly ($p<0.05$) from the initial values. The positively charged chromium ions of the solution probably adsorbed on the synthesized chitosan surface, which lead to decrease of dissolved ions in solution and therefore decrease of electrical conductivity. Because, chitosan has been used for the chelation of metal ions in near-neutral solution, the complexation of anions in acidic solution (cationic properties due to amine protonation), the coagulation of negatively charged contaminants under acidic conditions, and for precipitative flocculation at pH above the pKa of chitosan [42]. Most of the adsorption was completed within the first one hour and after one hour of adsorption the change in EC and TDS are not statistically significant.

The turbidity after adsorption was significantly changed ($p<0.05$) from the initial value (47.73 FTU). Turbidity was almost removed (99.3%) by adsorption with synthesized chitosan within 2 hours of adsorption (Fig 3).

In the temperature study for chromium removal, the adsorption increased with increasing temperature. A similar result was also found by Adamczuk [43]. The highest rate of chromium adsorption onto chitosan was observed at the highest temperature, 60 °C. A higher temperature increases the reaction rate of adsorption of chromium with the synthesized chitosan.

The pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption process, and thus, the role of the hydrogen ion concentration was examined in the batch experiment. In the pH study, adsorption of chromium ions increased with decreasing pH. Adsorption was the highest at pH 3 and the lowest at pH 8. Cr (VI), depending on the pH, is known to exist as anions. At a low pH (below 4), the amine group on chitosan is protonated to varying degrees. It is known that in acidic media, the free amine groups ($-NH_2$) in chitosan are protonated to form $-NH_3^+$ groups. Chitosan with positive charges can adsorb anions by charge neutralization. Stronger attraction between positive and negative charges leads to stronger adsorption. The $-NH_3^+$ group on the chitosan is chiefly responsible for Cr (VI) adsorption. Cr (VI) forms stable anions, such as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, and $HCr_2O_7^-$, and the fraction of any particular species is dependent upon the chromium concentration and pH [44]. From the pKa of chitosan, it can be calculated that the extents of protonation are 9%, 50%, 91%, and 99% at pH 7.3, 6.3, 5.3, and 4.3, respectively [45]. This leads to the interaction between $-NH_3^+$ functional groups and the chromate anions. With the increase in pH from 5 to 9, the degree of protonation of the adsorbent functional group decreased gradually and, hence, removal decreased.

In the dosage experiment, adsorption was carried out with adsorbent dosages ranging from 1 to 5 g of chitosan, while other variables were constant. Removal of chromium ions increased with increasing adsorbent dosage. Five grams of chitosan adsorbed almost all of the chromium ions in the effluent, because a large amount of chitosan provides a larger amount of reaction sites for adsorption [46]. Chromium removal with 1 g of chitosan was significantly different from those of the other treatments.

The chromium removal efficiency was 99.9% within one hour of batch adsorptionwith adsorbent chitosan.In this study, increasing adsorption time did not provide any remarkable difference in chromium removal, as the reaction reached its equilibrium point within one hour.So, 5 gm of chitosan has provided enough adsorption site to bind chromium and adsorption time did not affect the adsorption efficiency of chitosan in the effluent. A typical effective adsorbent must acquire a short equilibrium during the treatment with adsorbate. Likewise, the synthesized chitosan here in this study received equilibrium at the first one hour with chromium ions. After the equilibrium achieved, no significant differences were found among the removals in different soaking hours.

Yasmeen et al. 2016 synthesized a facile bioadsorbent of chitosan-microcrystalline cellulose composite for the removal of Cr (VI) from tanning effluent and the maximum adsorption was acquired of 5.434 mg/g Cr (VI) in solution [46]. Siraj et al. 2012 obtained 90% total removal of Cr using a fabricated chitosan-charcoal composite at a wide range of adsorbent dose from 5 to 45 g/L [47]. Kumari et al. 2016 reported 64.29 % removal of Cr (VI) using chitosan prepared from shrimp shells [48]. Quaternary ammonium salt modified chitosan magnetic composite adsorbents were able to uptake 166.37 mg/g [35]. The obtained efficiency here in this study with the crab shells derived chitosan was high (99%) in compare with the studies mentioned above and with other identical researches.

