Simultaneous determination of heavy metals and cationic dyes from industrial effluent by prawn shell derived chitosan-g-poly(acrylic acid) biocomposite

Mohammed Mizanur Rahman\textsuperscript{a,*}, Nurun N. Lata\textsuperscript{a}, Sunzida H. Rimu\textsuperscript{a,b}, Adib H. Chisty\textsuperscript{a,b}

\textsuperscript{a}Faculty of Engineering and Technology, Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Dhaka 1000, Bangladesh, emails: mizanur.rahman@du.ac.bd (M.M. Rahman), accelata@gmail.com (N.N. Lata), sunzidarimu12004@gmail.com (S.H. Rimu), adibchisty033@gmail.com (A.H. Chisty)

\textsuperscript{b}National Institute of Textile Engineering and Research, Nayarhat, Savar, Dhaka, Bangladesh

Received 18 May 2020; Accepted 30 November 2020

ABSTRACT

Poly(acrylic acid) (PAA) grafted modified chitosan biocomposite adsorbent was obtained by varying the amount of chitosan and acrylic acid (AA) to determine heavy metals and cationic methylene blue from aqueous solution and industrial effluent. The reaction was carried out in a homogeneous aqueous phase by using \textit{N,N}-methylenebisacrylamide as a cross-linker, and ammonium persulfate as an initiator. Fourier transform infrared (FTIR) revealed the presence of absorption band in the composite for \(-\text{OH}, \text{–NHCO}, \text{and } \text{–NH}_2\) of chitosan took part in grafting with acrylic acid. It was also observed that grafting percentage (G\%) decreases with increasing chitosan amount in the composite, however, the degree of swelling slightly increases with increasing chitosan amount due to the amphiphilic nature of the PAA modified chitosan. The adsorption behaviors for Cr(VI), Pb(II), and methylene blue (MB) on the biocomposite adsorbent were studied for 25 ppm standard solution with 0.05 g adsorbent dose and at pH 4, 6, and 9.1 for Cr(VI), Pb(II), and methylene blue (MB), respectively. The highest removal efficiencies 42\% and 36\% for Cr(VI) and Pb(II), respectively, were given by the composite (C-4) prepared from 2:1 chitosan and AA. On the other hand, the composite with higher AA (chitosan: AA = 1:7.2) showed a remarkable higher MB adsorption efficiency (64\%) than other composites. The composite adsorbent was applied to reveal its efficiencies for the real sample from tannery and textiles. The results revealed that 33\% Cr(VI) and 36\% Pb(II) can be eliminated by a single adsorption of 0.05 g C-4 (prepared from chitosan and AA at 2:1 ratio) after 2 h of adsorption. On the other hand, 53\% MB removal was observed for C-1 (obtained from chitosan and AA ratio of 1:7.2) with a similar adsorption conditions.

Keywords: Prawn shell; Poly(acrylic acid); Heavy metals; Methylene blue

1. Introduction

Chitosan is a polycationic naturally occurring biodegradable, non-toxic, non-allergenic biopolysaccharide derived from chitin which is found in abundance in nature [1]. It is readily obtained from shrimp and crab shell containing chitin which is a N-acetyl glucosamine polymer. The N-acetyl glucosamine gets converted in to glucosamine units by alkaline de-acetylation with NaOH (40\%-50\% concentration w/w) [2,3]. Chitosan is considered as most promising materials for its excellent biodegradability, biocompatibility, non-toxicity, antimicrobial activity, and its economic advantages [3]. The robust performance of chitosan, that is, two hydroxyl groups and the one primary
amine which can donate a free pair of electrons, make chi-
tosan soluble in diluted aqueous acetic acid solvents, and
allow the formation of coordination bonds, providing a
substantial probability of chemical modification. The mod-
ification of hydrophilic chitosan chains via hydrophobic
compounds such as carboxylic acids can impart amphi-
philic nature to chitosan. Such amphiphilic chitosan deriv-
atives are capable to self-assemble and form nanoparticles
(micelles) under appropriate conditions [4]. Chitosan was
employed as an effective adsorbent to remove heavy metals
and dyes due to its –NH, and –OH groups, that acts as the
active sites [5]. Chitosan can be readily dissolved in acidic
solution and it must be cross-linked in order to achieve
better resistance against acids, alkalis, and other chemi-
icals [6]. To develop the applicability of chitosan as wide
range of an adsorbent, cross-linking reagents such as glu-
taraldehyde, ethylene glycon diglycidyl ether, and isocya-
nates, etc., have been extensively used [7]. The cross-linking
agents can stabilize the polymer in acid solutions and make
it insoluble that can increase its mechanical properties [8].

