

Biopolymer Based Nanomaterials as Potential Biosorbents for Toxic Metal Ions

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ABSTRACT

In the present work ternary nanoparticles of chitosan, yeast and gelatin were prepared by emulsion crosslinking method and characterized by techniques like FTIR and TEM. Whereas the spectral studies confirm the presence of characteristic functional groups of the three biopolymers. The TEM analysis also reveal that the size of nanoparticles lie in the range 50 to 150 nm. The nanospheres so prepared were examined for removal of Cu (II) ions and it was found that the removal capacity of metal ions was more than 90 percent. The metal ion removal capacity of the nanoparticles was found to depend on the chemical composition of the adsorbent, concentration of the metal ion solution, pH and temperature of the medium and agitation speed of the suspension.

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INTRODUCTION

Clean water (i.e. water free of toxic chemicals and pathogens) is essential to human health. Clean water is also a critical feedstock in a variety of key industries including electronics, pharmaceuticals, metallurgical and food. The world is facing formidable challenges in meeting rising demand of clean water as the available supplies of fresh water are decreasing due to extended droughts, population growth, competing demands from a variety of users, etc¹.

Sachromyces cerevisiae (yeast) is readily available biopolymer used for removal of heavy metal ions such as Cu²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Cr²⁺ and Ni²⁺. The use of chelation while the harmless ions move on into the environment. Some of the known ion-exchange materials consist of different biopolymers like cellulose, alginates, proteins, chitin and chitin derivatives, etc. Among these biopolymeric materials chitosan has a prime rank as adsorbent for removal of toxic metal ions. Chitosan is a heteropolymer made of D-glucosamine and a small fraction of N-acetyl-D-glucosamine residues. Thus, due to the presence of free reactive amino group in chitosan it rapidly undergoes complex formation between metal ion and the polymer. The present study aims at investigating the removal of Cu²⁺ ions from aqueous solution by adsorption onto the nanoparticles composed of chitosan, gelatin and yeast. Copper being the most widely used heavy metal is mainly employed in electrical and electroplating industries and in large amount is extremely toxic for living organisms. The presence of copper (II) ions causes serious toxicological concern, which is usually known to deposit in brain, skin, liver, pancreas and myocardium.

EXPERIMENTAL

Materials

Biopolymers like chitosan, yeast, gelatin (Loba Chemie, India) . Glutaraldehyde (Loba Chemie, Mumbai, India) was used as crosslinking agent. Silicon oil (Aldrich, USA) viscosity 10,000 (at 25°C) was used as an oil phase for preparing the suspension. Copper sulphate and other chemicals were of high purity grade and throughout the work; double distilled water was used for making solutions.

Methods

Preparation of Nanospheres

A known solution of gelatin (3 g) and yeast (2 g) were mixed with a known solution of chitosan (1 g) on magnetic stirrer for about 20 min. 3 mL homogeneous mixture of glutaraldehyde and silicon oil was added dropwise into the suspension of yeast, gelatin and chitosan with the help of a syringe under constant stirring. Prepared nanoparticles were washed with acetone, then benzene and dried at 80°C for 2–3 h.

Adsorption Experiments

The adsorption was carried out by the batch contact method as described elsewhere². In brief, the stock solution was prepared by dissolving 0.6 g of copper sulphate in 1 liter distilled water. In to 6 mL of diluted stock solution (1:1), 100 mg of swollen nanospheres were added as adsorbent. The suspension was shaken in a rotary shaker (Tempstar, India) for 4 h which was found to be a sufficient time to attain equilibrium adsorption. After shaking is over, 3 mL supernatant was mixed with 1 mL reagent (NH₃ solution) and the amount of copper was assayed spectrophotometrically. The adsorbed Cu (II) was calculated by the following mass balance equation, where C_i and C_f being the initial and final concentrations of CuSO₄ solution (mg/mL). V being the volume of

adsorbed solution and m is the weight of swollen nanospheres, i.e. adsorbent.

$$\text{Adsorbed amount (mg/g)} = \frac{(C_i - C_f) V}{m} \quad \dots (1)$$

FTIR Spectral Analysis

The FTIR spectra of native (unadsorbed) and Cu (II) adsorbed nanospheres were recorded on a FTIR spectrophotometer (FTIR-8400S, Shimadzu).

Transmission Electron Micrograph (TEM)

In order to study morphology of the prepared nanospheres, the TEM analysis of the microspheres surface was carried out (STEREO SCAN, 430, Leica, USA).

