



Simultaneous detection of heavy metal and cationic dye from aqueous solution by hydrogel of poly(acrylic acid) grafted onto chitosan

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Poly(acrylic acid) (PAA) has been grafted to chitosan at varying ratios in order to prepare the hydrogel adsorbent to remove Cr(VI), Pb, and methylene blue from the waste water solution. The reaction was performed in a homogeneous aqueous phase using N, N-methylenebisacrylamide (MBA) as a cross-linker, and ammonium persulfate as an initiator. Grafting (%) decreases with an increase in the quantity of chitosan in the hydrogel, but the degree of swelling increases slightly with an increase of chitosan due to the amphiphilic nature of the modified chitosan. The hydrogel was characterized by a variety of techniques, such as FT-IR, SEM and TGA analysis. Adsorption behaviors for Cr(VI), Pb, and methylene blue (MB) on the prepared adsorbent were studied with respect to the standard solution and the actual industrial effluent sample. Maximum removal efficiencies for Cr(VI) and Pb were obtained from 2:1 chitosan and acrylic acid (AA) in the hydrogel. On the other hand, hydrogels with higher PAA had a remarkably higher MB adsorption capacity than others. Increased removal of heavy metals and MB by the hydrogel than chitosan was due to carboxyl groups that are easy to form bidentate carboxylates with metal ions. The adsorption result of the hydrogel for real industrial effluent showed that approximately 35% of heavy metals (Cr(VI), Pb) and 53 % MB can be removed by a single adsorption cycle.

Key words: Hydrogel, chitosan; poly (acrylic acid); heavy metals; methylene blue

Introduction

Due to increased global population, safe water must be produced to meet increasing population demand. Chitosan is a polycationic naturally occurring biodegradable, non-toxic, non-allergenic biopolysaccharide derived from chitin which is found in abundance in nature (Gaidhane et al., 2020). It is readily obtained from shrimp and crab shell containing chitin which is an N-acetyl glucosamine polymer (Kaisler et al., 2019; Yadav et al., 2019). The N-acetyl glucosamine gets converted in to glucosamine units by alkaline de-acetylation with NaOH (with 40-50% conc.)(Fei Liu et al., 2001; Ahmed et al., 2014). However, due to the high proportion of amine groups (-NH) and hydroxyl groups (-OH) and the addition of active agents with functional groups into chitosan composites, this natural biopolymer and derivatives would possibly provide more active adsorptive sites to make stable complexes with multi-component metal particles, resulting in an essentially higher degree of adsorption capacity. It is readily soluble in acidic solution and is not used as an adsorbent for wastewater treatment because of these distinct disadvantages (Zhang et al., 2015). To address the major drawbacks and to investigate the great adsorbability of chitosan, its adsorption efficiencies can be essentially improved when it can be modified by grafting (Kyzas et al., 2014; Islam et al., 2019), cross linking(Monteiro Jr and Airoidi, 1999), functionalization (Li et al., 2013) to form new composites. Many reagents such as formaldehyde(Singh et al., 2006), glutaraldehyde(Monteiro Jr and Airoidi, 1999), ethylene glycol(Kulkarni et al., 2005), and glycerol (Cui et al., 2011)have been used to improve its performance.

The chemical modifications leading the application of chitosan derived hydrogels using cross-linking, grafting of functional groups, and blending polymer or inorganics for the removal of heavy metals from wastewater has grown rapid attention. Chitosan can be chemically modified by polymerization due to the presence of -CH₂OH and -NH₂ groups for the removal of various water pollutants (Sharma and Singh, 2017). Therein, poly(acrylic acid) (PAA) has attracted increasing attention as modifier hydrogel, which contains a carboxyl group in each repeated unit and favor adsorption of metal ions (Dai et al., 2010). Extensive efforts have been made to blending or in situ grafting of PAA on chitosan to enhance metal ions adsorption ability.(Karmakar et al., 2019; Zhang et al., 2019) Large attention has been given toward graft copolymerization of vinyl monomers onto the chain of natural polymers such as starch (Kiatkamjornwong et al., 2002), cellulose(Kiatkamjornwong et al., 2002) and chitosan(Mahdavinia et al., 2004). Reactive -NH₂ and -OH of chitosan are convenient for graft polymerization of hydrophilic vinyl monomers, making this is an efficient way to acquire hydrogels with novel properties. PAA has been used to immobilize chitosan to form chitosan/PAA hydrogels to use as adsorbent for removal of heavy metals from wastewater.(Recillas-Mota1ID and Montiel-Herrera, 2019; Zhang et al., 2020)