Graft copolymerization of vinyl monomers onto the
chain of natural polymers such as starch [9], cellulose [9],
and chitosan [10] has been studied. The use of chitosan-
derived materials through cross-linking, grafting of func-
tional groups, and blending of polymer or inorganic mate-
rials for the removal of heavy metals from wastewater
has increased rapidly. Due to the high chelating effects
of carboxyl groups, various carboxylated chitosan prod-
ucts have been reported [10]. Poly(acrylic acid) (PAA) has
attracted increasing attention, which contains a carboxyl
group in each repeated unit and favor adsorption of metal
ions [11]. Extensive efforts have been made for in situ graft-
ning of PAA on to chitosan to enhance metal ions adsorp-
tion ability [12]. Reactive –NH, and –OH of chitosan are
convenient for graft polymerization of hydrophilic vinyl
monomers, making an efficient way to prepare chitosan
based hydrogels with novel properties. In this article, chi-
tosan–poly(acrylic acid) (CS–PAA) was synthesized via
graft copolymerization by varying the amount of chitosan
with acrylic acid in a homogeneous system using initiator
and cross-linking agent. The copolymer adsorbent was used
as an adsorbent for removing heavy metals (Cr(VI), Pb(II))
and cationic methylene blue dye from aqueous solution and
wastewater. The adsorption capacity of the adsorbent for
metal ions has been improved significantly than chitosan
after introducing carboxyl groups of PAA into the chitosan.

2. Materials and methodology

2.1. Materials

Prawn shell was collected from a prawn hatchery of
Satkhira District, Khulna Division, Bangladesh. Acrylic
acid (AA, from Sigma-Aldrich (India) and distilled under
reduced pressure before use), ammonium persulfate (APS,
recrystallized from distilled water before use) and N,N-
methylenbisacrylamide (MBA) were also supplied by
3050 Spruce Street, St. Louis, Sweden, hydrochloric acid
from Merck KGaA, 64271 Damstadt, Germany, and sodium
hydroxide was supplied by Loba Chemie Pvt., Ltd., 107,
Mumbai 400005, India. Methylene blue (MB), potassium
dichromate and lead nitrate all obtained from Merck KGaA,
64271 Damstadt, Germany and used as obtained without
further purification. Tannery Effluent was collected from
Karim Tannery, Hazaribag, Dhaka, Bangladesh in which
the liquor was collected from the final disposal line of the
Burianga River, Dhaka, Bangladesh. Another effluent was
collected from a knit dyeing industry Anliima Yarn Dyeing
Ltd., Karnapara, Savar, Dhaka, Bangladesh.

2.2. Extraction of chitosan from waste prawn shell

Chitosan was extracted from waste prawn shells fol-
lowing the method of Rashid et al. [13]. In a typical pro-
cess, the waste prawn shell was washed with distilled
water for 1 h at 50°C–60°C and dried in an oven at 100°C.
The washed prawn shell was treated with 4% NaOH
solution at a ratio of 1:16 (w/w) for 3 h at 70°C with con-
tinuous stirring in a mechanical stirrer to remove the pro-
tein. After filtration and washing with distilled water, the
prawn shells were dried in an oven at 105°C for 24 h. The
dried shells were treated with 3 M HCl at a ratio of 1:16
(w/w) with stirring for 3 h. The shells were washed and
dried in an oven at 100°C for 24 h to obtain chitin. The
shells were then crushed and deacetylated by heating
under boiling conditions (80°C–100°C) with 50% (w/w)
NaOH solution at a ratio of 1:20 (wt.%) for 4 h. The mix-
ture was then washed thoroughly with distilled water
to remove the NaOH completely, followed by drying in
an oven for 24 h at 60°C to obtain the product, chitosan.

The viscosity-average molecular weights of chitosan
solutions were calculated using the Mark–Houwink equa-
tion which provides the relationship between intrinsic vis-
cosity and molecular weight. The intrinsic viscosity [η] of
a polymer solution is related to the polymer molecular weight
(Mw) according to the Mark–Houwink equation 

\[ [\eta] = KA^a M_w^b \]

where \( K \) and \( a \) are constants for a given solute–solvent system and temperature. For chito-
san solution in acetic acid, \( K = 1.81 \times 10^{-3} \) g mL^{-1}, \( a = 0.93 \) [14]. So, viscosity average molecular weight of chitosan,
\( M_v = 155,245.5 \) Da. The data of intrinsic viscosity and molec-
ular weight are shown in Fig. 53.

