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Modifying polymer flocculants for the removal of inorganic phosphate from water

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ABSTRACT

Due to strong hydrogen bonding interactions, thiourea has been shown to have a high affinity for anions such as inorganic phosphate. The interaction between phosphate and thiourea has been used to develop technologies that can detect and even remove phosphate from water. This research investigates the use of thiourea derivatized polymer flocculants for the sequestering of inorganic phosphate from water. The study presented herein describes the development of a thiourea based monomer that was used to create a bi-functional polymer that flocculates suspended solid material as well as sorbs phosphate, removing both from water. The new polymer removed more than 60% of the phosphate from a simulated wastewater sample. The addition of a thiourea trapping group to the polymer more than doubled the amount of phosphate removed from solution compared to control polymers.

Introduction

Inorganic phosphate contamination leads to a variety of environmental problems with water resources including increased algal blooms, bacterial contaminations, and eutrophication.[1] Phosphate contamination can be attributed to a variety of factors including runoff from agricultural fields, land application of wastewater from confined animal feeding operations, and municipal wastewater. To help alleviate these adverse effects of phosphate on the environment, methods for the removal of inorganic phosphate from water are needed.

Thiourea/urea derived organic molecules have been used extensively in the area of molecular recognition for a variety of anions.[2–13] Due to the hydrogen bonding ability of urea/thiourea, these molecules have been used as molecular hosts for carboxylates, halogens, lactones, sulfur, and phosphorous containing anions. Recently, Gunnlaugsson and co-workers showed that strategically adding a third hydrogen-bonding moiety to a urea molecular host can greatly increase anion binding in a variety of solvents such as acetonitrile. Although a hydrogen bonding interaction was observed in non-polar and polar aprotic solvents, binding was completely reversible and the complex disseminated in highly polar solvents (methanol and H_2O).[13] To display the utility of these trapping groups, Kugimiya showed that thiourea molecular imprinted polymers can be used for the removal of inorganic phosphate from water.[14] In a simulated wastewater study the thiourea imprinted polymer was able to remove up to 75% of the inorganic phosphate.[15] The successful utilization of hydrogen bonding capabilities of thiourea in these diverse applications suggested that a derivatized polymer flocculant should increase its sorption capacity for phosphate. Polymer flocculants are routinely used to remove solid material from water. These polymers interact with the surface of suspended solids, organizing the individual particles into larger structures called flocs. The flocs then settle out of solution faster as the flocs have a larger diameter than the individual particles. The addition of the thiourea group to a polymer flocculent should increase the sorption capacity for phosphate, while maintaining the ability to remove sorbed phosphate through settling of suspended materials. Although polymer flocculants are generally used for the removal of solid material from solution, this is the first example of their modification with a thiourea-trapping group for the removal of inorganic phosphate ($H_2PO_4^-$) in solution.

Results and discussion

The synthesis of the thiourea monomers was conducted using a modified method developed by Elsabee and co-workers.[16] For the synthesis of the substituted thioureas (1 and 2); acroyl chloride was reacted with ammonium thiocyanate followed by aniline (1) or *o*-phenylenediamine (2). The yields for these reactions were excellent proceeding in 88% yield for (1) and 75% for (2) (Scheme 1).

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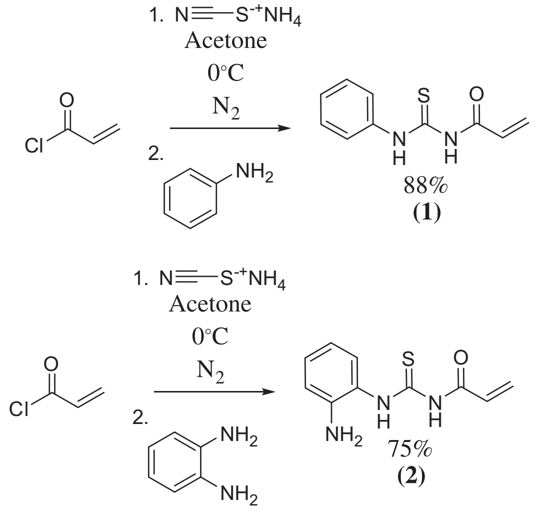


Scheme 1. Preparation of two- and three-point thiourea trapping groups.

