Phosphate Removal by Metal Cross-linked Biopolymers

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ABSTRACT

Novel metal cross-linked alginate beads (MCA) were successfully used for aqueous phosphate removal. Batch experiments were conducted using three different concentrations of phosphate (5, 50 and 100 mg PO_4^{3-}-P/L) with 0.11812 gm (dry weight) iron cross-linked beads. About 94% phosphate was removed in 6 h from the aqueous solution having an initial phosphate concentration of 5 mg PO_4^{3-}-P/L. With 50 mg PO_4^{3-}-P/L, the beads were found to remove only ~41% in 6 but achieved 89% phosphate removal in 96 h. The second order reaction model fitted better for all the concentrations and observed reaction rates were found to be 0.2979, 0.083 and 0.0181 per h for 5, 50, and 100 mg PO_4^{3-}-P/L, respectively. Interference of Cl^-, HCO_3^-, SO_4^{2-}, NO_3^- and natural organic matter (NOM) was investigated and no change in the removal efficiency of phosphate was observed. To investigate the feasibility of using the MCA beads in real-life situation (e.g., eutrophic lakes), “pouch experiments” were conducted in two conditions, namely shaking and static where MCA beads were introduced into the water in pouches. The efficacy of beads in pouches was found to be the same as free beads (used in earlier batch experiments). The successful sorption of phosphate by MCA beads is expected to have enormous implications for nutrient removal and recovery.

INTRODUCTION

Phosphorus (P) is essential for the growth of plants and microorganisms in most ecosystems. However, excess phosphorus becomes problematic when present in aquatic bodies leading to the overgrowth of algae and plant species that finally leads to eutrophication.[1] Phosphorus is also a nonrenewable resource and a recent assessment brought it to the fore that natural phosphate (PO_4^{3-}) deposits will last for approximately 60-240 years.[2] In this research work, novel biopolymer beads were synthesized for phosphate removal using Sodium (Na)-alginate cross-linked with metals (called metal cross-linked alginate or MCA). Na-alginate has drawn considerable attention owing to its biodegradability, hydrophilicity, presence of carboxyl and hydroxyl groups, low cost, natural and renewable nature. The objective of this research work is to determine if MCA beads can be used to remove aqueous phosphate. A series of batch experiments were also conducted with the MCA beads to determine the feasibility of using MCA beads in eutrophic lakes' reclamation.

EXPERIMENTAL SECTION

Synthesis of Metal-Cross-linked Alginate Beads. Fe cross-linked alginate (MCA) beads were synthesized following the method of Almeelbi et al. (2012).[3] The process and the product have been patented.

Adsorption Kinetics and Isotherm Studies. Adsorption kinetics were studied sing MCA beads. Three initial PO_4^{3-}-P concentrations (5, 50 and 100 mg PO_4^{3-}-P/L) were used. Ascorbic acid method was used for phosphate analysis.[4] A set of experiments were also conducted to understand the isotherm behavior of the MCA beads during PO_4^{3-} removal. Initial concentration of phosphate was varied from 5 to 100 mg/L in the isotherm studies.

Interference Studies. Effects of competing ions on phosphate sorption by the MCA beads were investigated by adding common coexisting anions (chloride, bicarbonate, sulfate, and nitrate). The effect of the presence of natural organic matter (NOM) was also investigated.

Pouch Studies. A feasibility study was conducted to see the efficacy of MCA beads in real-life condition (e.g., in eutrophic lakes). MCA beads were introduced into the PO_4^{3-} rich water in pouches made from synthetic fabrics. The pouches were withdrawn from the test water after 24 h and the phosphate concentration in the bulk solution was measured.

Characterization of Alginate Beads. Scanning electron microscopy along with energy dispersive spectroscopy (SEM/EDS, JEOL JSM-6300, JEOL Ltd.) was used to observe surface morphology and characterize the elemental composition of the beads.

RESULTS AND DISCUSSION

Synthesis and Characterization of Alginate Beads. MCA beads were synthesized successfully (**Figure 1**). All the MCA beads were approximately spherical in shape with average diameters of 3.96±0.21 mm (n = 22). Average number of MCA beads produced per batch was 86±6 (n = 26). Each batch of dry MCA beads weighed 0.11812±0.002 g.

Adsorption Kinetics and Isotherm Studies. Batch experiment data for different concentrations of PO_4^{3-} (C_0 = 5, 50 and 100 mg PO_4^{3-}-P/L) were fitted to kinetic models and the second order reaction model fitted better for all the concentrations. The observed reaction rates were found to be 0.2979, 0.083 and 0.0181 per h for 5, 50, and 100 mg PO_4^{3-}-P/L, respectively.