Several chitosan / polyacrylic acid adsorbents have been reported as mentioned above, but there is no such report on the application of hydrogel prepared from grafting of poly(acrylic acid) onto chitosan obtained from waste shrimp shells for adsorbent applications. In this article, chitosan-g-poly (acrylic acid) (CS-g-PAA) was synthesized by graft copolymerization of varying amounts of chitosan and acrylic acid in a homogeneous system in the presence of an initiator and a cross-linking agent that can form gel in aqueous media. The hydrogel was used as an adsorbent for heavy metals (Cr (VI), Pb) and cationic methylene blue dye removal from wastewater. The adsorption capacity of the hydrogel for metal ions was clearly improved than that of chitosan after the introduction of long-chain PAA carboxyl groups into chitosan. As textiles and tanning industries have expanded rapidly in Bangladesh and pollution-provoking plants, the hazardous reactions of toxic and heavy metal ions in water bodies are mandatory. For heavy metals and the removal of methylene blue dyes from tanning and textile wastewater the hydrogel can be used to provide optimum results.

2. Materials and Methods

2.1. Materials

Prawn shell was collected from a prawn hatchery of Satkhira District, Khulna Division, Bangladesh. Acrylic acid (AA, from Sigma- Aldrich and distilled under reduced pressure before use), ammonium persulfate (APS, recrystallized from distilled water before use) and N,N Methylene bis Acrylamide (MBA) were also supplied by 3050 Spruce Street, St. Louis, Sweden, hydrochloric acid from Merck KGaA, 64271 Darmstadt, 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, Hazaribaag, Dhaka, Bangladesh in which the liquor was collected from the final disposal line of the Buriganga River, Dhaka, Bangladesh. Another effluent was collected from a knit dyeing industry Anlima Yarn Dyeing Ltd.,Karnapara, Savar, Dhaka, Bangladesh.

2.2. Extraction of chitosan from waste prawn shell

Chitosan was extracted from waste prawn shells following the method of Rashid et al. (Rashid et al., 2012). In a typical process, the waste prawn shell was washed with distilled water for 1 h at 50-60 °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 continuous stirring in a mechanical stirrer to remove the protein. 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 (80-100 °C) with 50% (w/w) NaOH solution at a ratio of 1:20 (wt%) for 4 h. The mixture 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 degree of deacetylation (DD) of the chitosan was 87.87% as determined from the FTIR spectrum by using FT-IR spectrophotometer (FT-IR 8400S, Shimadzu Corporation, Japan) (Czechowska-Biskup et al., 2012) and the viscosity average molecular weight of chitosan was found to be 155 kDa.

2.3. Chitosan-graft-poly acrylic acid hydrogel 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 hydrogels are shown in Table 1. The mixture was magnetically stirred at 60 °C. Initiator ammonium persulfate was added to the mixture and waited for 10 minutes for the generation of free radicals. Then acrylic acid (AA) and N, N'-methylenebisacrylamide (MBA) were added to the flask and stirred at 70 °C for 3h 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 5h. Finally, the hydrogel was ground with mortar for adsorption experiment.

