



Role of humic acid entrapped calcium alginate beads in removal of heavy metals

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Abstract

Most of the available techniques for removal of heavy metals from solution such as leachates from waste sites are very expensive. The technique described in this paper is designed to study the removal of humic acid by alginate beads and the subsequent binding of the metals within the beads thus decreasing the leachability of heavy metals from a hazardous waste site. The entry of 500 mg/l humic acid into 3% calcium alginate beads in 24 h showed a distinct fluorescence as compared to the fluorescence shown by the entry of 100 and 250 mg/l of humic acid into alginate beads. Further, on treatment of calcium alginate beads containing 500 mg/l humic acid with metals such as Cu, Mn, Zn, Cr and Fe, quenching of fluorescence was noticed, which was maximum with Cu and minimum with Fe. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

With the increasing urbanization and industrialization, the land disposal of industrial wastes is becoming a serious problem. Heavy metals are of concern because of their increasing abundance in the environment and their relatively high toxicity even at low concentrations. Once released into the soil matrix, heavy metals can impact environmental quality and human health via ground water and surface water [1]. The factors influencing the bioavailability of hazardous metals to biota are important in ecotoxicity assessment.

Humic acid is a natural organic compound produced by biological and geochemical processes that contain structures that can complex metals, sequester anthropogenic organic

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compounds, oxidize and reduce elements to and from toxic forms, photosensitize chemical reactions and enhance and retard the uptake of toxic compounds or micronutrients to plants and microbial organisms. Recently considerable research has focussed on the use of biopolymer such as calcium alginate beads to remove toxic metals from wastes. Chen and Yiacomini [2] studied the Cu biosorption from aqueous solution by calcium alginate. Through potentiometric titration, they showed that the surface charge increases with decreasing pH. Several studies have indicated that sorbed or complex toxicants are less toxic than the soluble compounds due to reduced bioavailability [3–5]. Apel and Torma [6] evaluated the efficiency of calcium alginate beads in the treatment of Ba^{2+} , Cd^{2+} , UO_2^{2+} and Zn^{2+} from water and waste water. Pandey et al. [7] studied the removal of chromium and reduction of toxicity to microtox system from tannery effluent from the use of calcium alginate beads containing humic acid. In this study, the potential for removal of different metals by humic acid entrapped calcium alginate beads was compared by fluorescence quenching under microscopy.

2. Materials and methods

Humic acid (HA) isolated from local soil was used in the preparation of calcium alginate (CA) beads containing humic acid. Earlier studies showed this sample to be similar to reference sample of humic acid procured from Aldrich Chemical Company, Inc. (USA) [8]. Sodium alginate was procured from Central Drug House (P) Ltd., Delhi. Other chemicals used in the study were from Merck and Qualigens AnalaR grade.

2.1. Isolation of humic acid from soil

Haworth's method [9] was employed to extract humic acid from natural soil. Locally collected air dried soil (200 g) rich in humus was defatted with an ethanol–benzene mixture (1:1). The soil was then shaken with 2.4 l of 0.2N NaOH and centrifuged; the pH of the clear supernatant was adjusted to 1.0 with 2N hydrochloric acid. A gelatinous precipitate was obtained which was filtered on a sintered glass funnel and dried at 90 °C with the recovery of about 1.2% humic acid.

2.2. Preparation of humic acid solution

Humic acid stock solution (500 µg/ml) were prepared by dissolving humic acid isolated from soil in deionized water. A fresh solution was prepared prior to each experiment and stored in dark at 4 °C. The pH of the solution was 6.85. From this stock solutions of 100 and 250 µg/ml of humic acid was prepared.

2.3. Preparation of metal solution

Metal salts, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, FeCl_3 (anhydrous), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 (anhydrous) were dissolved in deionized water, the metal concentration was 100 µg/ml.

From this solution, the desired concentration. An amount of 10 $\mu\text{g/ml}$ solution of each metal for the study was prepared.

2.4. Preparation of calcium alginate beads

Calcium alginate beads were prepared by the method described by Aksu et al. [10]. A solution of 20% calcium chloride solution and 3% sodium alginate in deionized water was prepared. For preparation of the beads, 3% sodium alginate solution was added drop by drop into a stirred 20% calcium chloride solution. By doing so, the water soluble sodium alginate was converted into water insoluble calcium alginate beads (diameter 3 ± 0.2 mm). Finally, the beads were washed with deionized water several times to remove calcium chloride from the bead surface.

2.5. Entrance study

For entrance study, the beads were contacted with humic acid solution (100–500 mg/l) for 24 h and after washing the beads with distilled water, 8 μm thick sections of beads were cut mounted on a slide in distilled water and viewed for fluorescence under a Leitz Laborlux D fluorescence microscope (Germany), fitted with an exciting filter (BP 340-380) with a beam splitting mirror (RKP-400) and suppression filter (LP-430).