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectra of both native and Cu^{2+} adsorbed biopolymeric nanospheres are shown in Fig. 1(a) and (b), respectively. Whereas, the spectrum (a) confirms the presence of the biopolymer components, i.e. chitosan, yeast and gelatin in the nanospheres, the spectra (b) also indicate the sorption of Cu^{2+} ions into the nanospheres. The IR spectrum of nanospheres [Fig. 1(a)] shows peak around 1171 cm^{-1} corresponding to saccharide structure²⁵. A sharp peak appearing at 1615 cm^{-1} may be attributed to amide I band (N-C=O), characteristic of chitosan with acetylated unit. A cluster of peaks around 3422 cm^{-1} may be assigned to overlapped absorption bands due to N-H and O-H symmetrical vibrations. Peaks around 2910 cm^{-1} are the typical C-H stretch vibrations.

A close examination of spectrum (b) reveals that several specific bands appeared at 1615 cm^{-1} , 2910 cm^{-1} and 3422 cm^{-1} are shifted to longer wave numbers at 1683 cm^{-1} , 2940 cm^{-1} and 3544 cm^{-1} , respectively due to interaction of metal ions (Cu^{2+}) with biopolymer components.

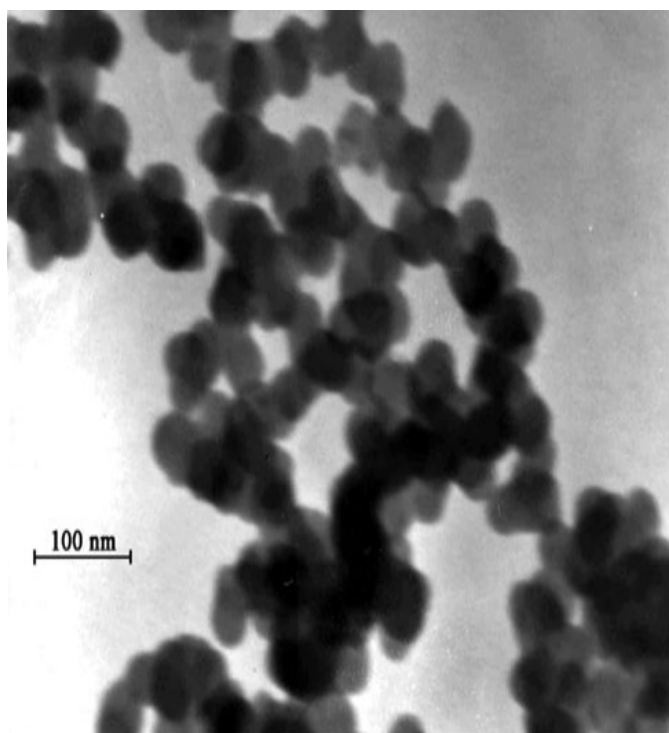
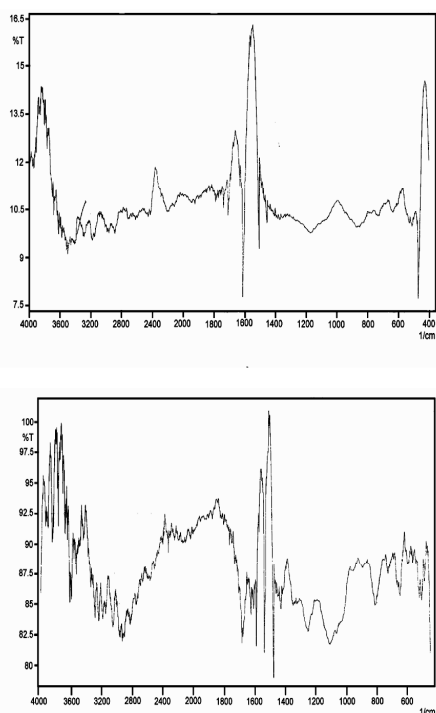


Fig. 1: FTIR spectra of nanosphere

Fig. 2: TEM image of prepared nanospheres

Transmission Electron Micrograph (TEM)

The TEM image of the nanospheres surfaces is shown in Fig. 2 which clearly indicates that the three components (yeast, gelatin, chitosan) of the nanospheres are very compatible to each other. Therefore, the surface appears quit homogeneous and even. The size of nanospheres varies from 30 to 150 nm.