Table 1: Composition of various components on different chitosan-graft-poly acrylic acid hydrogel

Chitosan: AA	Nomenclature	Chitosan (g)	AA (g)	APS (g)	MBA (g)	Chitosan concentration (w/v)
1 : 7	C-1	0.50	3.50	0.10	0.10	1.60
1 : 2	C-2	0.75	1.50	0.10	0.10	2.50
1 : 1	C-3	1.00	1.00	0.10	0.10	3.30
2 : 1	C-4	1.50	0.75	0.10	0.10	3.75

2.4. Determination of grafting efficiency

The efficiency of grafting (% E) can be calculated as the weight ratio of the increase in weight of the extracted copolymer sample and the initial monomer. This can be calculated using the relation:

$$\% E = 100 (W2 - W1)/W3$$

Where, W1, W2, and W3 are the weight of initial dry chitosan, grafted chitosan after water extraction and drying, and the weight of monomer, respectively. As is already known, 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 (W2 - W1)/W1 (Yazdani-Pedram et al., 2000).

2.5. Swelling determination

The swelling behavior of the hydrogel 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 (Ws - W0)/W0, where Ws and W0 are the weights of swollen and dry polymer, respectively.

2.6. Characterization techniques

An ATR-FTIR (Attenuated Total Reflectance/ Fourier Transforms Infrared) 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) was used for the determination of heavy metal concentration in standard samples of heavy metals (Pb, Cr) and effluent. The atomizer in which the analyte was atomized was flame. In a flame atomization fixed aliquot of measurement solution was converted into an aerosol in a nebulizer and transported into the flame. Then the aliquot was vaporized and atomized. The filtrate solutions obtained in adsorption were analyzed by AAS. For the detection, SHIMADZU AA-7000 atomic absorption spectrophotometer was used.

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

Chromium, stock solution corresponding to 1000 mg/L of chromium: 0.2892 g \pm 0.0002 g potassium dichromate, K₂Cr₂O₇ dissolved in a 400 mL glass beaker and 4 mL of DDD water was introduced then 0.5 mL of sulfuric acid (1N) was added and cooled. The mixture transferred to a 100 mL volumetric flask and fills to the mark with DDD water. Chromium, standard solution corresponding to 25 mg/L (25 ppm) of chromium (pH =4) has been prepared with the addition of 1N HNO₃. For preparing 25 ppm of chromium solution, 25.00 mL of the chromium stock solution has taken into a 1000 mL volumetric flask following the addition of 20 mL of nitric acid (1N) and filled to the mark with DDD water and mixed well and the pH of the solution adjusted by adding 1M NaOH solution.

Stock solution of Pb was prepared from lead nitrate by following a procedure described in the literature (Rao et al., 2008). In a typical process Pb (1000 ppm) has been prepared by dissolving 1.598 g of Pb(NO₃)₂, in 200 mL of DDD water, then 1.5 mL of conc. HNO₃ (63-65 %) was added to dilute it 1000 mL with DDD water. The standard solution of Pb corresponding to 25 mg/L (25 ppm) of lead was prepared with appropriate dilution with DDD water. Analytical grade HCl and NaOH solutions were used to adjust the solution pH to 6.

The stock solution of 100 ppm MB has been prepared by dissolving about 0.01 g of dye in 100 mL of DDD water. Serial dilutions have done to get the required lower concentrations in the range of 5 to 50 ppm. The concentration of MB was measured at λ_{max} of 663 nm using UV-visible spectrophotometer (Nahrain et al.). 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 by 1M NaOH solution.

2.8. Determination of Cr (VI), Pb and MB

20 mL and 25 ppm stock solution (chromium, lead and methylene blue) was taken in 100 mL conical flask with 0.05 gm of adsorbent and agitated at 27°C on a reciprocating shaker (Model no. SSL2, Stuart, Bibby Scientific, UK) for 2 h. The pH of the solution was adjusted by 0.1 mol/L NaOH or 0.1 mol/L HCl. 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 by AAS. For MB, 10 mL of the solution after filtration for the determination of the concentration dye in UV-Vis Spectrophotometer. The λ_{max} was selected to 663 nm. The adsorption capacity was calculated according to the following equation mentioned above. The adsorption capacity was calculated according to the following equation:

$$Q_e = V(C_0 - C_e) / W$$

where, Q_e (mg/g) is the adsorption capacity, C_0 (μ g/mL) is the initial concentration of Cr (VI), and Pb, C_e (μ g/mL) is the final concentration of Cr (VI) and Pb after 2 hours of adsorption, V (mL) is the volume of the solution of Cr(VI) and Pb, W (mg) is the weight of the adsorbent added.