The degree of deacetylation (DD), which determines
the content of free amino groups in the polysaccharide,
can be applied to differentiate between chitin and chitosan.
The DD of the chitosan samples was calculated using the
baseline of Baxter et al. [15]. The computation in Eq. (1) for
the baseline is as follows:

\[ DD = 100 - \left[ \frac{A_{1655}}{A_{3450}} \right] \times 100 \left[ \frac{1}{1.33} \right] \]

where \( A_{1655} \) and \( A_{3450} \) were the absorbance at 1,655 cm^{-1}
of amide-I band as a measure of the N-acetyl group content
and 3,450 cm^{-1} of the hydroxyl band as an internal stan-
dard to correct for differences in chitosan concentration
powder. The Fourier transform infrared (FT-IR) spectra
of chitin and chitosan are shown in Fig. 52. From FTIR spec-
trum, \( A_{1655} = 0.021 \) and \( A_{3450} = 0.125 \). Therefore, DD from
Eq. (1) is 87.37%.
2.3. Chitosan-graft-poly acrylic acid composite preparation

In a three-necked round bottom flask equipped with reflux and condenser, a specific amount of chitosan was dissolved in 1% (v/v) acetic acid. The composition of different components on the composites are shown in Table 1. The mixture was stirred at 60°C in a hot-plate magnetic stirrer. The initiator APS was added to the mixture and waited for 10 min for the generation of free radicals. Then acrylic acid (AA) and N,N-methylenebisacrylamide were added to the flask and stirred at 70°C for 3 h under the nitrogen atmosphere. The mixture was then extracted with distilled water to remove the homopolymer, unreacted monomer, and initiator. Then the product was spread on a petri dish and few drops of ethanol were sprayed on the top of the product and dried in an oven at 60°C for 5 h. Finally, the composite was ground with mortar for adsorption experiment.

2.4. Determination of grafting efficiency

The grafting efficiency (%GE) can be calculated using Eq. (2):

\[
\%GE = 100 \left( \frac{W_s - W_0}{W_0} \right)
\]

(2)

where \(W_s\), \(W_0\), and \(W_i\) are the weight of initial dry chitosan, grafted chitosan after water extraction and drying, and the weight of monomer, respectively. It is already known that, the composition of the grafted chitosan can be calculated in terms of the so-called percentage of grafting. This can be expressed on the basis of percent weight increase related to the initial weight of chitosan. Therefore, the extent of grafting can be calculated as percentage of grafting:

\[
\%G = 100 \left( \frac{W_s - W_0}{W_i} \right)
\]

[16].

2.5. Swelling determination

The swelling behavior of grafted chitosan samples was studied at 37°C as a function of time in distilled water. The well-known tea-bag method was used. An exact amount of pre-dried sample was placed into a tea bag made of 200 mesh nylon screen. This was then immersed in water at 30°C. After certain time, the tea bag containing swollen sample was taken out and hung up for 5 min in order to eliminate excess unabsorbed liquid and then weighed. The degree of swelling at time, \(t\), was calculated using the relation \((W_s - W_0)/W_0\) where \(W_s\) and \(W_0\) are the weights of swollen and dry polymer, respectively.

2.6. Characterization techniques

An attenuated total reflectance/Fourier transforms infra-red (ATR-FTIR) spectrophotometer of model FT-IR8400S spectrophotometer, Shimadzu Corp., Japan was used. Spectroscopic grade dry KBr of 200 mg and 1 mg of powdered sample were ground in an agate mortar. Pellets were formed from 100 mg of this ground mixture. Transmission band mode in the range 4,000–400 cm\(^{-1}\) was used to record the spectra with resolution being 4 cm\(^{-1}\) and hold time 5 min. Adsorption capacity was analyzed by a UV (Shimadzu 1700 UV) spectrophotometer. Scanning electron micrographs (SEM) images were taken at 20 kV with a JSM-6490LA, Jeol, Japan microscope. Differential scanning calorimetry (DSC) analysis was done using a DSC-60 (Shimadzu Corp., Japan) analyzer. The flow rate was maintained at 20 mL min\(^{-1}\), temperature rate at 10 min\(^{-1}\), and it was carried out in an aluminum pan. In dry nitrogen environment heat change per gram of sample was recorded at a constant temperature for 60 min with a computerized system. Thermogravimetric analysis (TGA) was done using TG-00260 machine form Shimadzu Corp., Japan. To maintain inert atmosphere nitrogen gas supplied and the samples were taken in an aluminum cell. The temperature increase rate was maintained at 10°C min\(^{-1}\), while the hold time was 5 min. Initial and final temperatures were room temperature and 600°C, respectively. Atomic absorption spectroscopy (AAS, SHIMADZU AA-7000 atomic absorption spectrophotometer, Shimadzu, Japan) was used for the determination of heavy metal concentration in standard samples of heavy metals (Pb, Cr) and effluent.

