

Novel modification of chitosan hydrogel beads for improved properties as an adsorbent

Nan Li and Renbi Bai*

Department of Chemical and Biomolecular Engineering

National University of Singapore

10 Kent Ridge Crescent

Singapore 119260

*Fax: (65) 6779 1936; E-mail: chebairb@nus.edu.sg

Abstract

Chitosan, a natural polysaccharide, has increasingly been studied as an adsorbent for heavy metal removal in recent years. The amine groups in chitosan are generally known to be the main adsorption sites for heavy metal ions. However, due to the instability of chitosan in acidic solutions, chemical crosslinking has often been used to enhance the acidic resistance of the material. Since most of the chemical crosslinking agents are prone to act on the amine groups instead of the hydroxyl groups in chitosan, some of the amine groups will be consumed in the crosslinking reaction, and therefore, the adsorption capacity of the adsorbent reduced. In this study, chitosan hydrogel beads were modified by formaldehyde solution to shelter the amine groups before the crosslinking reaction with ethylene glycol diglycidyl ether (EDGE), and then the amine groups of the modified chitosan hydrogel beads after the crosslinking were released by a strong acid treatment. Fourier Transform Infrared (FTIR) Spectroscopy and X-ray photoelectron spectroscopy (XPS) revealed that the crosslinking reaction took place with the hydroxyl groups in chitosan when the amine groups were sheltered. Batch adsorption tests for copper ion removal showed that the chitosan hydrogel beads through the novel crosslinking reaction had very good adsorption capacities in a wide solution pH range. Both the primary amine groups and the $-N=$ groups were found to interact with copper ions in the adsorption.

Keywords: Novel crosslinking; Chitosan hydrogel beads; Formaldehyde treatment; EGDE; Adsorption mechanism

Introduction

Chitosan, a derivative from N-deacetylation of chitin - a naturally occurring polysaccharide from crustacean and fungal biomass, has been found to be capable of chemically or physically adsorbing various heavy metal ions, including lead, mercury, platinum, cadmium, etc.¹⁻⁶ Compared with the conventional methods of heavy metal removal through processes such as chemical precipitation, ion exchange and activated carbon adsorption, bioadsorption using chitosan has shown the advantage of effectively removing metal ions at low concentrations, and the benefit of the material being widely available and environmentally friendly.⁶⁻⁷ Moreover, the amine groups in chitosan can provide reactive sites for specific adsorption of various metal ions.^{1,5,6,8} Traditionally, chitosan has been used in the form of flakes or powder in metal ion adsorption. Since raw chitosan can be characterized as a crystallized polymer, the adsorption of metal ions usually take place only at the amorphous region of the crystals.⁹ Progress has been made to produce chitosan

hydrogel beads to improve the adsorption capacity of chitosan because the gel formation process in producing chitosan hydrogel beads reduces the crystallinity of the polymer. The use of chitosan hydrogel beads also provide the potential for regeneration and reuse of the hydrogel beads after metal adsorption.^{1,9,10} One of the major material limitations of the hydrogel beads is however in their poor acidic resistance (the beads may dissolve at solution pH below about 4). Attempts were made to improve the chemical stabilities of the hydrogel beads in acidic conditions through chemical crosslinking of the surfaces with crosslinking agents, such as ethylene glycol diglycidyl ether (EGDE), glutaric dialdehyde (GA), and epichlorohydrine (ECH).^{5,7,10} Chemical crosslinking reaction was found to be able to reduce the solubility of the chitosan hydrogel beads in aqueous solutions of low pH values. However, most of the chemical crosslinking agents, e.g. EGDE, GA and even ECH, are prone to react with the primary amine groups instead of the hydroxyl groups in chitosan.¹⁰⁻¹³ Since the primary amine groups of chitosan are known to be the main chelating sites for many types of heavy metal ions, the adsorption capacity of the hydrogel beads will therefore be reduced by the crosslinking reactions. In this study, a new method was used in the crosslinking reactions to protect or prevent the amine groups in chitosan from being consumed by the crosslinking agent. Chitosan hydrogel beads were treated by formaldehyde solution to shelter the amine groups. Then, chemical crosslinking of the chitosan hydrogel beads were conducted with EGDE. Finally, the crosslinked hydrogel beads were treated in an HCl solution to release the sheltered amine groups. Adsorption experiments for copper ion removal were conducted to evaluate the effectiveness of the new crosslinking method in enhancing metal adsorption performance. Various analyse, such as scanning electronic microscopy (SEM), zeta potential measurement, Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS), were employed to characterize the surface properties of the hydrogel beads and the mechanisms of the surface treatment and crosslinking as well as copper adsorption on the surfaces.

Experimental Section

Materials. Chitosan flakes (85% deacetylated) were obtained from Sigma. Ethylene Glycol Diglycidyl Ether (EGDE), formaldehyde solution (20%), copper (II) standard solution (1000 mg/L), and acetic acid were supplied by Merck. All other chemicals were of reagent grade purity and deionized (DI) water was used to prepare all solutions.

