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Removal of hexavalent chromium using chitosan prepared from shrimp shells

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Contamination of the aqueous environment by heavy metals and due to the discharge of metal containing effluents into the water bodies is one of the environmental issues of the century. Thus, in this work, the main concern has been the preparation of chitin and chitosan from the raw materials of shrimp shells and the characterization of the prepared chitosan by field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FTIR). The work was then shifted to investigate the potentiality of Cr^{+6} adsorption with the prepared chitosan. The controlled parameters of adsorption process were studied. The percentage of Cr^{+6} removal using the shrimp chitosan was 64.29%.

Key words: Shrimp shells, chitosan, adsorption, chitin.

INTRODUCTION

Today water pollution is a major problem. There are many industries, such as textiles, leather, paper, plastics, electroplating, cement, metal processing, wood preservatives, paints, pigments, and steel fabricating industries (Shanker et al., 2005; Dima et al., 2015; Kim et al., 2015) that pollute water. Industrial waste water is a major source of various kinds of metal pollutions in natural water, such as lead (Pb), cadmium (Cd), zinc (Zn), and copper (Cu); these metals find their way into the water bodies through wastewaters (Mahvi et al., 2005). The presence of a low concentration of these heavy metals in water prevents the light and oxygen to penetrate into it. As a result, the photosynthetic activities are reduced in the aquatic environments (Alluri et al., 2007). These heavy metals also cause different direct and indirect toxic effects on humans, such as allergies, skin irritation, heart defects, tumour, cancer, jaundice, and mutation (Vakili et al., 2014). There are many conventional methods used in the water treatment, such as membrane filtration, oxidation, adsorption, coagulation/flocculation, chemical precipitation, electrochemical reaction, electro dialysis, reverse osmosis, biological treatment, and ion exchange.

These methods have limitations, such as high capital or operating cost, low efficiency and for small scale industries, it is difficult to handle the excessive sludge generated (Abbasi and Alikarami, 2012). Adsorption is preferred over all other methods, because of its comparatively low initial cost, and also it is non-toxic in

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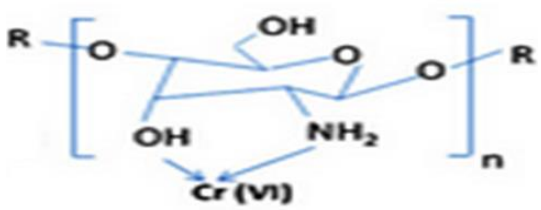

Figure 1. Structure of chitosan and combine with Cr(VI) (Samiey et al., 2014).

nature, highly selective, environmentally friendly, and has great adsorption ability due to bulky surface area. Chitin is the most abundant renewable, natural resource after cellulose. Chitin and its end product are biomolecules which have excessive potential, along with flexible biological activities that demonstrate biocompatibility and biodegradability. Chitosan (Figure 1) is a low-cost biopolymer that can be used as an ideal adsorbent for removing pollutants from the wastewater (Jung et al., 2007). It is the main module of the cell walls of fungi, the exoskeletons of crustaceans (crabs, lobsters and shrimps) and insects, the radulae of molluscs, and the beaks and internal shells of cephalopods, including squid and octopuses. Chitin is a long-chain homopolymer of the residues of N-acetyl-d-glucosamine, which are linked to each other by osidic-1, 4 bonds with the molecular formula of $(C_8H_{13}O_5N)_n$ (Dutta et al., 2004). Chitin and its end products like chitosan are broadly recognized to have huge applications in several fields (Benhabiles et al., 2013a, b; Vakili et al., 2014; Bouhenna et al., 2015). Chromium (Cr) is a transition element located in the group VI-B of the periodic table with a ground-state electronic configuration of Ar $3d^5 4s^1$. The stable forms of Cr are the trivalent Cr(III) and the hexavalent Cr(VI) species, although there are various other valence states which are unstable and short lived in biological systems Cr(VI) is considered the most toxic form of Cr, which usally occurs associated with oxygen as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) (Shanker et al., 2005).