To determine the percentage adsorption (removal efficiency %) of metal ions and dye by the adsorbents, the following equation as described by Chen and Wang was used (Chen and Wang, 2008).

where C_0 is the initial of metal ions or dye concentration in the synthetic wastewater (mg/L), C_e is final metal ions or dye concentration in each filtrate, after adsorption (mg/L).

To determine MB concentration from its standard solution, a calibration is necessary. To develop a calibration, a 100 ppm stock solution of methylene blue has been prepared. From the stock solution, 10 different solutions were ready to vary in concentration from 5 to 50 ppm. The λ_{max} was selected from a UV-Vis spectrophotometer and was obtained 663 nm and is employed for further studies. The absorbance found was plotted against the concentration and a straight-line graph was observed (in the fig S1 in the supporting information).

2.9. Application of adsorbent on effluent sample

The modified method of Deepali, K. K. Gangwar (Deepali and Gangwar) employed to digest tannery/textile effluent

(obtained from chrome tanning and from Buriganga river) and textile effluent. The effluent was diluted to 1000 times and 100 mL of the sample was taken followed by acidified with 1M HNO₃ to make the pH 2 and digest in a closed chamber for 30 min. The concentration of chromium and lead in the effluents 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 hydrogel

As can be seen from Fig. 1 (a), the absorption bands at 1647 cm⁻¹, 1598 cm⁻¹, 1380 cm⁻¹, 1094 cm⁻¹ and 1037 cm⁻¹ are ascribed to C=O of amide I, -NH₂, -NHCO of amide III, C3-OH and C6-OH of chitosan, respectively. In case of chitosan (b, c) it revealed the main absorption bands were at 3448.78 cm⁻¹ (O-H stretching overlapping the N-H stretching of primary amine), 2927.99 cm⁻¹ (C-H stretching vibration of CH₂ symmetry), 1634.69 cm⁻¹ (C=O stretching of amide bonds), 1084.01 cm⁻¹ (C6-O stretching overlapped with C=O stretching), 1006.85 cm⁻¹ (C-O-C bridge stretching), 1369.48 cm⁻¹ (asymmetrical C-H bending of the CH₂ group) and 1127.37 cm⁻¹ (C3-O stretching). After graft polymerization a new absorption band appeared at 1710 cm⁻¹ (-COOH stretching), 1450 cm⁻¹ (symmetric -COO- stretching), 1409 cm⁻¹ (-CH- bending), 1164 cm⁻¹ and 1080 cm⁻¹. The presence of these new absorption bands in the hydrogel indicated the successful polymerization process.



Figure 1: FTIR analysis of hydrogel (a) chitosan, (b) hydrogel C-1 and (c) hydrogel C-4

3.2. Morphology

The SEM images of chitosan and the hydrogel are shown in Fig. 2. It is observed that chitosan presented a smooth and nonporous surface. Chitosan-graft-poly acrylic showed a porous and tight surface which might make it suitable for the penetration of water into the polymeric network and then may have some influence on the swelling ability of corresponding hydrogels. SEM image of chitosan-g-acrylic acid hydrogel showed spherulites like structure, was rough and porous, providing great surface area for practically useful adsorption purposes. The images also revealed uniform distribution of acrylic acid onto the chitosan which might be improving the characteristic nature of chitosan as well as acrylic acid.