Preparation of Chitosan Hydrogel Beads. A 2 g amount of chitosan flakes was added into 100 mL 2 % (w/w) acetic acid in a beaker and the contents in the beaker were mixed on a hot plate stirrer at 70 °C and 200 rpm for 6 h to obtain a homogenous chitosan solution. Then, the chitosan solution was injected in droplets into a 1 M NaOH solution to form hydrogel beads through a vibration nozzle system (Nisco Encapsulation Unit, LIN-0018, with nozzle size of 300 µm). The chitosan hydrogel beads (denoted as CHBs) were allowed to stay in the NaOH solution with slow stirring for 12 h for hardening. The beads were finally separated from the NaOH solution and were washed with DI water in a large beaker until the solution pH became the same as that of the fresh DI water. Then, the beads were stored in DI water for further use.

Surface Treatment and Crosslinking of CHBs. 100 mL of the CHBs and 100 mL of 20% formaldehyde solution were added into a 500 mL conical flask. The contents in the flask were shaken in an orbital water bath shaker operated at 250 rpm and at room temperature

(22-23⁰C) for 2 h. Then, 150 mL of 1 M NaOH solution was added into the flask and the contents in the flask was shaken for another 2 h at the same shaking rate and temperature to solidify the hydrogel beads. Finally, the formaldehyde-treated chitosan hydrogel beads (denoted as FCHBs) were separated from the solution, washed with DI water for several times, and stored in a 250 mL conical flask containing DI water for further study.

For the chemical crosslinking with EGDE, 75 mL of the FCHBs was taken from the stock and added into 75 ml of DI water in a flask with the pH being adjusted to 12 by the addition of 0.1 M NaOH solution. After 5 min, a 1.2 g amount of EGDE solution was added into the flask and the crosslinking reaction in the flask was allowed to proceed at 70 °C for 6 h in a thermostatic water bath with continuous agitation. Finally, the mixture in the flask was cooled down to room temperature, and the EGDE crosslinked FCHB beads (denoted as EFCHBs) were separated and washed in an ultrasonic bath with sufficient DI water until the pH of the washing solution became around 6-6.5 (the same as the fresh DI water). The beads were then stored in DI water in a flask for further use.

To release the amine groups shielded by formaldehyde, 50 mL of the EFCHB beads was taken from the stock and added into 150 mL of a 0.5 M HCl solution in a 250 mL conical flask which was shaken in an orbital water bath shaker operated at 200 rpm and room temperature for 12 h. The HCl-treated EFCHB beads were separated and washed using sufficient DI water and were stored in DI water for further study. The beads with the amine groups released by the HCl treatment are denoted as NRCHB.

In order to compare the effectiveness of the new crosslinking method, the CHBs were also directly crosslinked with EGDE, without the treatment of formaldehyde, under the same conditions as presented above for analysis and adsorption study. The directly crosslinked CHB beads are referred to as DCHB.

SEM Observation. The surface morphologies of the CHB, FCHB, EFCHB and NRCHB beads were examined with a scanning electron microscope (SEM, JEOL JSM-5600LV) or a field emission scanning electron microscope (FESEM, JEOL JEM 6700) at 5 kV. Samples were vacuum-dried in a desiccator and were platinum-coated by a vacuum electric sputter coater (JEOLJFC-1300) to a thickness of at least 500 angstroms before glue mounted onto the sample stud for the SEM analysis.

Zeta Potential Measurement. Zeta potentials are often used as an important parameter in explaining the electrostatic surface interaction in adsorption. To estimate the zeta potentials of the CHB, DCHB and NRCHB beads, about a 0.1 g amount of each type of the dried beads was ground into powder and suspended into 100 mL of DI water, respectively. The mixtures were sonicated first for 4 h, followed by stirring for another 24 h, and then settled for 12 h. Samples were taken from the supernatants (which had colloidal fragments from the sample beads in it) and were used for zeta potential analysis. Before the analysis, each sample was distributed into several vials. The pH values of the sample in each of the vials were adjusted with a 0.1 M HCl or 0.1 M NaOH solution to a desired level. A Zeta-Plus4 instrument (Brookhaven Corp., USA) was used to measure the zeta potentials of all the samples. Zeta potentials so determined from the fragments in the samples were used to represent the zeta potentials of the sample beads in solutions of the same pH values.¹⁴

Adsorption Experiments. Kinetic adsorption experiments were conducted to evaluate the adsorption properties of the CHBs, NRCHBs and DCHBs. A number of plastic bottles, each with 10 mL copper ion solution with an initial copper concentration of 15 mg/L

and an initial solution pH of 6, were used. A 0.1 g (wet) amount of each type of the beads was added as scheduled into each of several bottles, respectively. The mixture in each bottle was shaken on an orbit shaker operated at 200 rpm and room temperature for various periods of time up to 12 h or until adsorption equilibrium was established. The histories of copper ion concentration in the solutions were established by analyzing the solution samples taken from each bottle with different adsorption times, using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima 3000DV). The amounts of adsorption on each type of the beads, q (mg/g), were calculated from the following equation:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

where C_o (mg/L) and C_t (mg/L) are the initial concentrations and concentration at adsorption time t of the solution, respectively, V (L) is the volume of the copper solution in each bottle, and m (g) is the dry weight of the beads added into each bottle.