2.6. Quenching study

Metal solutions (10 $\mu\text{g/ml}$) were placed in a test tube and calcium alginate beads containing 500 mg/l of humic acid were added. After 24 h, the beads were cut and mounted in distilled water on a slide and viewed under fluorescence microscope as above to see the quenching of fluorescence intensity (diminution of brightness of fluorescence) in the case of each metal.

3. Results

A qualitative assessment of entry of humic acid into the calcium alginate beads/entry of metals in the humic acid entrapped beads by the measurement of fluorescence intensity is shown in Tables 1 and 2. The UV fluorescence of humic acid in the calcium alginate beads prepared using concentration of 500 mg/l solution of humic acid at 24 h was much more

Table 1
Entry of different concentrations of humic acid in calcium alginate beads and its fluorescence intensity

System	Humic acid concentration (mg/l)	Duration of contact of humic acid with beads (h)	Fluorescence intensity
Calcium alginate beads	Nil	24	Nil
Calcium alginate beads	500	24	(+++) Maximum
Calcium alginate beads	250	24	(++)
Calcium alginate beads	100	24	(+) Minimum

Table 2
Removal of metals by humic acid entrapped calcium alginate beads

System	Metal concentration	Duration of contact of metals with beads (h)	Quenching of fluorescence Intensity
Calcium alginate beads + humic acid (500 mg/l)	Nil	24	Nil
Calcium alginate beads + humic acid (500 mg/l)	Cu (10 mg/l)	24	(++++) Maximum
Calcium alginate beads + humic acid (500 mg/l)	Mn (10 mg/l)	24	(+++)
Calcium alginate beads + humic acid (500 mg/l)	Zn (10 mg/l)	24	(++)
Calcium alginate beads + humic acid (500 mg/l)	Cr (10 mg/l)	24	(+) Minimum
Calcium alginate beads + humic acid (500 mg/l)	Fe (10 mg/l)	24	(+) Minimum

distinct as compared to the fluorescence of humic acid prepared using concentrations of 100 and 250 mg/l. However, calcium alginate beads without humic acid did not show any fluorescence. Further, on the treatment of calcium alginate beads containing 500 mg/l humic acid with metals such as Cu, Mn, Zn, Cr, and Fe at 24 h, quenching of fluorescence was noticed, which was maximum with Cu and minimum with Fe. The trend of quenching of fluorescence was in the decreasing order Cu, Mn, Zn, Cr, Fe but no quantitative significance is attributed.

4. Discussion

Diffusion plays an important role in the kinetics of removal of metal ions from matrices. Gel beads contain mostly water so mass transport is determined by metal ion diffusion in water which is faster than in dry beads. External mass transport affects the initial sorption phase and results in most of the metal ion removal while the diffusion influences the rate of sorption in the final phase [11]. Tanaka et al. [12] reported that the substrates with molecular weight lower than 2×10^4 can diffuse freely into and from the gel beads. The diffusion is not disturbed by increasing the calcium alginate concentration in the beads and the calcium chloride (CaCl_2) concentration used in gel preparation. The fluorescence of humic acid in the beads in our study suggests the entry of humic acid in the calcium alginate beads through diffusion. Chen et al. [13] calculated the diffusivities of metal ions in biopolymer gels by the use of linear absorption model (LAM) to describe the process of metal binding to spherically shaped biopolymer particles. They found that the diffusion coefficient for Cu^{2+} ranged from 1.19×10^{-9} to $1.48 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (average $(1.31 \pm 0.21) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$). Kinetic studies indicated that mass transfer plays an important role in the biosorption rate [2]. Previous studies on the kinetics of metal ion uptake by alginate showed that uptake begins with a rapid phase followed by a relatively slow phase. The rapid phase lasts for several minutes to a few hours while the slow phase may continue for several hours to 1 day [11]. Konoshi et al. [14] showed that the uptake of neodymium and ytterbium by alginate reaches equilibrium in 2 h. Chen et al. [13] reported that the equilibrium time for copper ion uptake by calcium alginate beads is 10 h. FTIR spectrophotometry on calcium loaded alginate demonstrated that Cd binding arises by bridging or bidentate complex formation with the carboxyl group of the alginate [15].

The quenching of fluorescence of humic acid after the addition of metals to the beads containing humic acid could be due to the binding of metals with the functional groups of humic acid. The maximum quenching of fluorescence in case of Cu and minimum in case of Fe may be explained on the basis of affinity of humic acid with Cu and Fe. Xue et al. [16] reported that copper and other metal ions become bound first to the surface ligands with higher affinity and subsequently to those of lower affinity. To explain the mechanism, it is believed that the metal ions migrate within the humic structure and form stable inner sphere complexes. Hering and Kraemer [17] studied the kinetic behaviour of humic acid metal interaction and found a remarkably slow migration of metal ions in the humic structure.

5. Conclusion

Fluorescence microscopy was used to compare the response of humic acid entrapped in alginate beads on interacting with metals. As observed from the quenching of fluorescence by different metals, as graded usually, Cu and Mn were more active and Fe and Cr least. Even though qualitative, this differential response may make the technique of binding of humic acid useful for selective metal removal from disposal sites.

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