2.7. Preparation of standard solution of Cr(VI), Pb(II), and MB

Cr(VI) stock solution (1,000 ppm) was prepared by taking 0.2892 ± 0.0002 g potassium dichromate (K\(_2\)Cr\(_2\)O\(_7\)) in 100 mL volumetric flask. Stock solution was diluted to prepare desired 25 ppm (corresponding to 25 mg L\(^{-1}\)). The solution pH 4 was adjusted by addition of 0.1 M NaOH and 0.1 M H\(_2\)SO\(_4\) as described in the literature [17]. Stock solution of Pb(II) was prepared from lead nitrate by following a procedure described in the literature [18]. In a typical process Pb(II) (1,000 ppm) has been prepared by dissolving 1.598 g of Pb(NO\(_3\))\(_2\) in 200 mL of DDD water, then 1.5 mL of concentration of HNO\(_3\) (63%–65%) was added to dilute it 1,000 mL with DDD water. The standard solution of Pb(II) corresponding to 25 mg L\(^{-1}\) (25 ppm) of Pb(II) was prepared with appropriate dilution with DDD water. Analytical grade 1 M HCl and 1 M NaOH solutions were used to adjust the solution pH to 6.0. The stock solution of 100 ppm MB has

Table 1

<table>
<thead>
<tr>
<th>Chitosan:AA</th>
<th>Nomenclature</th>
<th>Chitosan (g)</th>
<th>AA (g)</th>
<th>APS (g)</th>
<th>MBA (g)</th>
<th>Chitosan concentration (w/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:7.2</td>
<td>C-1</td>
<td>0.50</td>
<td>3.50</td>
<td>0.10</td>
<td>0.10</td>
<td>1.60</td>
</tr>
<tr>
<td>1:2</td>
<td>C-2</td>
<td>0.75</td>
<td>1.50</td>
<td>0.10</td>
<td>0.10</td>
<td>2.50</td>
</tr>
<tr>
<td>1:1</td>
<td>C-3</td>
<td>1.00</td>
<td>1.00</td>
<td>0.10</td>
<td>0.10</td>
<td>3.30</td>
</tr>
<tr>
<td>2:1</td>
<td>C-4</td>
<td>1.50</td>
<td>0.75</td>
<td>0.10</td>
<td>0.10</td>
<td>3.75</td>
</tr>
</tbody>
</table>
been prepared by dissolving about 0.01 g of MB in 100 mL of DDD water. Serial dilutions have done to get the required lower concentrations in the range of 5–50 ppm. The concentration of MB was measured at λ_max of 663 nm using UV-visible spectrophotometer as shown in Fig. S1 [19]. For preparing 100 mL of 25 ppm standard solution 25 mL of stock solution has been taken in a 100 mL volumetric flask and made up to the mark with DDD water. The pH of the solution was adjusted to 9.1 by adding 1 M NaOH solution.

2.8. Adsorption studies for Cr(VI), Pb(II), and MB

20 mL of 25 ppm stock solution of each substance was taken in 100 mL conical flask with 0.05 g of adsorbent and agitated at room temperature (27°C) on a reciprocating shaker (Model no. SSL2, Stuart, Bibby Scientific, UK) for 2 h. After shaking the mixture was allowed to settle and a small volume of the sample was separated from the top of the settled solution for determining the concentration of Cr(VI) and Pb(II) by AAS. For MB, 10 mL of the solution after filtration for the determination of the concentration dye in UV-vis spectrophotometer (Shimadzu Corp., Japan). The λ_max was selected to 663 nm. The adsorption capacity (Q_e) was calculated according to the following equation (Eq. (3)): 

\[ Q_e = \frac{V(C_0 - C_e)}{W} \]  

(3)

where \( C_0 \) and \( C_e \) are initial and equilibrium concentration of Cr(VI), Pb(II), and MB, respectively (mg L\(^{-1}\)). \( V \) is the volume of aqueous solution (L) and \( W \) (0.05 g) is the weight of the adsorbent (g). To determine the percentage adsorption (removal efficiency R %) of metal ions and dye by the adsorbents, Eq. (4) as described by Chen and Wang [20] was used:

\[ R\% = \frac{C_0 - C_e}{C_0} \times 100 \]  

(4)

where \( C_0 \) is the initial of metal ions or dye concentration of the aqueous solution (mg L\(^{-1}\)), \( C_e \) is final concentration in each filtrate, after adsorption (mg L\(^{-1}\)). To determine MB concentration from its standard solution, a calibration curve is necessary. In order to develop a calibration curve, a 100 ppm stock solution MB was prepared. From the stock solution, 10 different solutions were made by varying concentration from 5 to 50 ppm. The λ_max from UV-vis spectrophotometer was obtained 663 nm and the absorbance data was plotted against the concentration that yields a straight-line (as shown in Fig. S2).