The adsorption performance of copper ions with the CHBs, NRCHBs and DCHBs were also investigated at various initial solution pH values. A 0.1 g amount of each type of the beads was added, respectively, into a number of 25 mL plastic bottles, each of them contained 10 mL copper ion solution with the same initial copper concentration of 15 mg/L, but a different initial solution pH values in the range of 3 to 10, respectively. The contents in the bottles were stirred on an orbital shaker at 200 rpm and room temperature for 24 h for adsorption to proceed (the equilibrium adsorption time was usually less than 10 h). The pH of the solution in each bottle was not controlled during the adsorption process in order not to introduce any additional ions into the solution. The initial and final copper ion concentrations in the solution in each bottle were analyzed using ICP-OES mentioned early.

FTIR Analysis. In order to investigate the surface modification and crosslinking mechanisms, FTIR analysis was conducted. The CHB, FCHB, EFCHB and NRCHB beads were ground into powder, respectively. For each type of the powder, a 1 mg amount of the powder was blended with a 100 mg amount of IR-grade KBr in an agate mortar and pressed into a tablet. FTIR spectra were obtained for the tablets from a FTS3500 FTIR Spectrometer.

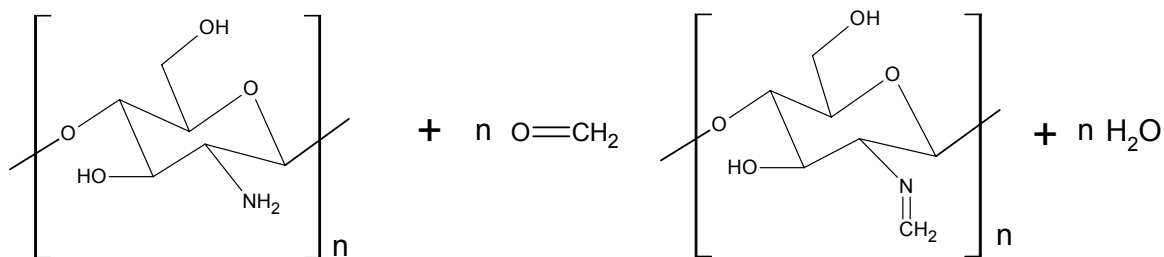
XPS Study. XPS analyses of the CHB, FCHB, EFCHB and NRCHB beads were carried out on a VGESCALAB MKII spectrometer with an Al $K\alpha$ X-Ray source (1486.6eV of photons) to further verify the surface modification and crosslinking mechanisms. The XPS spectra peaks were decomposed into subcomponents by fixing the 0% Lorentzian-Gaussian Curve-fitting program with a linear background to the spectra through an XPSpeak 4.1 software package. The full width half maximum was maintained at 1.4. The NRCHB beads after copper ion adsorption were also analyzed with XPS to examine the adsorption mechanisms.

Results and Discussion

Surface Treatment and Crosslinking Mechanisms. FTIR spectra have widely been used as a tool to identify the presence of certain functional groups or chemical bonds on a solid surface in material modifications because each specific chemical bond often shows a unique energy adsorption band.¹⁵⁻¹⁷ In this study, FTIR analysis was used to examine the characteristic chemical structures of the four types of the hydrogel beads (i.e. CHB, FCHB, EFCHB, and NRCTB) to elucidate the mechanisms occurred on the surfaces. The typical

