



Effect of pH on Binary Biopolymeric Beads of Alginate and Gelatin as Adsorbent for Removal of Cu²⁺

SHIPRA JHA*, S.N. DIKSHIT and G. PANDEY

Department of Chemistry, Government Model Science College, Gwalior-474 001, India

*Corresponding author: Fax: +91 120 4392295; E-mail: sjanvi79@gmail.com

(Received: 13 December 2010;

Accepted: 20 May 2011)

AJC-9975

Biopolymeric beads of alginate and gelatin were prepared and characterized by dispersion spectrometer and scanning electron micrograph techniques. On to the surface of beads were performed dynamic adsorption studies of Cu²⁺ ions at fixed pH and ionic strength of aqueous metal ions solutions. The nature of adsorption was quantified in terms of rate constants for absorption. The influence of various experimental parameters such as pH, temperature and chemical composition of biopolymeric beads on adsorption of copper ions was investigated.

Key Words: Gelatin particles, Alginate, Adsorption, Copper.

INTRODUCTION

Over the past several years, the increasing contamination in various environmental segments due to unscrupulous discharge of trace metals from several sources is a matter of concern. Environmental significance of traces metal is assessed in terms of toxicity as well as the extent of their exploitation, applications and consequent immobilization in to air, water and land. At least 20 metals are classified as toxic and half of these are entitled in to the environment in quantities that pose risks to human health¹. Various heavy metals such as cadmium, chromium, zinc, lead, copper, iron, nickel and cobalt enter the environment through industrial wastes, mill tailings and landfill run off may cause serious health problems to living organism^{2,3}.

One of the most widely studied biopolymers are polysaccharide-based biosorbent such as alginate, which have binding sites for divalent cation because of the presence of amino, carboxyl, phosphate and sulfate functional groups within them. Alginate is a linear polyurinate obtained from marine algae and contains variable amounts of D-manuronic acid and L-guluronic acid which is cross linked by using calcium ions. Thus present work aims at investigating the removal of Cu²⁺ ions from aqueous solutions by adsorbents into biopolymeric matrix⁴ composed of sodium alginate and cross-linked gelatin in the form of spherical beads.

EXPERIMENTAL

All the reagents were of analytical grade and used without further purification. Sodium alginate and gelatin was purchased and used, metal such as copper sulphate (adsorbate) for the

metal sorption experiments, calcium chloride (cross linking agent for gelatine), etc were of high purity grade. Triple distilled water was used throughout the experiments. All experiments were performed in a shaking bath and metal concentrations were determined by atomic absorption spectrometry.

Synthesis of various polymeric particles: Gelatin nanoparticles were prepared using a desolvation technique. Gelatin type A (1.25 g) was dissolved in distilled water (25 mL) under constant heating. Acetone (25 mL) was added to the gelatin solution as a desolvating agent to precipitate the high molecular weight gelatin. The supernatant was discarded and the high molecular weight gelatin re-dissolved by adding 25 mL distilled water and stirring at 600 rpm under constant heating. The pH of the gelatin solution was adjusted at 2.5. Acetone (75 mL) was added drop-wise to form nanoparticles. At the end of the process, gluteraldehyde solution (250 µL) was used for preparing nanoparticles as a cross linking agent and stirred for 12 h at 600 rpm. The particles were purified by threefold centrifugation and redispersion in acetone (30 %) in milliQ water. After the last redispersion, the acetone was evaporated using concentrator (speed vacuum). The resultant nanoparticles were stored at 2-8 °C. with triple distilled water. These binary biopolymeric beads were stored in triple distilled water.

Metal binding batch experiments: The metal salts were dissolved in distilled water and stock solution of different concentrations of single metal solutions were prepared. pH of the metal solutions was adjusted to the desired value using 0.1M NaOH and 0.1M HNO₃. Samples of biopolymeric beads

were contracted with 100 mL of metal solution in 200 mL Erlenmeyer flask shaking at 190 rpm at 25 °C overnight for complete equilibration and metal content of the final solution was determined.

Sorption kinetics experiments: Stock metal solution was prepared and the pH was adjusted by addition of a known quantity of 0.1M NaOH and 0.1M HNO_3 . Samples of biopolymeric beads were contracted as described above for different contact times. The beads were then removed from the solution by filtering and metal concentrations were determined.

Statistical analysis: For the effect of pH data, analysis of variance (ANOVA) methods were applied. Model diagnostics were applied to check the ANOVA and ANCOVA model assumptions. Adjustments for multiple treatment comparisons were made (Tukey) and testing was performed at the 5 % level of significance. Data analysis was done using SPSS 13.0 software.

RESULTS AND DISCUSSION

Characterization of biopolymeric bead: Biopolymeric beads employed as adsorbent were prepared in two steps. In the first step, a known solution of mixture of sodium alginate (4.0 g) and gelatin (1.0 g) was added drop wise into a 0.05 M CaCl_2 solution with the help of a syringe and under constant stirring. The beads so produced were of almost identical spherical dimensions and allowed to harden by leaving them in CaCl_2 solution for 24 h and thereafter filtered and washed thrice with triple distilled water. The washed beads were further placed in as gluteraldehyde bath overnight and then filtered carefully and washed thrice with distilled water at room temperature and used as such. Beads were examined and tested in terms of size. The particle size distribution, determined by means of a sieving system, ranged from 0.5 to 0.9 mm. The surface of beads was examined using dispersion microscope (Fig. 1) The weight drying show that the wet beads contain of 96.48 % water. When left in water to swell the beads regained 2.35 % of water.