2.9. Application of adsorbent on effluent sample

The modified method of Deepali and Gangwar [21] employed to digest tannery/textile effluent (obtained from chrome tanning and from Buriganga River) and textile effluent. The effluent was diluted to 1,000 times and 100 mL of the sample was taken followed by acidification with 1 M HNO_3 to make the pH 3 as it was found in the literature suitable for effluent sample [22]. The concentration of Cr(VI) and Pb(II) in the effluent was measured by AAS and upon dilution to the desired concentration, the adsorption capacity was measured for the C-4.

3. Results and discussion

3.1. FTIR analysis of chitosan-graft-poly acrylic acid composite

The FT-IR spectra of chitosan and composite C-1 and C-4 are shown in Fig. 1. As observed from Fig. 1a, the absorption bands at 1,647; 1,598; 1,380 and 1,037 cm\(^{-1}\) are ascribed to C=O of amide I, \(-\text{NH}_2\), \(-\text{NHCO}\) of amide III, \(\text{C}_\text{C}-\text{OH}\) and \(\text{C}_\text{C}-\text{OH}\) of chitosan, respectively. In case of composite (Figs. 1b and c) the main absorption bands were observed at 3,448.78 cm\(^{-1}\) (O–H stretching overlapping the N–H stretching of primary amine), 2,927.99 cm\(^{-1}\) (C–H stretching vibration of \(\text{CH}_3\) group), 1,634.69 cm\(^{-1}\) (C=O stretching of amide bonds), 1,084.01 cm\(^{-1}\) (\(\text{C}_\text{C}-\text{O}\) stretching overlapped with C=O stretching), 1,006.85 cm\(^{-1}\) (C=O-C bridge stretching), 1,369.48 cm\(^{-1}\) (asymmetrical C–H bending of the \(\text{CH}_3\) group) and 1,127.37 cm\(^{-1}\) (C–O stretching), respectively. After graft polymerization a new absorption band appeared at 1,710 cm\(^{-1}\) (\(-\text{COOH}\) stretching); 1,450 cm\(^{-1}\) (symmetric \(-\text{COO}^-\) stretching); 1,409 cm\(^{-1}\) (\(-\text{CH}\)– bending); 1,164 and 1,080 cm\(^{-1}\). These new absorption bands indicated the existence of poly acrylic acid chain with chitosan [23].

3.2. Surface morphology by SEM

The SEM images of chitosan and the composite C-4 are shown in Fig. 2 and composite (C-1–C-4 in supporting information). It was observed that chitosan presented a smooth and nonporous surface. However, chitosan-graft-poly acrylic acid showed spherulites like, rough and porous structure, providing great surface area that might be useful adsorption purposes. This surface morphology change by PAA onto chitosan may influence the penetration of water into the polymeric network, and then may has some influence on swelling ability of corresponding composites.

![Fig. 1. FTIR analysis of composite (a) chitosan, (b) composite C-1, and (c) composite C-4.](image-url)
3.3. Efficiencies of grafting on chitosan concentration

The extracted copolymer samples showed insolubility in dilute acetic acid, a difference to chitosan. This solubility characteristic together with the increase in weight of the product, as compared with that of the initial chitosan, and their infrared spectra were taken as evidence of grafting. The influence of chitosan concentration on grafting percentage (%G) and grafting efficiencies (%GE) are shown in Fig. 3. Grafting behavior of PAA on chitosan followed a trend such that grafting yield reaches the highest value, 130% for higher monomer ratio (for C-1 at AA:chitosan ratio of 7.2:1). It is apparent that higher the amount of monomer than chitosan the higher %G due to larger availability of monomer for grafting and an opposite phenomena was observed if chitosan concentration is increased.

3.4. Swelling behavior

The grafted products were insoluble in water and in dilute acid solutions, a difference of chitosan and PAA which readily dissolve in these media. However, the grafted chitosan samples swell considerably in these media (as shown in Fig. S4). The composite C-1 and C-4 with %G of 130 and 20, respectively, were subjected to swelling test in deionized water and the degree of swelling was measured and plotted in Fig. 4. It observed that the swelling was extremely high in the initial 5 min then the increase slows down and after 25 min it become plateau. Interestingly, the composite C-4 with extremely low %G than C-1 showed a higher swelling degree than the one with high %G. This could be due to the amphiphilic nature of the modified chitosan. This characteristic is due to the fact that the composite prepared in this work contains both, chitosan as cationic and PAA as anionic polyelectrolyte counterparts. Naturally, inter-chain salt bonds between amino groups of chitosan and carboxyl groups of PAA forms. Therefore, complex behavior resulting from inter- and/or intra-molecular as well as possible electrostatic interactions should take place. A similar behavior was observed by Yazdani-Pedram et al. [24]. It can be seen from this figure that the sample with a lower degree of grafting swells more in aqueous media. This could be due to the more compact structure of the sample with higher grafting, as was discussed above.