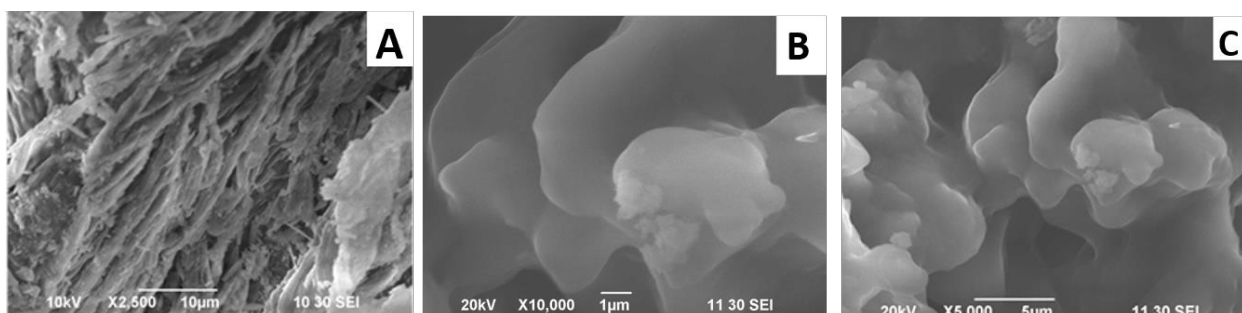


Figure 2. Scanning electron micrographs for chitosan and chitosan-graft-poly acrylic hydrogel: (a) chitosan, (b) and (c) hydrogel C-4

3.3. Grafting efficiencies

The influence of chitosan concentration on % G and % GE is shown in Fig.3. Grafting behavior of poly acrylic acid on chitosan followed a trend such that grafting yield reaches the highest value, 130% (for C-1 at AA: chitosan ratio of 7.2:1), at a chitosan concentration of 1.6% (w/v). Further increases in the concentration of chitosan solution, result in substantially lower grafting yield values. Although the number of sites susceptible to oxidation increases with the amount of chitosan, the initiator limits the number of free radical sites available for grafting. The fact that the grafting yield decreases rather than leveling off with increasing chitosan concentration, may be attributed to the increased viscosity of the solution with higher polymer concentration which restricts the number of effective collisions.

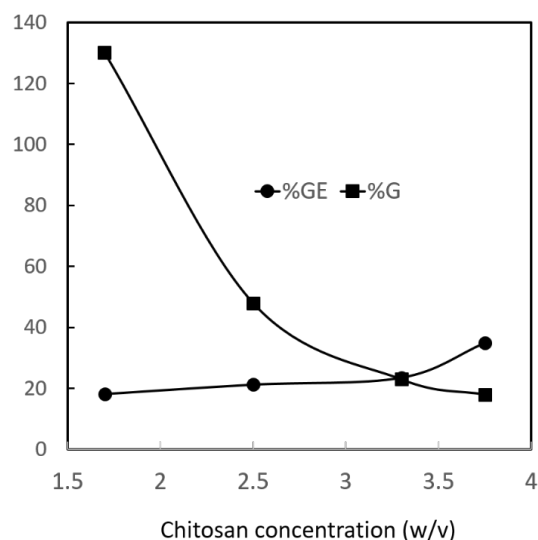


Figure 3: Effect of chitosan concentration on percentage of grafting and grafting efficiency

3.4. Swelling behavior of the adsorbent

Chitosan and all the grafted products were insoluble in water, however, the grafted chitosan samples swell considerably in water (as shown in Fig. S2 in the supporting information). The hydrogel C-1 with %G 130 and C-4 with %G 20 were subject to swelling test in deionized water and the degree of swelling was measured and plotted in Fig 4. It was observed that the swelling was extremely high initial 5 min then the increase slows down and after 25 min it become plateau. Interestingly the hydrogel 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 hydrogel 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 intramolecular as well as possible electrostatic interactions should take place. A similar behavior was observed by Yazdani-Pedram et al.(Yazdani-Pedram et al., 2000) 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.