Objectives of the present work are preparation of chitin and chitosan from the raw samples of shrimp shells, calculating the yield of chitin and chitosan from the raw samples of shrimp shells, characterization of the prepared Chitosan by using field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FTIR) analyses and studying the effect of amount of adsorbent dose and contact time on the adsorption process.

MATERIALS AND METHODS

Fresh samples of shrimp shells were obtained from the local market (Rourkela). The samples were washed thoroughly with water and then dried for 24 h. Hydrochloric acid (analytical reagents, Rankem) and sodium hydroxides pellets (Rankem) were purchased from Rankem chemicals.

Deproteinization

Deproteinization of chitin is the process in which 2% NaOH was used along with heating at 100°C. A magnetic bead was put inside the solution, and the process was carried out on the electromagnetic stirrer for a time period of 30 min. The solution was continuously stirred and heated for 30 min. The resulting solution was then washed several times with distilled water till the neutrality of the solution was obtained (that is, pH 7) and then it was washed with ethanol.

Demineralization

Demineralization is the process in which dilute HCl (2% HCl solution) solution was used without heating. Mineral content present in the shells of the crustaceans is not the same for each of the species, so all the chitin resources do not require the same type of treatments. Here, the sample of shrimp shells was treated with HCl solution at ambient temperature. A magnetic bead had been put inside the solution, and the process was carried out on the magnetic stirrer for a time period of 30 min. The solution was continuously stirred. The resulting solution was washed for several times with distilled water till the neutrality of the solution was attained (that is pH 7) and then it was washed with ethanol. The demineralized sample was then filtered and dried in an oven for a period of 5 h at 60°C. The chitin synthesized was then weighed.

Deacetylation

Deacetylation is the process with which chitosan can be prepared from chitin; which has been prepared from the raw and ground samples of shrimp shells. In this process, the sample is treated with concentrated NaOH (40%) (Sagheer et al., 2009). Detailed procedure followed for deacetylation was reported in author's previous publications (Suneeta and Kumar, 2014; Kumari et al., 2015).

Preparation of stock solution

A stock solution of a heavy be prepared for the different batch experiments conducted for the adsorption process. 100 ppm of stock solution was prepared, that is, 100 mg (0.1 g) of chromium (Cr^{+6}) powder was added to 1000 ml of distilled water and the sample is taken in a beaker. The solution was stirred for producing a homogeneous concentration.

Batch experimental procedure

The adsorption of heavy metal (Cr^{+6}) was studied using the chitosan sample (shrimp shells) in the batch operation for a contact time of 60 min. 30 ml of heavy metal solution was taken in the 150 ml conical flask and then a known amount of the chitosan was added to the conical flask. The conical flask was put into the shaker at 100 rpm. Sample of liquid (1 ml) was pipetted out at regular time interval of 60 min. Collected liquid sample was subjected to centrifuge till clear liquid was separated from chitosan. Using UV-Spectrophotometer at λ_{max} 370 nm the absorbance of clear liquid sample was estimated. In order to obtain the dye concentration, the calibration curve was plotted, and the absorbance of the unknown dye solution obtained from spectroscopic analysis was used to estimate the dye concentration.