Adsorption isotherm was analyzed by Langmuir and Freundlich adsorption isotherm. It was found that Langmuir adsorption isotherm correlation coefficient value (R^2) was 0.9537 and for Freundlich adsorption isotherm R^2 value was 0.9888. Thus, the Freundlich model was the most acceptable one to explain the adsorption process of Cr onto Chitosan surface suggesting a multilayer adsorption process. Accordingly, the adsorption process here in this study followed both monolayer (chemisorption) and multilayer (physisorption) adsorption on heterogeneous surfaces. In addition, adsorption kinetics depends on the interaction of adsorbate-adsorbent in aqueous adsorption system and plays an important role in water purification process. Reaction rate and adsorption mechanism can be elucidated by fitting data into both Pseudo first and second order kinetics models. The adsorption of Cr with the synthesized chitosan was highly fitted into the Pseudo Second order kinetic model and thus showed the chemisorption kinetics.

Cost-effectiveness and reusability are very important for a synthesized adsorbent in real applications. A facile synthesis method was followed in this study to extract chitosan from crab shells. Crab shells are ubiquitous in nature and are now-a-days commercially derived using simple methods which involve low cost. Reusability of any adsorbent is of great importance in view of sustainability and cost-effectiveness. Several researches have shown multi-reusability property of synthesized chitosan including our previous own work [49-50]. Likewise, the synthesized chitosan in this study also revealed elevated level of reusability. Desorption studies was also carried out for several cycles and sufficiently high desorption (78%) was found for the consecutive five cycles and then decreased slightly after the sixth one.

5. Conclusion

Chitosan was successfully synthesized from available crab shells. Chromium is highly concentrated in tannery effluents, but after treating with crab shell chitosan, the concentration of chromium in the tannery effluent decreased drastically within a short time, and no major difference in chromium concentration was observed as time elapsed. It was observed that the adsorption efficiency increased with decreasing pH and increasing adsorbent dosage and temperature. Chitosan may offer an alternative to traditional coagulants in wastewater treatment, as it is cheaper and easier to extract from crab shells or similar biological samples. Its unique properties together with its availability make chitosan an exciting and promising agent for the adsorption of heavy metals from wastewater.

Acknowledgement

This work was supported by the Department of Environmental Sciences, Jahangirnagar University. The authors are largely indebted to the departmental laboratory and its staffs for their support during this research. In addition, the efforts from the faculty members and other research associates continually took part in useful discussion and direction to conduct this research and thus highly appreciated.

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Figure legends

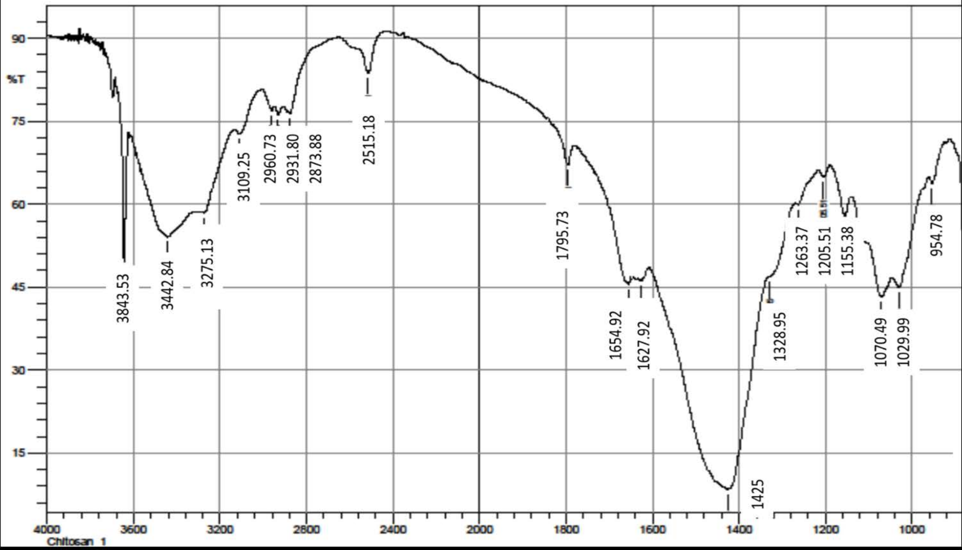
Fig. 1 FTIR spectra of synthesized chitosan.

Fig. 2 Physico-chemical parameter changes after the adsorption with synthesized chitosan from crab shell. (a) pH, (b) TOC, (c) TDS and (d) EC; experimental conditions: temperature- 30^{o} C, adsorbent dose- 5 g/ 100 mL, soaking duration- 6 hrs. Error bars indicate mean ± standard deviation (n=3). Statistical significance was evaluated by t-test: Two sample assuming unequal variances, where * denotes $p < 0.05$

Fig. 3 Turbidity removal from tannery waste with synthesized chitosan from crab shell; experimental conditions: temperature- 30^{o} C, adsorbent dose- 5 g/ 100 mL, soaking duration- 6 hrs. Error bars indicate mean ± standard deviation (n=3). Statistical significance was evaluated by t-test: Two sample assuming unequal variances, where * denotes $p < 0.05$

Fig. 4(a) Effect of pH; experimental conditions: temperature- 30^{o} C, adsorbent dose- 5 g/ 100 mL, soaking duration- 6 hrs, and (b) effects of temperature; experimental conditions: pH - 4.56, adsorbent dose- 5 g/ 100 mL, soaking duration- 6 hrs on the adsorption of Cr (VI) by synthesized crab shell chitosan. Error bars indicate mean ± standard deviation (n=3). Statistical significance was evaluated by t-test: Two sample assuming unequal variances, where * denotes $p < 0.05$.