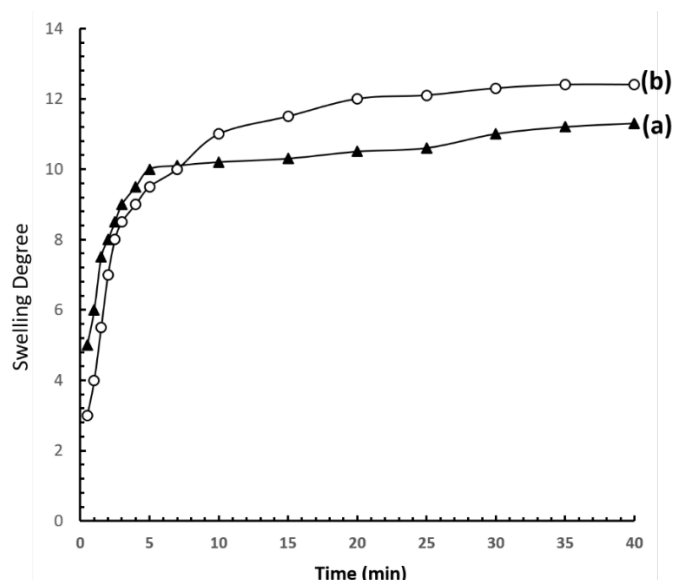


Figure 4. Swelling behavior of chitosan grafted poly (acrylic acid) hydrogel (a) hydrogel C-1 and (b) hydrogel C-4.

3.5. Thermogravimetric analysis

The thermal degradation behavior of chitosan-g-PAA of C1-C4 are shown in Fig. 5 and chitosan in Figure S3 (in the supporting information). Chitosan 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 hydrogels are shown in Fig.5, where hydrogels showed mainly three stages of weight loss. The first-stage weight loss ~10% started from 30 to 204.3°C was attributed to the loss of water is 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 to 332.5°C. The temperature of 50% weight loss of polysaccharide is found in the range 370-380 C which attribute to the degradation of the glycosidic bond of chitosan. The third-stage degradation behavior from 332.5 to 600 °C was mainly due to the chain scission both in PAA and chitosan. It was found that the higher the monomer feed, the lower the char yield at 600 °C. This is because the char yield of pure PAA is much lower than that of pure chitosan. It can be inferred from the curves of the hydrogels that the C-4 hydrogel show greater thermal stability than others. With the increase of chitosan concentration, the thermal stability of the hydrogel increases.

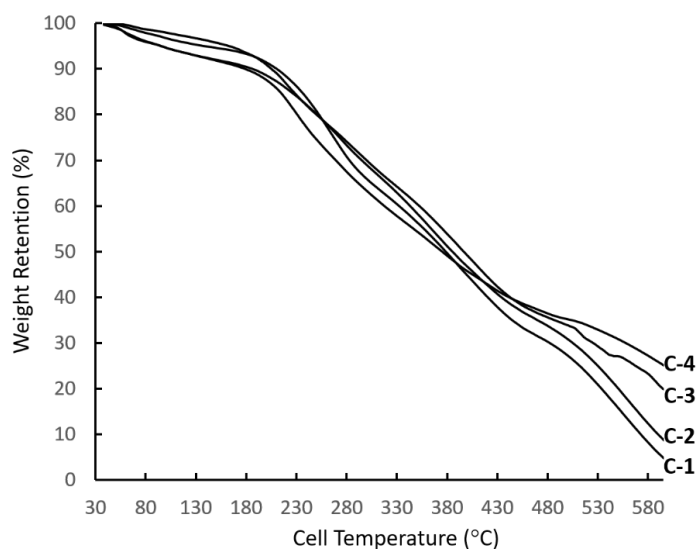


Figure 5. TGA curve of chitosan-g-PAA hydrogels.