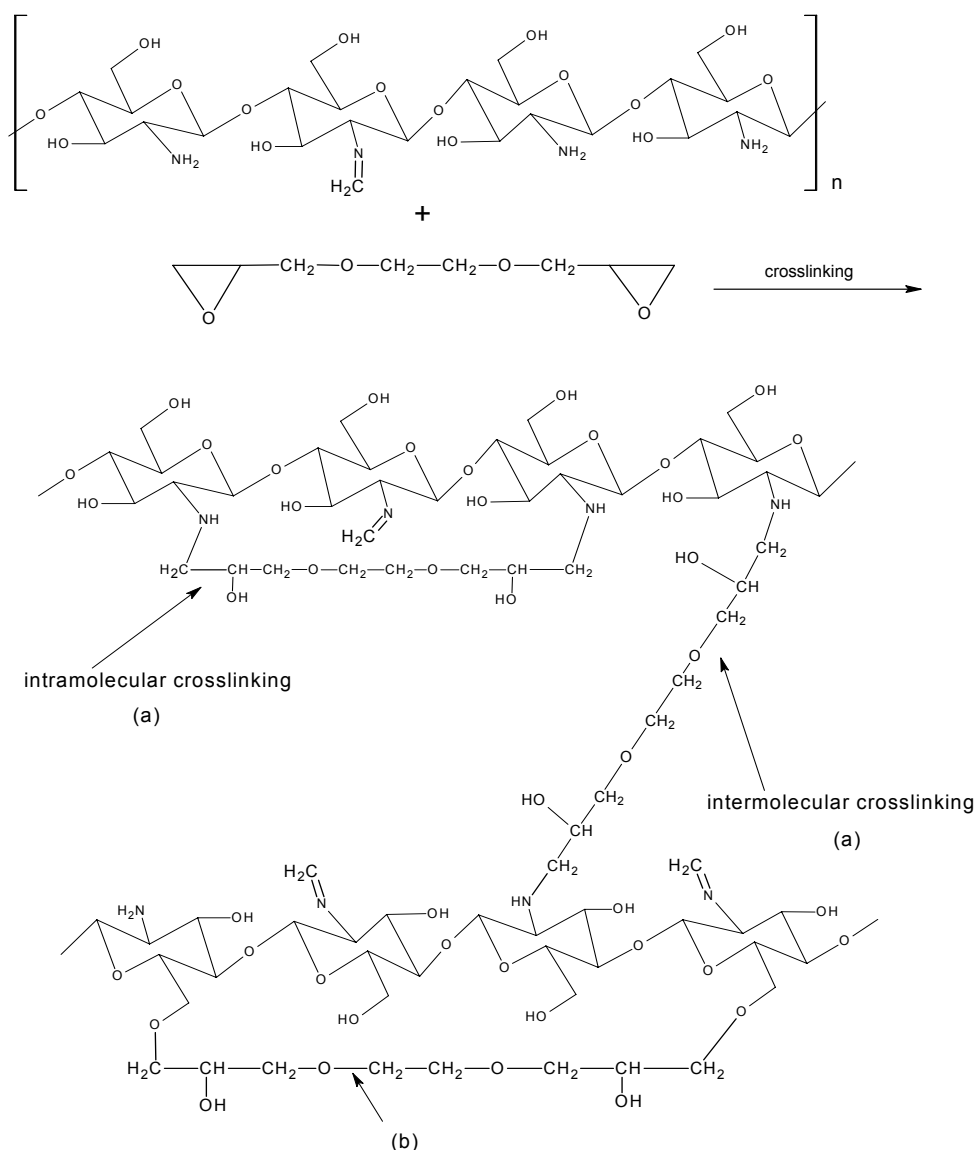
FTIR results of the CHB, FCHB, EFCHB, and NRCHB in this study are shown in Figure 1. The major peaks for the CHBs in Figure 1a can be assigned as follows: 3450.4 cm^{-1} (-OH and N-H stretching vibrations), 2882.9 cm^{-1} (C-H stretching vibration in -CH, and -CH₂), 2354.3 cm^{-1} (asymmetric N-H stretching vibration in -NH₃⁺), 1652.9 cm^{-1} (N-H bending vibration in -NH₂), 1429.1 cm^{-1} (N-H deformation vibration in -NH₃⁺), 1379.8 cm^{-1} (C-H symmetric bending vibration in -CHOH-), 1321.5 cm^{-1} and 1159.6 cm^{-1} (C-N stretching vibration), 1061.4 cm^{-1} and 1025.6 cm^{-1} (C-O stretching vibration in -C-OH), and 897.6 cm^{-1} (C-N stretching vibration).¹⁸

After the formaldehyde treatment of the CHB beads, the spectrum of the FCHB in Figure 1b shows some major changes due to the reaction. The peak at 3450 cm^{-1} for the CHB was broadened and shifted to 3405.1 cm^{-1} . A new peak at the wavenumber of 1563.8 cm^{-1} appeared after the formaldehyde treatment. The peak at 1563.8 cm^{-1} can be assigned to the C=N- stretching vibration, indicating that some of the C-NH₂ groups were changed into the C=N- groups. In addition, the peaks at the wavenumbers of 1429.1, 1159.6 and 897.6 cm^{-1} shown in Figure 1a weakened after the formaldehyde treatment. All of these changes are related to the chemical bonds with nitrogen, indicating that the amine groups were involved in the reaction with formaldehyde treatment. The possible reaction mechanism can be given in Scheme 1. It was observed that no peaks appeared at wavenumber of 1739 cm^{-1} (C=O stretching) and 538 cm^{-1} (C=O twisting) after formaldehyde treatment. Therefore, one can conclude that formaldehyde attached on the surface of the beads and the hydrogel is safe for use.



Scheme 1. Conversion of CHB to FCHB in formaldehyde treatment

With the EGDE crosslinking, the spectrum of the EFCHB in Figure 1c shows that the band for O-H and N-H stretching vibration around the wavenumber of 3400.2 cm^{-1} and the peaks for the N-H bending vibration in -NH₂ at the wavenumber of 1652.9 cm^{-1} were significantly weakened. The other two bands at the wavenumbers of 1419.1 and 1321.5 cm^{-1} , relating to the amine groups, were also weakened after the EGDE crosslinking reaction. However, the peak representing the -C=N- stretching vibration at the wavenumber around 1597.9 cm^{-1} was almost not affected by the crosslinking reaction. Hence, the FTIR result in Figure 1c suggests that the EGDE crosslinking reaction occurred with the -NH₂ in the -C-NH₂ groups and perhaps the -OH in the -C-OH groups as well but not with the -C=N- group. In other words, some amine groups in chitosan were converted to the -C=N- groups by the formaldehyde treatment and were not participated in the crosslinking reaction. The possible crosslinking mechanisms are proposed in Scheme 2.



Scheme 2. Possible crosslinking mechanisms in the new method (a) with amine groups (b) with hydroxyl groups

From the FTIR spectrum in Figure 1d for the acid-treated beads (i.e. NRCHB), some important information can be clearly obtained. Firstly, the peak at the wavenumber of 1655.4 cm^{-1} was significantly increased (compared to that in Figure 1c), indicating that more $-\text{NH}_2$ groups were generated by the acid treatment. Secondly, the strengthened peak at the wavenumber of 2351.5 cm^{-1} suggests that more protonated $-\text{NH}_3^+$ groups appeared on the surfaces of the beads after the acid treatment. Thirdly, the peak at the wavenumber of 1536.1 cm^{-1} , representing the $=\text{N}-\text{CH}_2$ bond, disappeared almost completely. All these results provide evidence that the $=\text{N}-\text{CH}_2$ groups formed in the formaldehyde treatment were returned to the $-\text{NH}_2$ groups (or $-\text{NH}_3^+$ in the protonated form) by the acid treatment.