Fig. 5(a) Effect of adsorbent dose; experimental conditions: pH - 4.56, temperature- 30^{o} C, adsorbent dose- 1-5 g/ 100 mL, soaking duration- 6 hrs; and (b) effects of soaking time; experimental conditions: pH - 4.56, temperature- 30^{o} C, adsorbent dose- 5 g/ 100 mL, soaking duration- 1-24 hrs, on the adsorption of Cr (VI) by synthesized crab shell chitosan. Error bars indicate mean ± standard deviation (n=3). Statistical significance was evaluated by t-test: Two sample assuming unequal variances, where * denotes $p < 0.05$.


%T
90
75
60
45
30
15
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
Chitosan_1
3843.53
3442.84
3275.13
3109.25
2960.73
2931.80
2873.88
2515.18
1795.73
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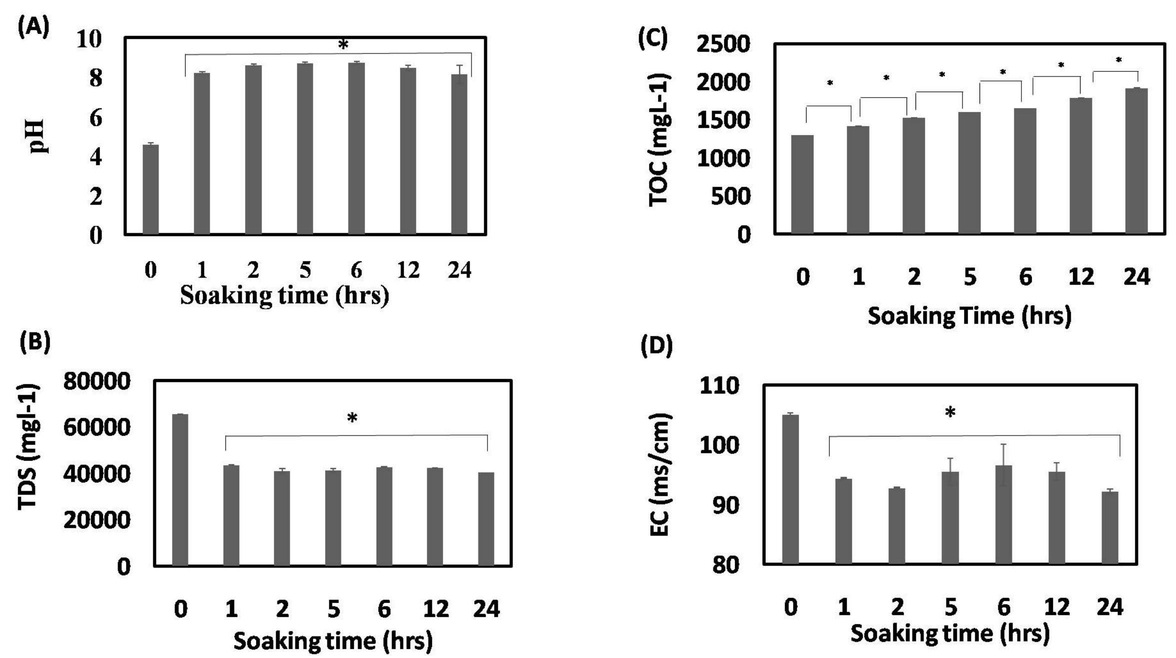
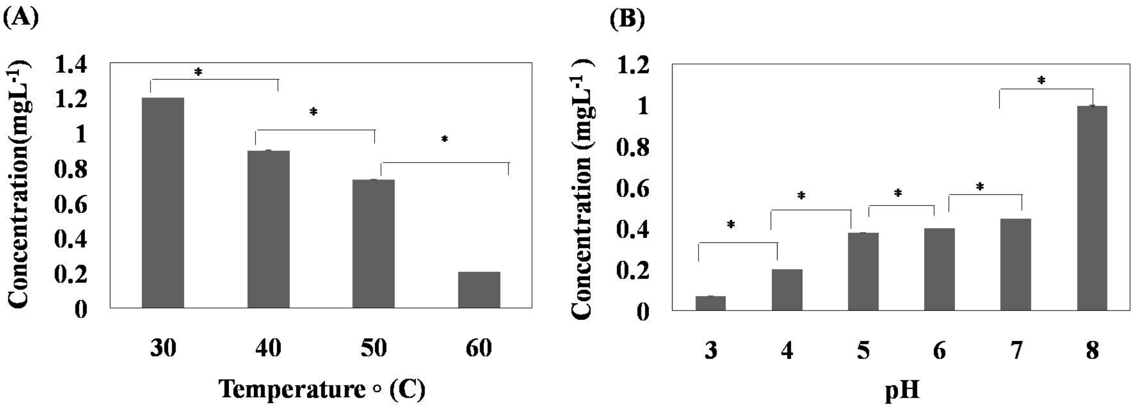