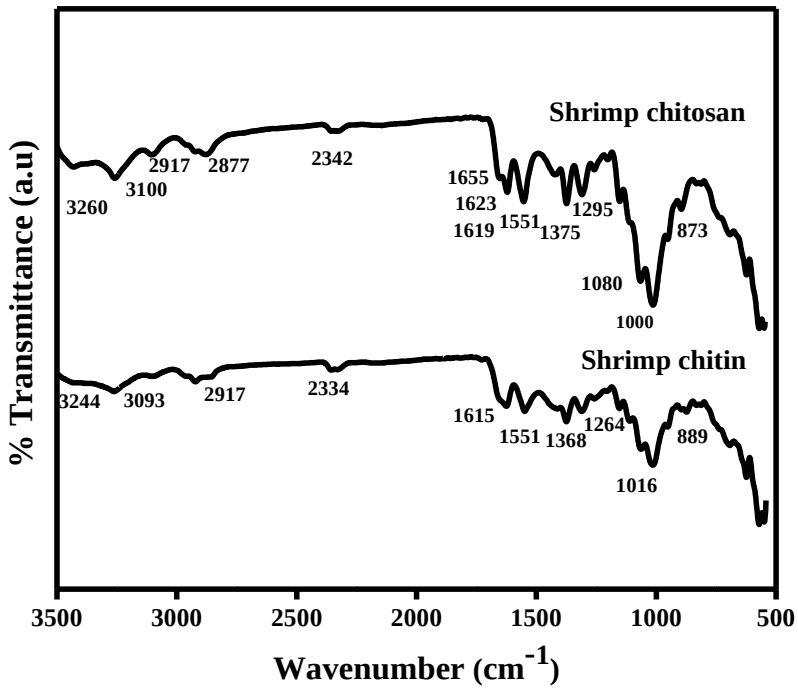

Figure 2. Shrimp shell chitin and chitosan (2% HCl and 2% NaOH).

Study of the effect of contact time

For the study of the effect of contact time on the adsorption of Cr^{+6} over chitosan, 30 ml from 100 ppm Cr^{+6} solution was taken in a conical flask and 0.1 g of chitosan (shrimp) is added in the flask at solution pH. The flask was kept at 25°C in the shaker at 100 rpm shaking speed. Then, the samples were pipetted out at the interval of 60 min. The chromium concentration in the samples collected was analyzed by using UV-spectrophotometer.

Study the effect of adsorbent dosage

Effect of adsorbent dosage on the adsorption of Cr^{+6} was studied by taking 30 ml from 100 ppm Cr^{+6} solution in a conical flask, and then different amounts of chitosan were added in different conical flasks at certain pH. Conical flask was kept in a shaker at 100 rpm at a temperature of 25°C, the samples were collected at a time interval of 60 min to obtain the Cr^{+6} concentration remaining in the solution after adsorption.

Characterization of chitosan

FTIR

Infrared spectra were obtained using a Perkin-Elmer type FTIR 1000 spectrometer at room temperature and using KBr pellet scanning method. Pellets were scanned at room temperature (25°C) in the spectral range of 400 to 4000 cm^{-1}.

FESEM

FESEM characterizes a wide range of samples with unique low vacuum capabilities and ultra-high resolution low voltage imaging; low voltage [1 kV] resolution is 1.4 nm in high vacuum mode, while for non-conductive materials, the Nova Nano SEM is unique in offering the highest resolution (1.8 nm) at low voltages (3 kV).

RESULTS AND DISCUSSION

FTIR

The FTIR spectra of chitin and chitosan are shown in Figure 2. FTIR pattern of shrimp chitin was presented for better comparison. Chitosan has exhibited FTIR peaks at 3260, 3100, 2917, 2877, 2342, 1615, 1551, 1375, 1295, 1080, 1000 and 873 cm^{-1}. The characteristic bands at 1551 and 1615 cm^{-1} and in the vicinity of 3093 and 3244 cm^{-1} correspond to the stretching vibration of C=O and NH in ($NHCOCH_3$), respectively. Complete demineralization was confirmed by the absence of mineral associated bands. Chitin has exhibited FTIR peaks at 3244 cm^{-1}, 3093 cm^{-1}, 2917 cm^{-1}, 2334 cm^{-1}, 1615 cm^{-1}, 1551 cm^{-1}, 1368 cm^{-1}, 1264 cm^{-1}, 1016 cm^{-1} and 889 cm^{-1}. In chitosan, the absorption feature observed around 1623 cm^{-1} (bending vibration of NH of $R\text{-}NH_2$) indicates the high degree of deacetylation (Sagheer et al., 2009; Kumari et al., 2015). The degree of deacetylation of chitosan was found to be 65 %. The degree of deacetylation was calculated by using FTIR.