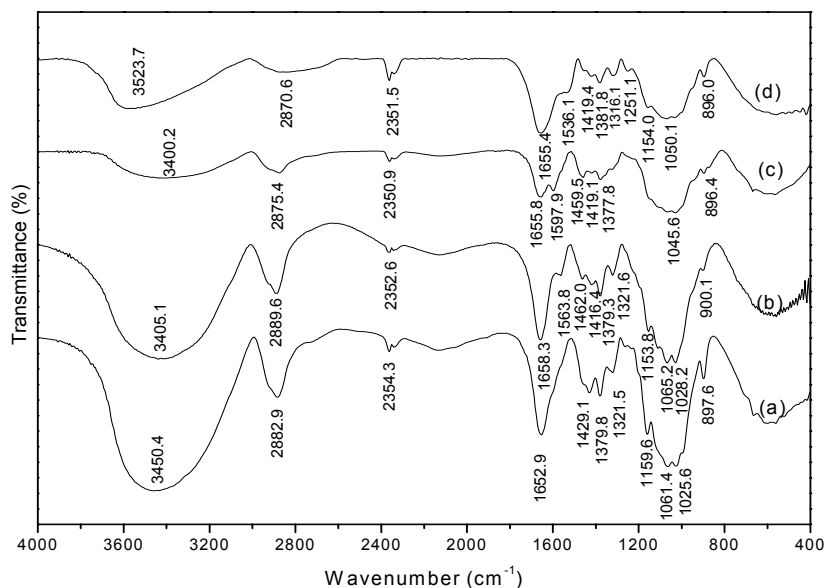


Figure 1. FTIR spectra of (a) CHBs, (b) FCHBs, (c) EFCHBs, and (d) NRCHBs

To verify the findings from the FTIR spectra, X-ray photoelectron spectroscopy (XPS) was employed. Since most reactions discussed above involved the nitrogen atom, the N 1s core-level XPS spectra of the CHB, FCHB, EFCHB, and NRCHB beads are examined in Figure 2. As seen in Figure 2a, the N 1s core-level XPS spectrum of the CHB can be fitted to only one peak with binding energy of 399.42 eV for the nitrogen in the $-\text{NH}_2$ groups. After the treatment with formaldehyde, the N 1s core-level XPS spectrum of the FCHB beads in Figure 2b can be assigned to peaks at the BEs of 398.52 and 399.79 eV for the nitrogen in the $=\text{N}-$ and $-\text{NH}_2$ groups, respectively,^{19,20} indicating the formation of the $-\text{N}=\text{CH}_2$ groups by the formaldehyde treatment, as shown in Scheme 1. After the EGDE crosslinking (see Figure 2c), the peak at 398.52 eV representing the $=\text{N}-$ groups did not change noticeably, but the weak peak shifted a little bit down to 399.31 eV, suggesting that, the $-\text{N}=\text{CH}_2$ groups were not affected by the crosslinking reaction, but some of the $-\text{NH}_2$ groups in FCHB beads were changed to $-\text{NH}-$ by the crosslinking reaction. This result is in accordance with the FTIR results discussed in Figure 1c. The change of $-\text{NH}_2$ to $-\text{NH}-$ during the EGDE crosslinking process is suggested by the crosslinking mechanism as shown in Scheme 2a. Some of the $-\text{NH}_2$ groups were not “sheltered” by the formaldehyde treatment and hence they were crosslinked by EGDE in the case. Figure 2d shows the N 1s core-level XPS spectrum of the NRCHB beads. It is observed that the peak at the binding energy of 398.41 eV is very weak and the one at 399.85 eV is strengthened after the HCl treatment, in comparison with the peaks at the similar BEs in Figure 2b and 2c. The strong peak in Figure 2d can be attributed to the nitrogen in the $-\text{NH}_2$ and $-\text{NH}_3^+$ groups,^{15,19} indicating that the nitrogen atoms in the $-\text{N}=\text{CH}_2$ groups were converted back to $-\text{NH}_2$ (or the protonated form of $-\text{NH}_3^+$). The weak peak at the BE of 398.41 eV may be attributed to the nitrogen atoms in the $=\text{N}-\text{CH}_2$ groups, suggesting that a small number of the $=\text{N}-\text{CH}_2$ groups remained after the acid treatment in this case.