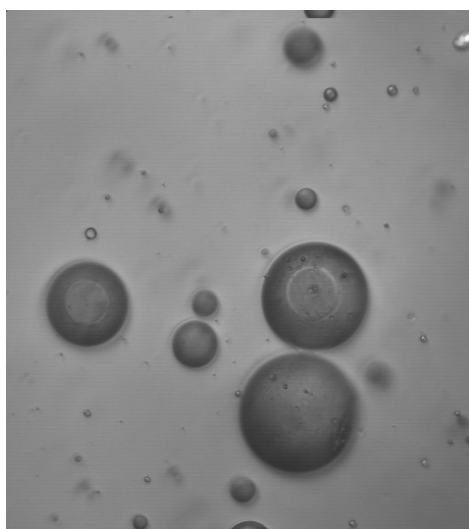


Fig. 1. Variation in size of biopolymeric bead at various initial concentration of Cu^{2+} ions

Effect of pH: Properties of adsorbant, pH, concentration of adsorbant and presence of co-ions solution affect the biosorption of metal ions from aqueous solution. Beads was contacted Cu^{2+} ions in separate solution (75 mL) at metal ions concentration of ca. 10 mg/L for 14 h with initial pH value of the solutions ranging from 3.0-8.0 (Fig. 2) show the effect of pH on biosorption of Cu^{2+} ions. At an initial pH biosorption occurred. A sharp increased in biosorption capacity took place in pH range 3.0-8.0. Above pH 6.0 biosorption of copper was to be relatively constant and still increase but to lesser extent.

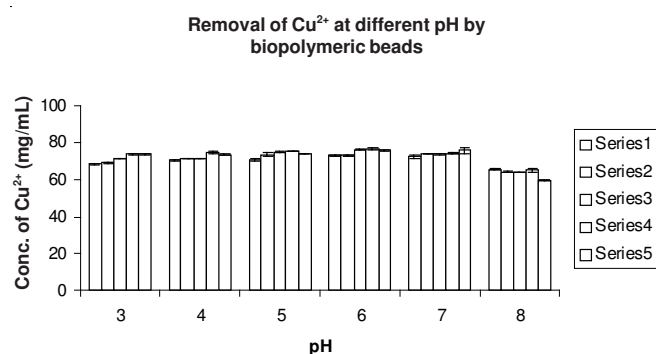


Fig. 2. Represent absorption of Cu^{2+} at different pH at different time interval

Conclusion

Biopolymeric beads can be used for removal of copper and showed a high adsorption capability. pH was found to be critical in biosorption, with an optimum pH being 6 or higher. Biosorption of metal ions is dependent to a larger extent on pH of metal ion solution. The pH plays an important role mainly by its influence on metal or cell wall. We have performed Anova test (Table-1) and once we have determined that differences exist among the means (Fig. 3), post hoc range tests and pairwise multiple comparisons (Table-2) can determine which means differ. We applied Tukey's honestly significant difference test to find out At-Par list which is given below: 6-3-5-4-8. So if we compare maximum metal absorption, pH 6 is most significant at which maximum absorption of copper takes place than pH 3 followed by pH 5, pH 4 and at last pH 8. pH 3 and pH 7 is not effective for biosorption of copper.

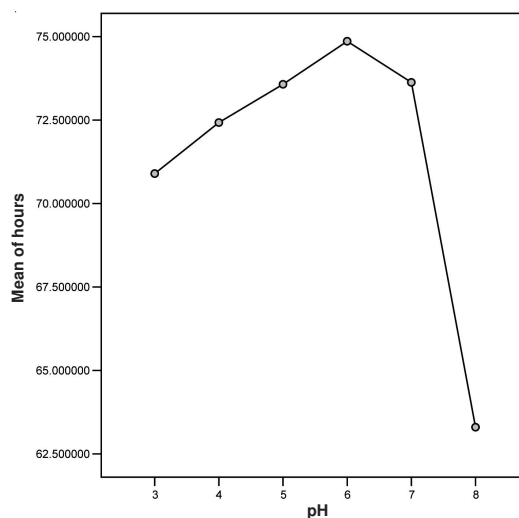


Fig. 3. Distribution of pH for different timing of removal of copper by biopolymeric bead

TABLE-1
ANOVA TEST RESULTS

	Sum of Squares	df	Mean Square	F	Sig.
Between groups	442.583	5	88.517	31.952	.000
Within groups	66.487	24	2.770		
Total	509.070	29			

TABLE-2
TUKEY HONESTLY SIGNIFICANT DIFFERENCE TEST

pH	N	Subset for alpha = .05		
		1	2	3
8	5	63.30222400		
3	5		70.89666800	
4	5		72.42444400	72.42444400
5	5		73.57111000	73.57111000
7	5		73.62889000	73.62889000
6	5			74.85999800
Sig.		1.000	.137	.227

Means for groups in homogeneous subsets are displayed.
aUses Harmonic Mean Sample Size = 5.000.

ACKNOWLEDGEMENTS

The authors are thankful to Dr. Gayatri V. Singh for her support in statistical analysis.

REFERENCES

1. S.M. Nomanbhay and K. Palanisamy, *Electron. J. Biotech.*, **8**, 137 (2005).
2. B.J. Alloway and D.C. Ayres, *Chemical Principles of Environmental Pollution*, Springer, edn. 2 (1993).
3. D.A.J. Wase and C.F. Forster, *Biosorbents for Metal Ion*, Taylor & Francis Ltd., London, U.K., pp. 141-163, 238 (1997).
4. J. Bajpai, R. Shrivastava and A.K. Bajpai, *Physicochem. Eng. Aspects*, **236**, 81 (2004).