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

The adsorption capacity of chromium (VI), Pb and MB by chitosan and different hydrogel (C1 to C4) were studied and compared in Fig. 6 and removal efficiencies in Fig. 7. In this study, the pH was maintained at 4.9 for Cr (VI) better result was observed for hydrogel C-4 (4.15 mg/g) compared to chitosan. It showed more than double capacity than chitosan and the removal efficiency is about 42%. The better adsorption for C-4 can be described from its composition. The chromium (VI) exist as Cr_2O_7^- in the acidic solution. This adsorption was carried out in acidic pH (below 7). At lower pH value, it is observed that the adsorption capacity decreases appreciably. This fact is ascribed to that the reactive functional groups within the polymeric networks are shown as protonated form, which can hinder the interaction between the adsorbent and cation. Besides, the non-ionic bonding mechanism (e.g. hydrogen bonding) among carboxylic groups occurs at lower pH value, which is also responsible for lower metal ion adsorption capacity. With an increase in pH values, the adsorption capacity increases since the dissociation of carboxylic groups is favored at higher pH values, by which ionic bonds form between the polymer backbone and metal ions. So, the amine groups in the hydrogel converted to the NH_3^+ . As, this hydrogel was made by the addition of a higher percentage of chitosan. So, freer amine groups from the chitosan were available which in turn converted to the NH_3^+ and thus adsorb chromium from the solution by electrostatic action. Whereas, in the case of C-2, the percentage of acrylic acid was higher than that of the chitosan. So, less free amine sites were available for adsorbing chromium.

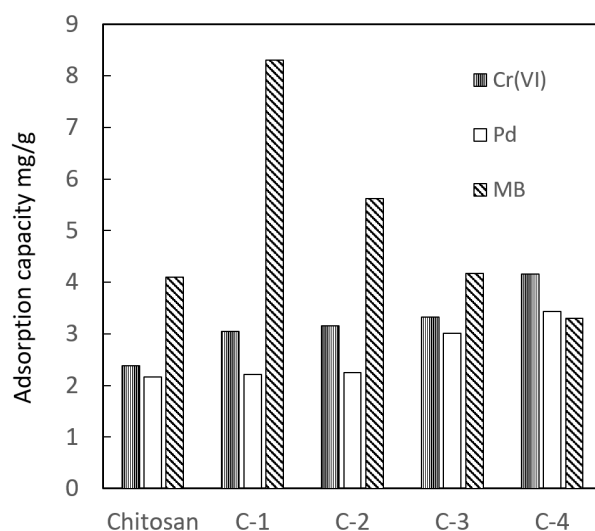


Figure 6. Adsorption capacity for heavy metals and cationic dyes of chitosan and various chitosan-g-PAA hydrogels.

For Pb the best adsorption was observed for C-4 (3.43 mg/g) compared to chitosan and other chitosan-g-PAA and the hydrogel yield 36% removal efficiencies of Pb from aqueous solution. In the case of chitosan the adsorption occurred at the free amine site of the chitosan. Lead ions coordinated to the amine site on chitosan surface, resulting in the lone electron pair of the nitrogen atom being shared by the attached lead species.

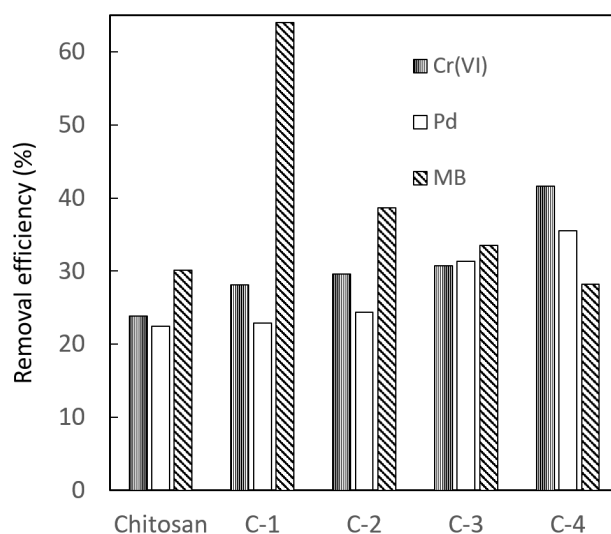


Figure 7. Removal efficiencies of heavy metals and cationic dyes of chitosan and various chitosan-g-PAA hydrogels.