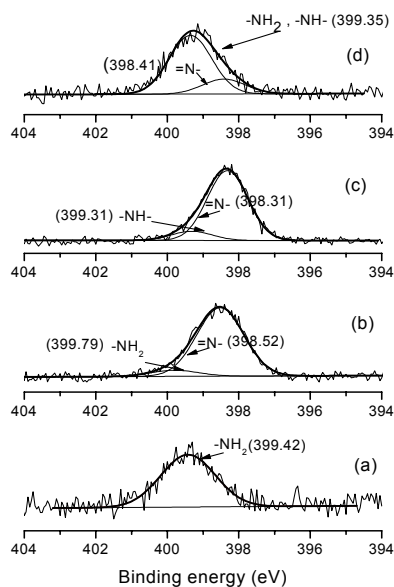


Figure 2. XPS N 1s spectra for the CHBs (a), FCHBs (b), EFCHBs (c) and NRCHBs (d)

As the -OH groups in chitosan are also suspected to be possibly involved in the crosslinking reaction from the FTIR results in Figure 1, the O 1s XPS spectra of the CHB, FCHB, EFCHB and NRCHB beads are examined in Figure 3.

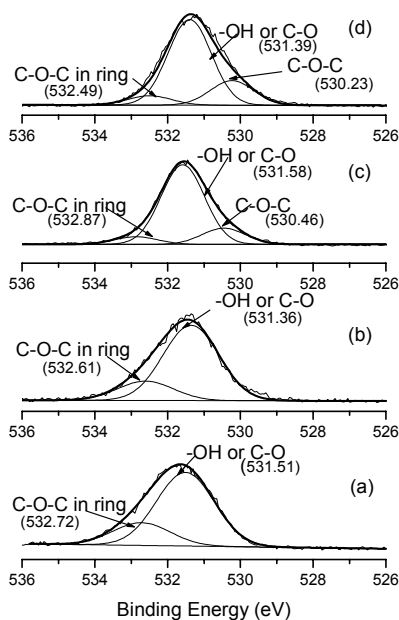
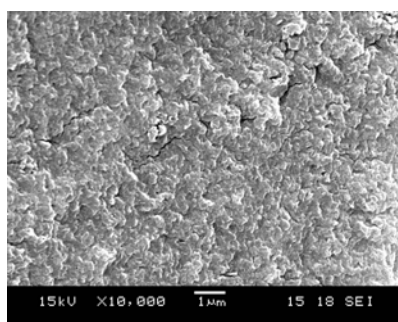


Figure 3. XPS O 1s spectra for the CHBs (a), FCHBs (b), EFCHBs (c), and NRCHBs (d)

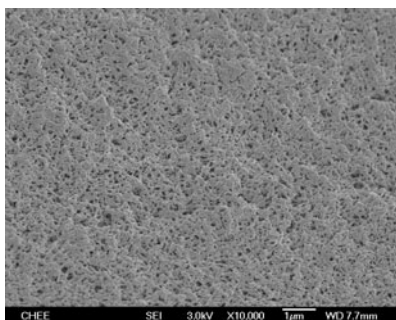
There are two peaks at the BEs of 532.72 and 531.51 eV, respectively, in the O 1s of the CHBs (see Figure 3a). These two peaks can be assigned to the oxygen in the C-O-C groups in the glucose ring and in the -OH or C-O groups on the surfaces of the CHBs. The

O 1s peaks of the FCHBs in Figure 3b are very similar to that of the CHBs, indicating that the formaldehyde treatment did not react with any oxygen-containing functional groups. After the EGDE crosslinking, a new peak is observed at the BE of 530.46 eV, which can be assigned to the oxygen in the C-O-C groups,²¹ see Figure 3c. The formation of the C-O-C groups on the surfaces may be attributed to the chemical binding of EGDE with the CH₂OH groups on the surface of the beads. This crosslinking mechanism is also shown in Scheme 2 (as 2b). Since the amine groups on the surfaces of the beads may not be enough for the crosslinking reaction, the remaining or extra EGDE molecules in the solution therefore used the -OH groups for the crosslinking reaction. From Figure 3d the O 1s XPS spectrum, as the O1s peaks did not show noticeable changes after the acid treatment, in comparison with those in Figure 3c before acid treatment, one may conclude that the crosslinked beads were stable and were not affected even by the HCl treatment. The results provide evidence that the crosslinking reaction was also effective.

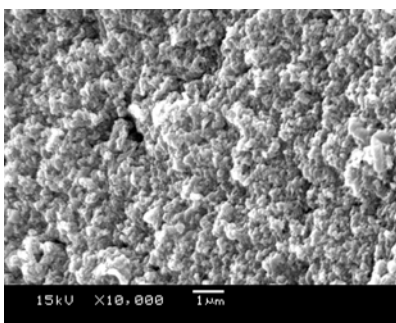
The SEM images in Figure 4 show the morphological differences of the surfaces of the various types of beads, i.e. CHB, FCHB, EFCHB and NRCHB, resulting from the surface treatment and crosslinking reactions.



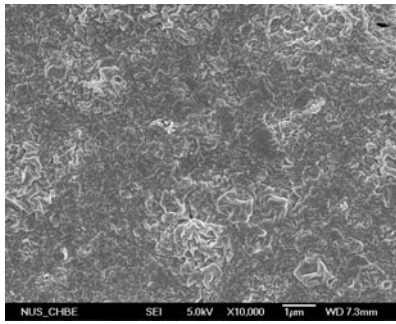
(a)



(b)



(c)



(d)

Figure 4. SEM images showing the surface morphologies of (a) CHBs, (b) FCHBs, (c) EFCHBs, and (d) NRCHBs

Zeta Potentials. As the DCHB and NRCHB beads were used in the adsorption experiments to compare their adsorption performances, the zeta potentials of the two types of the beads as a function of the solution pH values are presented in Figure 5. Both the DCHBs and NRCHBs have positive zeta potentials in acidic conditions but negative zeta potentials in basic conditions, with a point of zero zeta potential at pH around 7.8. From the electrostatic interaction point of view, the adsorption of metal ions on the chitosan hydrogel beads may be improved with the increase of solution pH values, due to the reduction of the repulsive or increase of the attractive surface electrostatic interactions. It is observed that, in general, the NRCHBs have greater zeta potential value than the DCHBs. This can be another evidence that more amine groups are available on the NRCHBs than DCHBs for protonation.