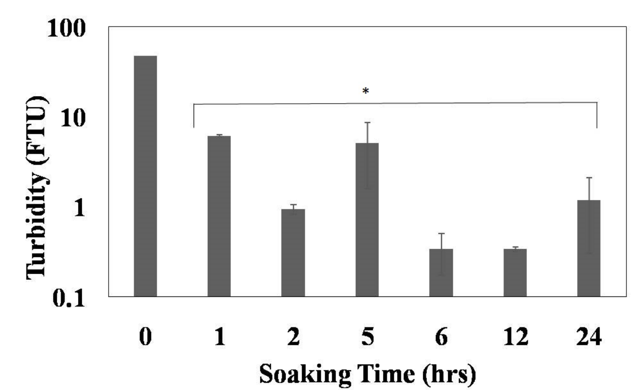
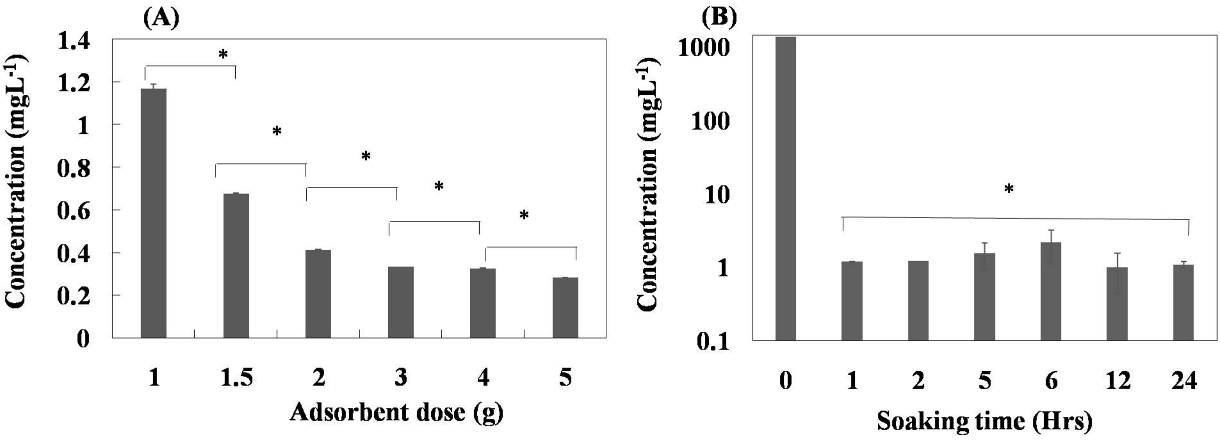

(A)
pH
10
8
6
4
2
0
*
0
1
2
5
6
12
24
Soaking time (hrs)
(B)
TDS (mgl-1)
80000
60000
40000
20000
0
*
0
1
2
5
6
12
24
Soaking time (hrs)
(C)
TOC (mgL-1)
2500
2000
1500
1000
500
0
*
*
*
*
*
*
0
1
2
5
6
12
24
Soaking Time (hrs)
(D)
EC (ms/cm)
110
100
90
80
*
0
1
2
5
6
12
24
Soaking time (hrs)


(A)
Concentration(mgL-1)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
*
*
*
30
40
50
60
Temperature ◦ (C)
(B)
Concentration (mgL-1)
1.2
1
0.8
0.6
0.4
0.2
0
*
*
*
*
*
3
4
5
6
7
8
pH



Turbidity (FTU)
100
10
1
0.1
*
0
1
2
5
6
12
24
Soaking Time (hrs)



(A)
Concentration (mgL-1)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
*
*
*
*
*
1
1.5
2
3
4
5
Adsorbent dose (g)
(B)
Concentration (mgL-1)
1000
100
10
1
0.1
*
0
1
2
5
6
12
24
Soaking time (Hrs)