FESEM

The extracted shrimp shell chitosan was observed to

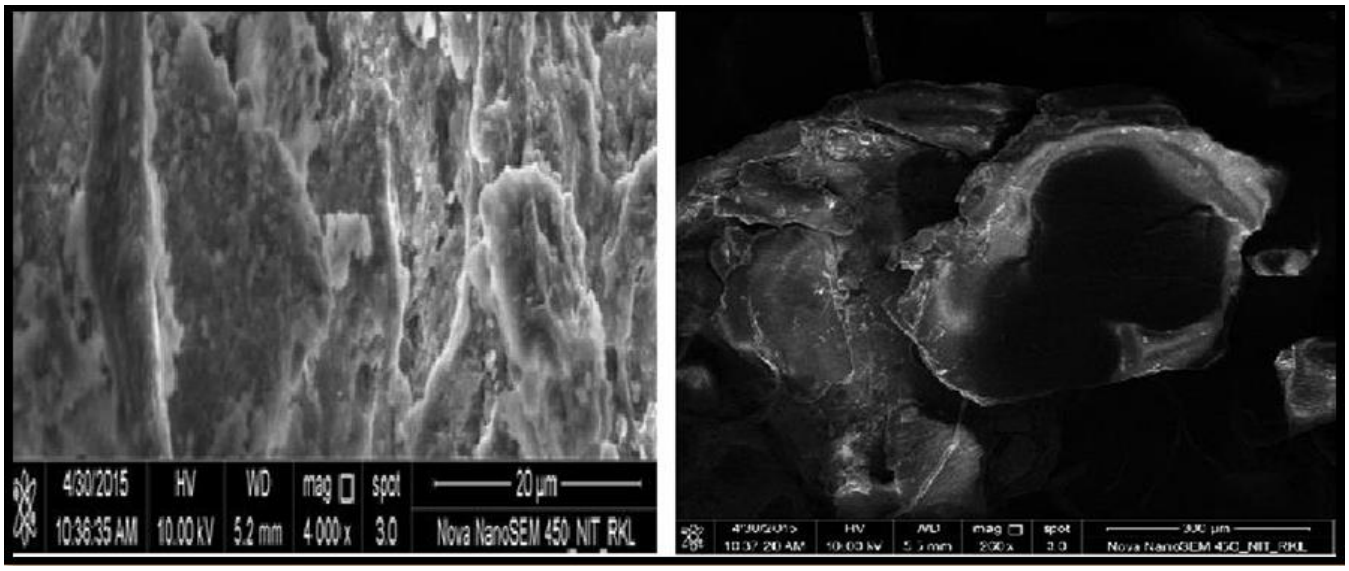

Figure 3. FESEM images of shrimp chitosan.

have layers of flakes, and its porous nature could be seen in some areas. In some portions of chitosan, fibril structures can easily be distinguished. With the increased magnification, crumbling flakes were observed with fibril structures in some portions of chitosan, similar observation reported in the study of Yen et al. (2009) (Figure 3).

Effect of adsorbent dose

The effect of adsorbent dosage on the adsorption of Cr^{+6} has been studied by taking 30 ml of 100 ppm Cr^{+6} solution in a conical flask, and different amounts of chitosan (that is, from 0.1 to 0.4 g) were added in different conical flasks. Separate studies have been carried out for different samples of chitosan (that is, chitosan from shrimp at pH=4, which is acidic medium). The conical flask was kept at 25°C in the shaker at 100 rpm for the time period of 30 min to obtain the uniformity in the solution after adsorption. The graph obtained was shown in Figure 4. As the dose of the adsorbent increased, keeping the time and speed of the shaker (rpm) constant, the adsportion of Cr^{+6} was also found to be increased, that is, percentage of removal of Cr^{+6} followed an increasing trend with the increased amount of adsorbent taken. Removal of Cr^{+6} was found to be 73.89% at a chitosan dosage of 0.4 g, that is, the Cr^{+6} removal is 5.54 mg/g of shrimp chitosan.