3.5. Thermogravimetric analysis

The thermal stability of chitosan-g-PAA was investigated by TGA and the TGA curves of composite C1–C4 are shown in Fig. 5 and chitosan in Fig. S5. Chitosan

Fig. 2. Scanning electron micrographs for chitosan (a) and chitosan-graft-poly acrylic composite C-4 in (b and c).

Fig. 3. Effect of chitosan concentration on percentage of grafting (%G) and grafting efficiency (%GE).

Fig. 4. Swelling behavior of chitosan grafted poly(acrylic acid) composite (a) composite C-1 and (b) composite C-4.
started to degrade at 250°C and had a broad degradation temperature range with a high char yield at 600°C. The degradation mechanism is very complex including dehydration, deacetylation, and chain scission. The thermal degradation curves of various composites are shown in Fig. 5, where composites showed mainly three stages of weight loss. The first-stage weight loss (~10%) started from 30°C to 204.3°C was attributed to the loss of water ascribed to the elimination of water molecules adsorbed to the polysaccharide. Both the degradation of chitosan and the dehydration as well as the decarboxylation of PAA chains caused the second-stage degradation from 204°C to 332.5°C. As the temperature increased to 370°C–380°C, the weight of the composites decreased gradually (about 50%) implying a loss of moisture, dehydration of saccharide rings, and breaking of C–O–C glycosidic bonds in the main chain of chitosan [25]. With further increasing temperature to 600°C, CTS-g-PAA exhibits a third step decomposition implying the decomposition of carboxyl groups of PAA chains. Similar thermal behavior has been reported by Chen and Tan [26] for carboxymethyl chitosan-g-PAA. It can be inferred from the TGA curves of the composites that the C-4 composite showed greater thermal stability than others that indicated that with the increase of chitosan concentration, the thermal stability of the composite was increased.

3.6. Adsorption of Cr(VI), Pb(II), and MB from standard solution

The adsorption capacity of Cr(VI), Pb(II), and MB by chitosan and different adsorbents (C1–C4) were studied and compared in Fig. 6 and removal efficiencies in Fig. 7. In this study, the pH of the Cr(VI) solution was maintained to 4.0 and the highest adsorption (4.15 mg g⁻¹) was observed for composite C-4 than other composite and chitosan. The composite C-4 showed about 200% higher adsorption for Cr(VI) than chitosan and the removal efficiency was obtained to 42%. The higher adsorption for C-4 than other composites was due to the presence of higher amount of chitosan and acidic condition Cr(VI) exist as Cr₂O₇⁻ and at low pH value. At low pH, a large number of hydrogen ions can neutralize the oppositely charged surface and thus enhance the electrostatic attraction between the adsorbent and adsorbate overcoming electrostatic repulsion between them [27]. The dissociation of carboxylic groups is favored at pH values about 5.0, by which the amine groups in the composite was converted to the NH₃⁺. As, this composite was made by the addition of a higher percentage of chitosan the free amine groups from the chitosan were available which in turn converted to the NH₃⁺ and thus adsorb chromium from the solution by electrostatic action. The pH lower than 4.0 the adsorption of Cr(VI) was found to decrease because the reactive functional groups within the polymeric networks are shown as protonated form, which can hinder the interaction between the adsorbent and cation. In the case of C-2, the percentage of acrylic
acid was higher than that of the chitosan and less free amine sites were available for adsorbing chromium.

The maximum adsorption for Pb(II) was also observed for C-4 (3.43 mg g⁻¹) and removal efficiency (36%) compare to chitosan and other chitosan-g-PAA composites (C1-C3). In the case of chitosan, the adsorption occurred at the free amine site however lead ions coordinated to the amine site of chitosan surface, resulting in the lone electron pair of the nitrogen atom being shared by the attached lead species.

The experiment for MB was performed at pH 9.1 which was found suitable for MB adsorption from aqueous solution [28]. The higher tendency of adsorption at basic pH value may be attributed that at higher pH, most of the carboxylic groups of the composites are ionized and interacted with the dye molecules, which increase the adsorption for MB. Besides at higher pH, the –COOH groups present in acrylate dissociate to form COO⁻, increasing the number of fixed ionized groups. This generates electrostatic repulsion forces among the adjacent ionized groups of polymer networks, inducing an expansion of the polymer chains within the composite structure, which also increases the adsorption for MB. In case of chitosan in basic solution the –NH₂ became neutral or in acidic media it became positively charged (NH₃⁺). Hence adsorption on chitosan was believed to be lowered due to the absence of any interaction between the –NH₂ and cation of dye in solution. Although, it can be suggested that –OH group in chitosan might result in some adsorption. So, with increasing chitosan concentration, methylene blue adsorption decreased, and increasing acrylic acid the adsorption increases significantly. The highest adsorption was observed for C-1 (8.30 mg g⁻¹) and yielded 64% removal efficiencies (as shown in Fig. S6). It showed more than five times higher adsorption MB than chitosan.