The increasing tendency of adsorption capacity with increasing the pH value may be attributed to the following facts. At higher pH, most of the carboxylic groups of the hydrogels are ionized and interacted with the dye molecules, which increase the absorption for MB. Besides at higher pH, the $-\text{COOH}$ 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 hydrogel structure, which also increases the adsorption for MB. The MB existed in the solution as a positive cation. Cationic dyes were attracted to the anionic layers of the clay. Where in the case of chitosan in basic solution the $-\text{NH}_2$ became neutral or in acidic media it became positively charged (NH_3^+). So, Dye adsorption on chitosan was believed to be lowered due to the absence of any interaction between the $-\text{NH}_2$ and cation of dye in solution. Although, it can be suggested that $-\text{OH}$ group in chitosan might result in some adsorption. So, with increasing chitosan concentration, methylene blue adsorption decreased and increasing acrylic acid caused the best adsorption. The best adsorption was observed for C-1 (8.30 mg/g)

compared to chitosan and yielded 64% removal efficiencies (as shown in Fig. S4 in the supporting information). It showed more than five times the adsorption of cationic dye MB than chitosan. In the case of chitosan the adsorption occurred at the free amine site of the chitosan. So, with an increase in the available amine groups in the hydrogel, the adsorption capacity increases. The lowest adsorption capacity among the hydrogels was found for C-4. As, this hydrogel was made by the addition of a higher percentage of chitosan than acrylic acid. So, freer amine groups from the chitosan were available which in turn form co-ordination bond Pb^{2+} ion. Whereas, in the case of C-1, the percentage of acrylic acid was higher than that of the chitosan. So, less free amine sites were available for adsorbing lead.

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

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 EPA (Environmental Protection Agency). The adsorbent C-4 was applied for treating tannery effluent and after a single adsorption experiment the concentration of Cr (VI) reduced to 0.0738ppm meaning about 33% removal was observed at acidic pH (0.5) with 2 hours of shaking period. The result showed a decrease in value from that of the standard solution. Such deviation may be suggested as a result of the low pH of the solution and due to the interference of other metals present in the effluent. AAS showed the effluent sample contains 40.5 ppm lead and after treatment with C-4 the concentration of lead reduced to 0.081 ppm which means it can remove about 36% lead from effluent.

3.7.2. Textile effluent

Since hydrogel C-1 with a higher percentage of AA yielded greater efficiencies for MB than others it was used for practical application. 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. In this work the adsorbent was used to assess the MB removal efficiencies from textile effluent was C-1. 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 which means it can reduce MB concentration to about 52% only treated for 2 h and is significantly lowered than the initial value. In this case it is evident C-1 is an effective adsorbent for MB removal from textile effluent.

4. Conclusion

The chitosan skeleton endows the biodegradability for hydrogels; meanwhile, the poly(acrylic acid) provides abundant adsorption sites. Thus, the maximum removal efficiencies by CS-g-PAA for standard solutions were found 42, 36 and 64% respectively for Cr(VI), Pb and MB. It indicated that the heavy metal adsorption behavior of adsorbent was monolayer chemisorption. The high adsorption capacity of CS-g-PAA was ascribed to the formation of bidentate carboxylates with metal ions. The environment-friendly component of hydrogel is proposed to have promising potential for the simultaneous removal of heavy metals and dye from aqueous solution and industrial effluent.

Conflict of Interest

The author declares no conflict of interest

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- Supporting Information

Simultaneous detection of heavy metal and cationic dye from aqueous solution by hydrogel of poly(acrylic acid) grafted on chitosan

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