Effect of contact time

For the study of contact time on the adsorption of

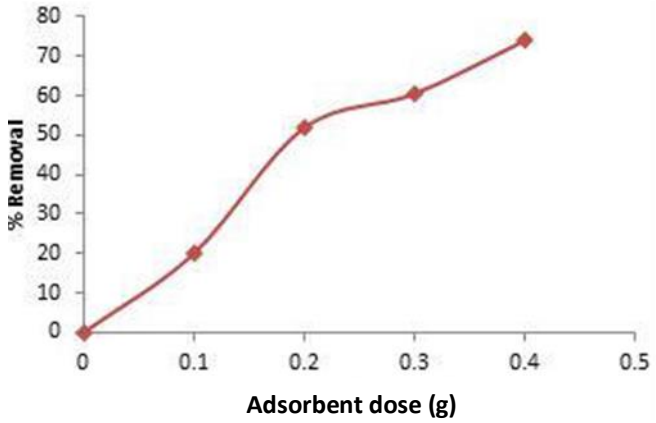

Figure 4. Effect of chitosan dosage over % Cr^{+6} removal.

chitosan, 30 ml of 100 ppm Cr^{+6} solution was taken in a conical flask and 0.1 g of chitosan (shrimp) was added in the flask at solution pH (pH= 4, which is acidic medium). The flask was kept at 25°C in the shaker at 100 rpm shaking speed for time period of 60 min. The sample (1 ml) was pipetted out at the interval of 60 min to obtain the concentration remaining in the solution after adsorption. From the graph shown in Figure 5, it was found out that by keeping the amount of adsorbent and speed of the shaker (rpm) constant as the time progresses, the concentration of the heavy metal solution decreased, but after 2 h of the time, there was no significant change in the percentage of removal. The percentage of removal of the heavy metal for the shrimp chitosan was found as 64.29% (The Cr^{+6} removal is 19.29 mg/g of shrimp chitosan).

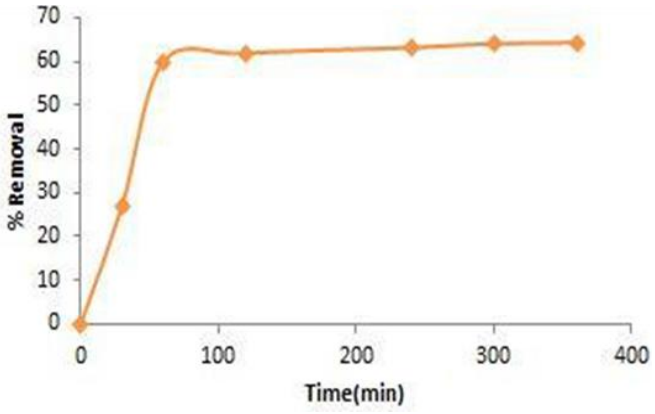

Figure 5. Effect of time over the % removal of Cr^{+6}.

Conclusion

Shrimp shell waste is a good source of chitin and chitosan synthesis. Deproteinization, demineralization of shrimp shell, followed by deacetylation resulted in the formation of chitosan and chitosan formation is confirmed from the FTIR patterns. The percentage of removal of Cr^{+6} is increased with increase in adsorbent dosage (keeping the time and shaker speed (rpm) constant). Removal of Cr^{+6} was obtained at the maximum of 73.89% for the case of 0.4 g shrimp chitosan dosage (Cr^{+6} removal is 5.54 mg/g of shrimp chitosan). It is concluded that keeping the amount of adsorbent (0.1 g) and speed of the shaker (rpm) constant, with increased time of contact, the percentage removal of Cr^{+6} increased but after 2 h, no significant change in Cr^{+6} concentration was observed. 64.29% removal of Cr^{+6} was removed with 0.1 g shrimp chitosan dosage as adsorbent (Cr^{+6} removal is 19.28 mg/g of shrimp chitosan).

Conflict of interests

The authors have not declare any conflict of interest.

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