Langmuir Isotherm

Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherm which is usually the relation between quantity adsorbed and that remaining in solution at fixed

temperature at equilibrium. The most common type is the Langmuir³ isotherm as shown in Fig. 3.

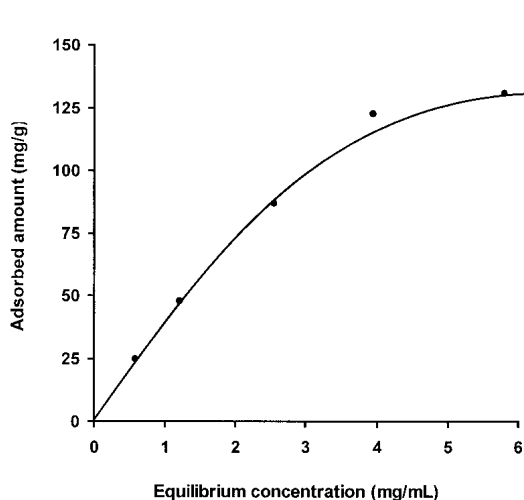


Figure 3 Langmuir adsorption isotherm plot

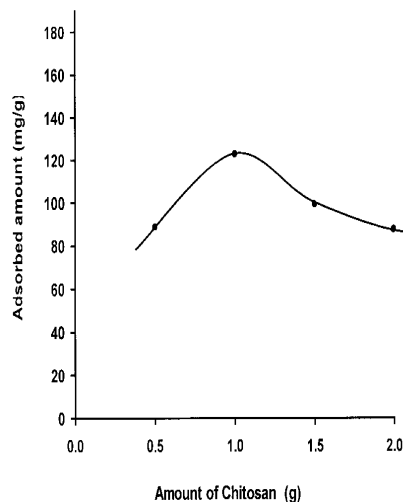


Fig. 4 Effect of chitosan on adsorption

$$\frac{C_e}{a} = \frac{1}{a_s K} + \frac{C_e}{a_s} \quad \dots (3)$$

Where a is the adsorbed amount of Cu^{2+} (mg/g) at any equilibrium concentration, a_s is the adsorbed amount of metal ion at saturation (adsorption capacity), K is the adsorption coefficient which is equal to k_1/k_2 , where k_1 and k_2 are rate constants for the adsorption and desorption, respectively. The linear plot of C_e/a vs C_e shows that adsorption follows Langmuir adsorption. The values of a_s and K may be determined from the slope and intercept values and found to be 250 mg/g^{-1} and $0.2 \text{ (mg}^{-1} \text{ dm}^3)$, respectively.

(i) Effect of Chitosan

When chitosan is varied in the range 0.5 g to 2.0 g, adsorption of Cu^{2+} ions varies as shown in Fig.4. The results clearly show that with increasing concentration of chitosan, adsorption initially increases and then decreases. The results may be explained by the fact that amino sugar of chitosan and chitin are major effective binding sites for metal ion and form stable complex with metal ions by co-ordination.

Thus, obviously with increasing chitosan content in the nanospheres, the adsorption of metal ions also increases, whereas beyond an optimum concentration of chitosan (1.0 g) the observed decrease may be attributed to the reason that at higher chitosan content, the intermolecular forces become much stronger and this causes shrinkage in the pore size of the nanospheres. This clearly results in a fall in the adsorbed metal ions

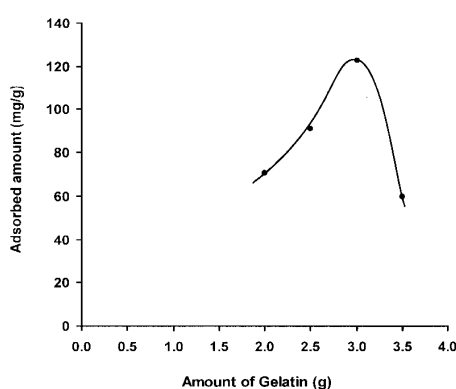


Fig. 5 Effect of gelatin on adsorption of metal ions

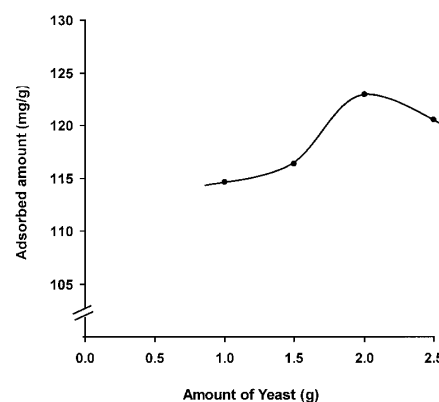


Fig. 6 Effect of yeast on adsorption of copper

(ii) Effect of Gelatin

In the case of gelatin, the amount was varied in the range of 2.0 g to 3.5 g. The results shown in Fig. 5 indicate that the adsorption of Cu^{2+} increases with increasing gelatin concentration up to 3.0 g and then increase

in gelatin concentration results in a decrease in the adsorption.