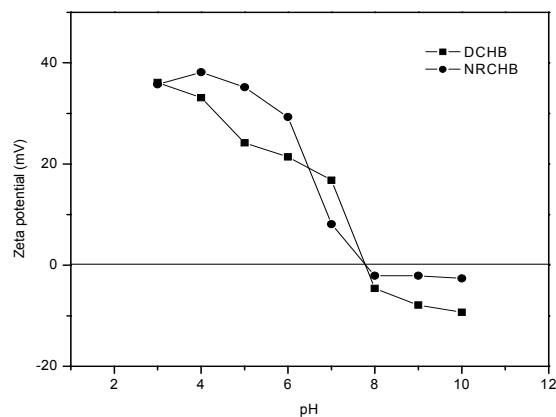


Figure 5. Zeta potentials of CHBs and NRCHBs

Adsorption Performance. As an evaluation, the adsorption performances for copper ion removal with the CHBs (chitosan hydrogel beads without crosslinking), DCHB (chitosan hydrogel beads directly crosslinked with EGDE), and NRCHB (chitosan hydrogel beads prepared with the new corsslinking method in this study) as the adsorbents are presented in Figures 6 and 7. Figure 6 shows the typical results of the time-dependent adsorption performances of the three types of the beads. The adsorption capacity for the NRCHBs is

found to be slightly less than that of the CHBs, but is significantly greater than that of the DCHBs, confirming that the new crosslinking method with the amine groups “sheltered” or “protected” before the EGDE crosslinking only consumed a very small number of the amine groups in chitosan (with NRCHB compared to CHBs) but preserved most of the amine groups (with NRCHBs compared to DCHBs) for metal adsorption, and, as a result, enhanced the adsorption performance of the crosslinked chitosan hydrogel beads.

It is observed that for all types of the beads, the adsorption of copper ions on the adsorbents increased very fast in the initial stage of adsorption. After a fast adsorption period, the adsorption rates gradually reduced. This type of adsorption behavior in the later stage is typical of the specific adsorption process in which adsorption rate is dependent upon the number of available adsorption sites on the surfaces of the adsorbent and the amount of adsorption is usually controlled by the attachment of the metal ions on the surface. In view of the fact that the weight and surface area of the DCHB and NRCHB beads were similar in the kinetic adsorption experiments but the adsorption capacity of the NRCHB beads was much greater than that of the DCHB beads, it can be concluded that there are more adsorption sites on the NRCHBs than on the DCHBs, and the adsorption was attachment controlled since the transport of copper ions from the bulk solution to the surface of the two types of the adsorbent was essentially the same in the experiments.

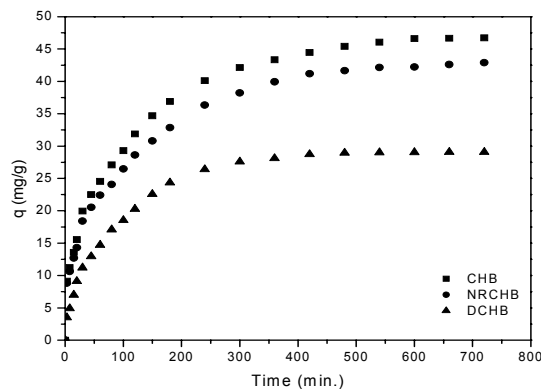


Figure 6. Typical kinetic adsorption results of copper ions on the CHBs, NRCHBs and DCHBs (initial solution pH = 6, initial copper ion concentration = 15 mg/L)

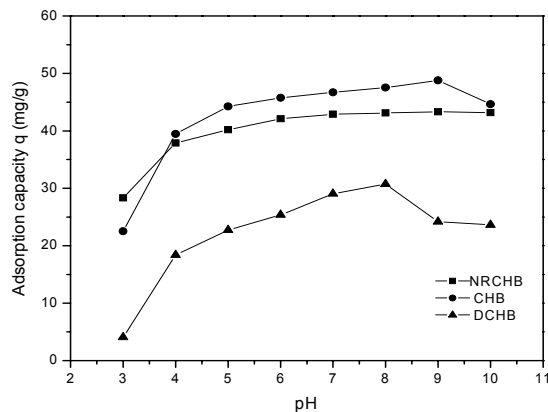


Figure 7. Effect of initial solution pH values on copper adsorption capacities on the NRCHBs, DCHBs, and CHBs (initial copper ion concentration in the solution = 15 mg/L)