3.7. Application of the chitosan-g-PAA composite for the treatment of tannery and textile effluent

3.7.1. Tannery effluent

The analysis by AAS showed that, the effluent sample after contains 0.11 ppm of chromium, So, in real effluent the concentration was 55 ppm, which is significantly higher than the permissible limit (0.00001 ppm) of chromium in drinking water by Environmental Protection Agency (EPA). The adsorbent C-4 was applied for treating tannery effluent and after a single adsorption experiment, the concentration of Cr(VI) reduced to 0.0738 ppm meaning about 33% removal was observed at acidic pH (3.0) with 2 h of shaking. The result showed a decrease in value from that of the standard solution due to the interference of other metals present in the effluent. AAS showed the effluent sample contains 40.5 ppm Pb(II) and after treatment with C-4 and the concentration of Pb(II) reduced to 0.081 ppm which means that it can remove about 36% Pb(II) from effluent.

3.7.2. Textile effluent

Since composite C-1 with a higher percentage of AA yielded greater efficiencies for MB than others it was used for real textile effluent sample analysis. The textile dyeing and finishing industry from where waste sample was collected (Anlima yarn dyeing and finishing) uses various cationic and anionic dyes among those methylene blue (MB) was one. The concentrate of MB in textile effluent before treated with adsorbent was 0.20 ppm and after treatment with C-1, it was found 0.092 ppm. The percent removal was around 52% at slightly acidic pH (6) following a 2 h shaking period with the adsorbent. After analyzing all the above results, it can be inferred that the fabricated composites have potential applicability for industrial wastewater treatment. The removal percentage of every species for real sample are lower than standard solution. The reason for this can be said to be the interference of other dissolved species present in real effluents like salts, surfactants, other dye molecules, and heavy metals, etc. Moreover, as the adsorption process was highly pH-dependent, the deviation from standard pH for effluents was also responsible for this reduced performance. Some pretreatments used to exclude these interfering species, as well as adjust the pH for maximum adsorption efficiency, may increase the performance. According to recent reports focusing on potential adsorbents, more than 93% of MB can be removed from wastewater by a chitosan-based composite, which is a much higher percentage than that relating to our composite under investigation [29]. In the case of removing Pb(II) from groundwater, maximum efficiency of 94% has been reported by Badmus et al. [30]. However, all these data were obtained under optimized conditions and present maximum efficiency. Our studies showed promising results than many other commercial absorbents while removing the selected metal or dye ions. We are in the process of studying a detailed adsorption isotherm and the performance evaluation for Cr(VI), Pb(II), and MB, respectively, and hope that the adsorption efficiency for these species will also be promising compared to other available adsorbents. We will present detailed outcomes in our future report.

4. Conclusion

From the present study, it can be concluded that the biocomposite beads of chitosan with modified Bijoypur clay act as a promising adsorbent to remove Cr(VI) and Pb(II) ions and methylene blue dye from both standard solution and real effluent. FTIR revealed that –OH, –NHCO, and –NH₂ of chitosan took part in grafting with acrylic acid. It was also observed that grafting (%) decreases with increasing chitosan amount in the composite, however, the degree of swelling slightly increases with increasing chitosan amount due to the amphiphilic nature of the modified chitosan. SEM micrographs clearly explained the surface morphology of the prepared composites. The composite which was rich in chitosan (C-4) showed a better performance for heavy metals (Cr(VI) and Pb(II)) and C-1 for MB in which the percentage of AA is significantly high. In addition, adsorption studies were performed for real tannery and textile effluent showing a lower removal percentage compared to the standard solution. From tannery and textile effluent, C-4 (obtained from 2:1 chitosan and AA) can remove 33% and 36% of Cr(VI) and Pb(II), respectively, and C-1 (with a chitosan and AA ratio of 1:7.2), 52% of MB. Thus, the maximum removal efficiencies by chitosan-g-PAA for standard solutions were found at 42%, 36%, and
64%, respectively for Cr(VI), Pb(II), and MB. The environment-friendly component of the material is proposed to have promising potential for the simultaneous removal of heavy metals and dye from aqueous solution and industrial effluent.

Acknowledgments

The author acknowledges the Ministry of Education of the Peoples Republic of Bangladesh for its research grant under the program “Grant for Advanced Research in Education (GARE)” to support the work.

References

Supporting information

S1. Fourier transform infrared spectra analysis of chitin and chitosan

The results of Fourier transform infrared (FTIR) spectra of chitin and chitosan are shown in Fig. 3.1a and b, respectively. The FTIR spectra of chitin exhibited a characteristic band at 3,448.78 cm\(^{-1}\) attributed to –NH and –OH groups stretching vibration and the band 2,885 cm\(^{-1}\) were an aliphatic C–H stretching bands that converges to OH stretching with N–H. The characteristic carbonyl C=O stretching of chitin at 1,630.84 cm\(^{-1}\) are attributed to the vibrations of the amide I band.