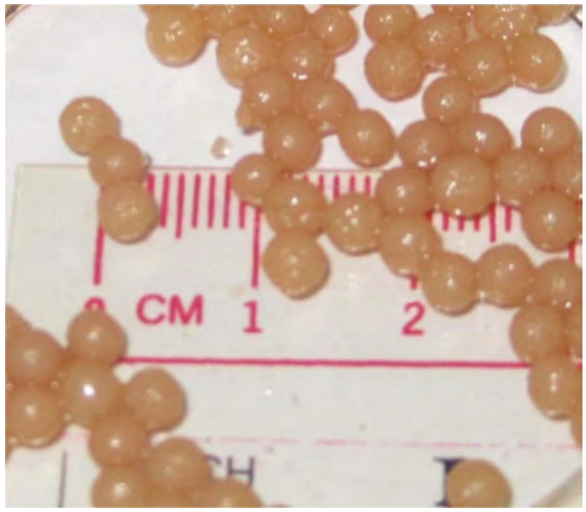

Figure 1. Image of the synthesized metal-cross-linked alginate (MCA) beads

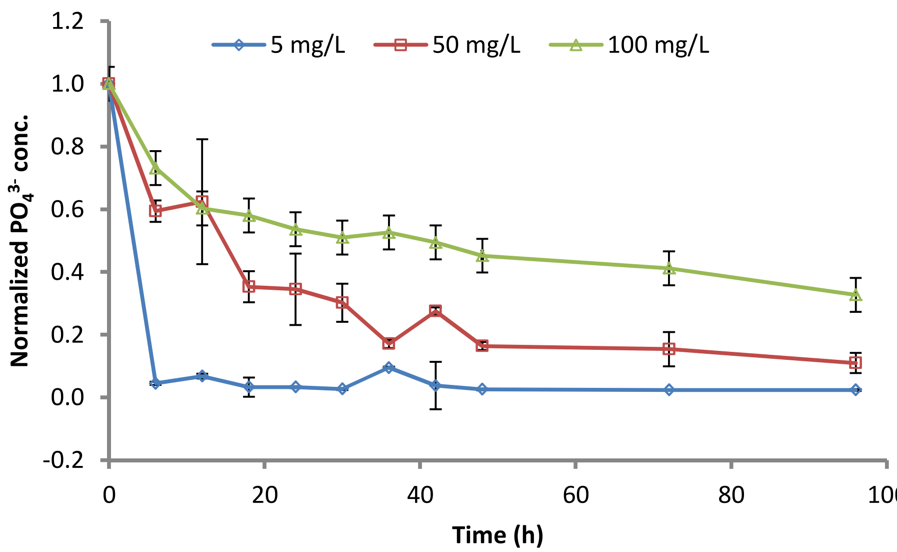

Figure 2. Phosphate removal by MCA beads from solutions with different initial PO_4^{3-} concentrations (*diamonds:* 5 mg PO_4^{3-}-P/L, *squares:* 50 mg PO_4^{3-}-P/L, and *triangles:* 100 PO_4^{3-}-P/L)

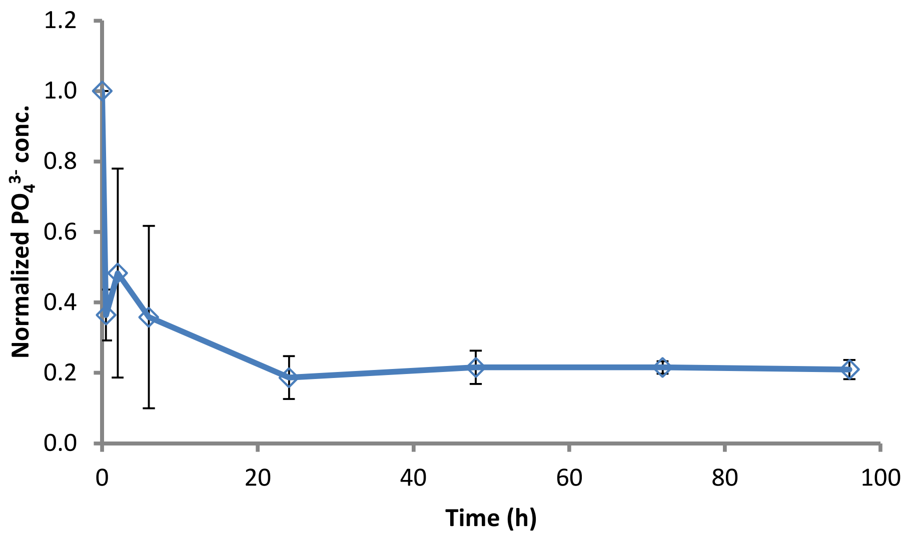

Figure 3. Phosphate removal by MCA beads from solutions with 100 µg PO_4^{3-}-P/L as the initial concentration

Rapid phosphate removal by MCA beads was observed for different concentrations of interest **(Figures 2** and **3)**. About 96% of phosphate was removed within 6 h at the lowest loading of phosphate (5 mg PO_4^{3-} -P/L). At 50 mg PO_4^{3-} -P/L, ~41% of phosphate was removed within 6 h. Freundlich isotherm was found to most closely fit with experimental data (R^2 = 0.8707). Maximum adsorption capacity was found to be 14.77 mg/g of dry MCA beads.

Interference Studies. No interference in the removal of PO_4^{3-} (C_0 = 5 mg PO_4^{3-} -P/L) was observed in the presence of Cl^-, HCO_3^-, SO_4^{2-}, NO_3^- and NOM.

Pouch Studies. From the "Pouch studies" conducted, the bagged beads were found to work almost as effectively as the free loose beads in shaking condition. In 24 h, bagged beads removed ~58% phosphate from the solution whereas loose beads removed ~60% phosphate.

Effect of pH. The effect of pH on phosphate removal (C_0 = 5 mg PO_4^{3-}-P /L) by MCA was investigated at pH of 4, 7, 8 and 9. The change in pH did not affect the removal of PO_4^{3-} by MCA beads, and 100% removal was achieved in all pH values.

ENVIRONMENTAL SIGNIFICANCE

Metal cross-linked alginate (MCA) beads were successfully synthesized and utilized for phosphate removal. About 94% removal of aqueous phosphate was achieved after 6 h. Further, there was no interference by Cl^-, HCO_3^-, SO_4^{2-}, NO_3^- and NOM in phosphate removal by MCA beads. From the “pouch studies” results it can be concluded that the MCA beads hold great promise for use in the reclamation of eutrophic lakes. Additional research is required to find out the exact mechanism of phosphate removal and the feasibility of using these MCA beads in actual field.

ACKNOWLWDGEMENTS

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