(iii) Effect of Yeast

In the case of yeast, the variation in the amount was in the range 1.0 g to 2.5 g. The results are shown in Fig. 6 which reveals that the adsorption of Cu^{2+} ions increases with increasing yeast concentration up to 3.0 g and then further increase in yeast concentration results in a decrease in the adsorption.

Effect of pH

pH seems to be the most important parameter in the biosorption process. It affects the solution chemistry of the metal ion, the activity of the functional groups in the biomass and competition of metallic ions. Cu^{2+} exhibits different type of pH dependence equilibria in aqueous solution. As pH is shifted the equilibrium will also shift. The effect of pH on the adsorbed amount of Cu^{2+} ions have been investigated in the range 1.2 to 5 as shown in Fig. 7

. Effect of Temperature

In the present work, the effect of temperature on adsorption was studied in the range 5° – 40°C . The results are shown in Fig. 9 which indicates that adsorption increases from 5 to 22°C and then starts decreasing.

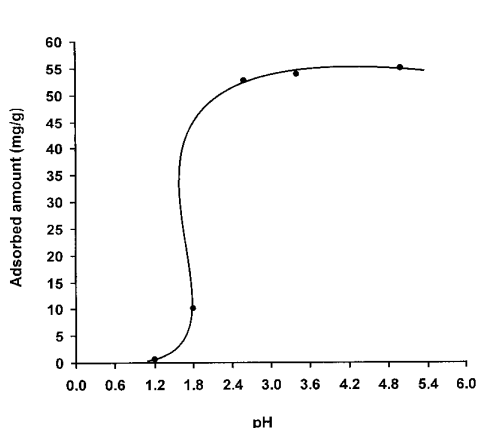


Fig. 7 Effect of pH on adsorption

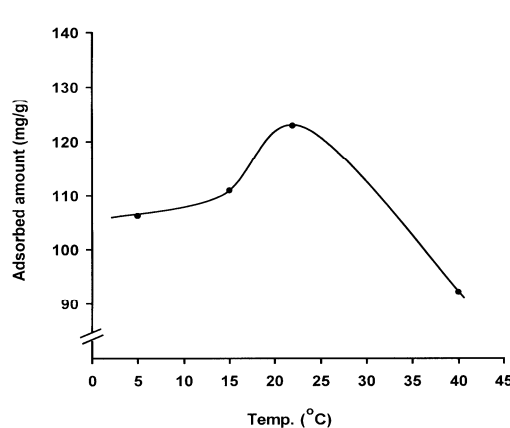


Fig. 8 Influence of temperature

CONCLUSIONS

Chemical crosslinking of a water/oil suspension of a gelatin, yeast and chitosan produces regular shaped nanospheres of size up to 150 nm. The prepared nanospheres show potential for the removal of Cu^{2+} ions from aqueous solutions.

The adsorption of Cu^{2+} ions onto the water-swollen nanospheres increases with increasing initial metal ion concentration in the range 1.0 to 8.0 mg/mL. It is noticed that in the higher concentration range (8 mg/mL), the adsorbed amount nearly levels off. The adsorption process is found to follow Langmuir adsorption isotherms equation characterized by the appearance of a well marked plateau portion. The adsorption of Cu^{2+} ions also exhibits a significant change with changing concentration of the nanospheres biopolymeric constituents. It is observed that there is a definite concentration of chitosan, gelatin and yeast at which the adsorption of Cu^{2+} ions is optimum and on both the sides of this optimum concentration, the adsorption is comparatively low. The adsorbed amount of Cu^{2+} ions is significantly affected by pH of the metal ion solution when varied in the range 1.2 to 5.4. It is noticed that the adsorbed amount steeply increases in the range 1.2 to 2.4 while a marginal increase occurs beyond pH 2.4. An optimum amount of Cu^{2+} ion is adsorbed at 25°C while it decreases on both the sides of this temperature.

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