The sharp band at 1,427 cm\(^{-1}\) corresponds to a symmetrical deformation of the CH\(_3\) group and at 1,542.11 cm\(^{-1}\) corresponds to the N–H deformation of amide II. The vibrations bands at 1,084.01 cm\(^{-1}\) showed C–O–C vibration inside chitin ring and produced many peaks caused by the presence of hydroxide from chitin which contains a single bond C=O \[31\]. In case of chitosan (Fig. 3.1a) it revealed the main absorption bands were at 3,452.58 cm\(^{-1}\) (O–H stretching overlapping the N–H stretching of primary amine), 2,922.15 cm\(^{-1}\) (C–H stretching vibration of CH\(_2\) symmetry), 1,633.70 cm\(^{-1}\) (C=O stretching of amide bonds), 1,383.88 cm\(^{-1}\) (asymmetrical C–H bending vibrations of the CH\(_3\)) 1,089.78 cm\(^{-1}\) (C–O–C bridge stretching) and 1,149.57 cm\(^{-1}\) (C–O–C stretching). The significance differences observed in FTIR spectra of chitin and chitosan was at region 3,350–3,500 cm\(^{-1}\). In case of chitosan, it was broader than chitin. That indicated the increased deacetylated part in chitosan because that specific region corresponded to the O–H stretching overlapping the N–H stretching. The reduction in intensity of peaks related to C–H bonds, that is, 2,922.15 and 1,383.88 cm\(^{-1}\), and the appearance of new peak at 1,593.20 cm\(^{-1}\) related to the N–H bending vibration of primary amine indicated the deacetylation from chitin to chitosan \[32\].

The degree of deacetylation, which determines the content of free amino groups in the polysaccharide, can be applied to differentiate between chitin and chitosan. For instance, the degree of deacetylation of chitosan ranges from 56% to 99% with an average of 80%, depending on the crustacean species and the preparation methods. The DD of the chitosan samples was calculated using the baseline of Duarte et al. \[33\]. The computation equation for the baseline is \[34\]:

\[
DD = 100 - \left[ \frac{A_{1655}}{A_{3450}} \times \frac{100}{1.33} \right] \%
\]  

(S1)

where \(A_{1655}\) and \(A_{3450}\) were the absorbance at 1,655 cm\(^{-1}\) of amide-I band as a measure of the N-acetyl group content and 3,450 cm\(^{-1}\) of the hydroxyl band as an internal standard to correct for differences in chitosan concentration powder.

From FTIR spectrum:

\[A_{1655} = 0.021\]
\[A_{3450} = 0.125\]

So, \(DD = 100 - \left[ \frac{A_{1655}}{A_{3450}} \times \frac{100}{1.33} \right] \% = 87.37\% \)

The physiochemical, biological, and rheological properties of chitosan vary significantly as a function of its...
molecular weight and molecular weight distribution. The intrinsic viscosity $[\eta]$ was found at the zero concentration of reduced viscosity and it was obtained at 121 g/mL.

The intrinsic viscosity $[\eta]$ of a polymer solution is related to the polymer molecular weight ($M_v$) according to the Mark–Houwink–Sakurada equation $[\eta] = K M_v^a$.

For chitosan solution in where $K$ and $a$ are constants for a given solute–solvent system and temperature. For chitosan solution in acetic acid, $K = 1.81 \times 10^{-3}$ g/mL, $a = 0.93$ [14].

So, viscosity average molecular weight of chitosan, $M_v = 155,245.5$ Da.

S2. Determination of chemical oxygen demand

- Two conical flasks were taken and 1 mL of effluent is taken in each of them and diluted with 49 mL water.

- Chemical oxygen demand (COD) of one flask is measured readily (initial COD), and the other is measured after 4 h sunlight exposure with ZnO nanoparticle (final COD).

- For COD measurement 10 mL of dilute sulfuric acid is added in the flask, then 10 mL of 0.02 M potassium permanganate is added and heated in water bath for 30 min.

- After heating 10 mL of 0.05 M ammonium oxalate is added and then titrated with standard potassium permanganate to the first pink coloration.

- COD was calculated by the following formula in mg/L or ppm.

$$\text{COD (mg/L)} = \frac{\text{mL of KMnO}_4 \text{ used in the last step} \times 1,000}{\text{mL of sample used}}$$ (S2)

Fig. S4. Composite: (a) before and (b) after water absorption.

Fig. S5. TGA curves of chitosan.

Fig. S6. SEM images of C1–C4.

Fig. S7. Methylene blue: (a) after and (b) before adsorption.
References