The effect of solution pH values on the adsorption of copper ions on the three types of the beads is shown in Figure 7. Generally, the adsorption capacity of copper ions on the adsorbents increased with the increase of pH values, in accordance with the analysis in zeta potential results in Figure 5. However, the difference between the largest adsorption capacity and the smallest adsorption capacity in the pH range studied for the NRCHBs is smaller than that for the CHBs and DCHBs. This is also in agreement with the smaller differences in the zeta potentials for the NRCHBs in the pH range studied. Since the zeta potentials of the NRCHBs were positive at pH less than 7.8 (shown in Figure 5), the electrostatic interactions between the NRCHBs and the copper ions to be adsorbed were electrically repulsive in this pH range. With the increase of the pH values, the electrical repulsion forces decreased and the copper ions were easier to be transported to the surfaces of the adsorbents from the bulk solution, and, thus, attached to the functional groups on the adsorbent surfaces. More importantly, in the pH range examined, the NRCHBs always showed much greater adsorption capacities than the DCHBs. In addition, unlike the CHBs which was observed to be slowly dissolved in pH less than 4, the NRCHBs was found to be very stable in the pH range (even in much lower pH solutions than shown in this figure). Therefore, it is reasonable to conclude that the NRCHBs are very good adsorbent with both high adsorption capacity and acidic resistance.

Adsorption Mechanisms. XPS has often been used to identify the interaction of a metal ion with the surface chemical groups on an adsorbent during adsorption. The creation of a chemical bond between a metal ion and an atom on the surface of the adsorbent would change the distribution of the electrons around the corresponding atom, i.e., the electron-donating ligands can lower the binding energy (BE) of the core level electrons while the electron-withdrawing ligands can raise the BE.^{15,20}

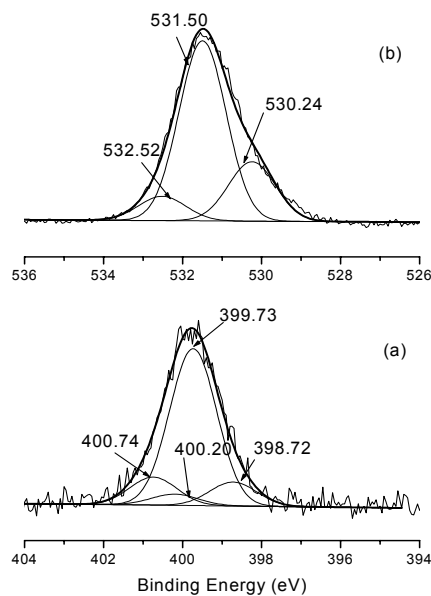


Figure 8. XPS N 1s (a) and O 1s (b) spectra for the NRCHBs after copper adsorption (pH=6)

In Figure 8, the N 1s and O 1s spectra of the NRCHBs after copper adsorption are shown. Compared to Figure 2d, the N 1s XPS spectrum in Figure 8a shows two new peaks at the BEs of 400.2 and 400.74 eV, respectively, after copper adsorption, indicating that copper ions were adsorbed to the nitrogen atoms on the surface of the NRCHBs. As the lone pair of electrons in a nitrogen atom on the NRCHBs can be donated to form a shared bond (surface complex) between a copper ion and the nitrogen atom, the electron cloud density of the nitrogen atom can be reduced and a peak at a higher BE in the XPS spectrum can be observed. The two new peaks in the N 1s spectra may be an indication that two types of nitrogen-containing functional groups were involved in the copper-adsorbent interactions. The major new peak at the BE of 400.74 eV can be assigned to the nitrogen atoms in the NH_2 groups attached with copper ions, and the other minor new peak at the BE of 400.2 eV may be assigned to the nitrogen atoms in the $-\text{NH}-$ or $=\text{N}-$ groups with copper ions attached. In other words, the primary amine groups are the most effective surface functional group in copper adsorption. However, the O 1s spectrum of the NRCHBs with copper adsorption in Figure 8b does not show noticeable difference with that in Figure 3d before copper adsorption. This result may suggest that the OH groups were not involved in copper ion adsorption, at least through surface complexation or other chemical mechanisms.

Conclusions

The nitrogen atoms in the primary amine groups in chitosan were most effective in copper ion adsorption through surface complexation. Formaldehyde treatment of the chitosan hydrogel beads before EGDE crosslinking converted the $-\text{NH}_2$ groups to $-\text{N}=\text{CH}_2$ and sheltered or prevented them from being consumed in the crosslinking reaction. The crosslinking reaction was therefore forced to take place at the unsheltered amine groups and the hydroxyl groups on the beads. The final HCl treatment after the crosslinking reaction effectively released most of the sheltered nitrogen atoms in the $-\text{N}=\text{CH}_2$ groups into those in the $-\text{NH}_2$. The new crosslinking method was found to be able to preserve most of the amine groups on the chitosan hydrogel beads for metal adsorption, in comparison with the traditional direct EGDE crosslinking process. Adsorption experiments for copper ion removal confirmed that the chitosan hydrogel beads crosslinked with the new method had significantly greater adsorption capacities than the beads crosslinked with the traditional method. The analysis with XPS spectra proved that copper ion adsorption on the beads were indeed through attachment mainly to the nitrogen in the primary amine groups in chitosan, through the formation of surface complexes. The new crosslinking method has great potential in many other cases where the amine groups are the useful functional group but they may usually be preferentially consumed when a traditional crosslinking method is used.

Acknowledgement

The financial support of the Academic Research Funds, National University of Singapore, is acknowledged.

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