To test the affinity of the two- and three-point hydrogen bonding thiourea monomers (1 and 2) ^{1}H NMR studies were performed. ^{1}H NMR studies were conducted at room temperature using each monomer individually and increasing amounts of tetra-*n*-butyl ammonium phosphate (0, 0.5, 1.0, and 2.0 equiv). The first NMR spectrum contains the two-point thiourea (1) without any inorganic phosphate, while the remaining shows an increase in $H_2PO_4^-$ from 0.5–2.0 equiv (Fig. 1). As observed in the NMR spectra an increase in $H_2PO_4^-$ concentration leads to a significant decrease in both of the thiourea (11.60 and 12.65 ppm, H_a and H_b) signals indicating a hydrogen bonding interaction between the monomer and $H_2PO_4^-$.

Figure 2 displays the ^{1}H NMR of the three-point monomer (2) with increasing levels of $H_2PO_4^-$ (0.0, 0.5, 1.0, 2.0 equiv). The thiourea protons are once again labeled H_a (11.90 ppm), H_b (11.52 ppm), and the amino moiety H_c (5.00 ppm). Similar results were observed with the three-point thiourea (2) upon the addition of $H_2PO_4^-$. As the concentration of $H_2PO_4^-$ increases, a significant decrease in the thiourea proton signal (H_a and H_b) is observed (Fig. 2). The major difference in the two- (1) versus three-point (2) monomer is the decrease in the amino (labeled H_c) signal. The decrease in the amino proton signal indicates a third site for hydrogen bonding to $H_2PO_4^-$. Based on the NMR studies, two- and three-point thioureas were pursued as our trapping groups for the polymer flocculent studies and their possible removal of inorganic phosphate from water.

Thiourea monomers (1 and 2) were polymerized with acrylamide and [2-(acryloyloxy)ethyl] trimethylammonium chloride utilizing AIBN as the initiator (Scheme 2).

Once the modified polymers were prepared, experiments were conducted to test the sorption of phosphate to the polymer (Table 1). To test the sorption of phosphate on the polymers an aqueous suspension of solid material was prepared. The solid material used was kaolinite (1:1 aluminosilicate) that was weighed and added to

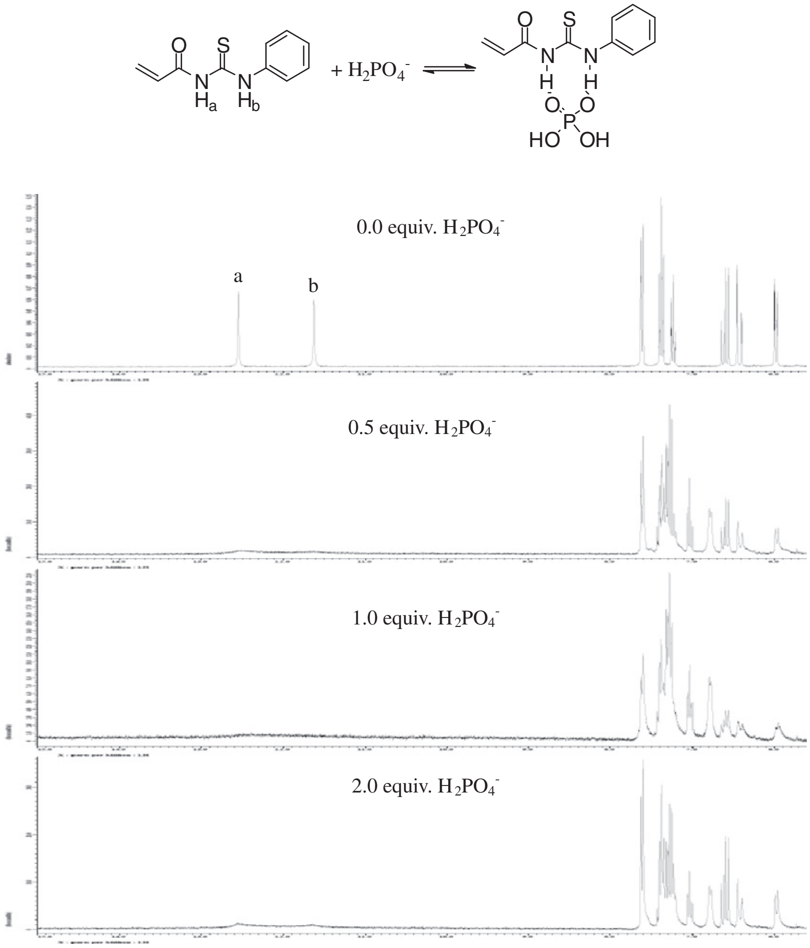


Figure 1. ^{1}H NMR (DMSO-d_6) of two-point thiourea monomer (1) and increasing concentrations of $H_2PO_4^-$. NMR's were run at 7.40×10^{-3} M concentration based on (1).

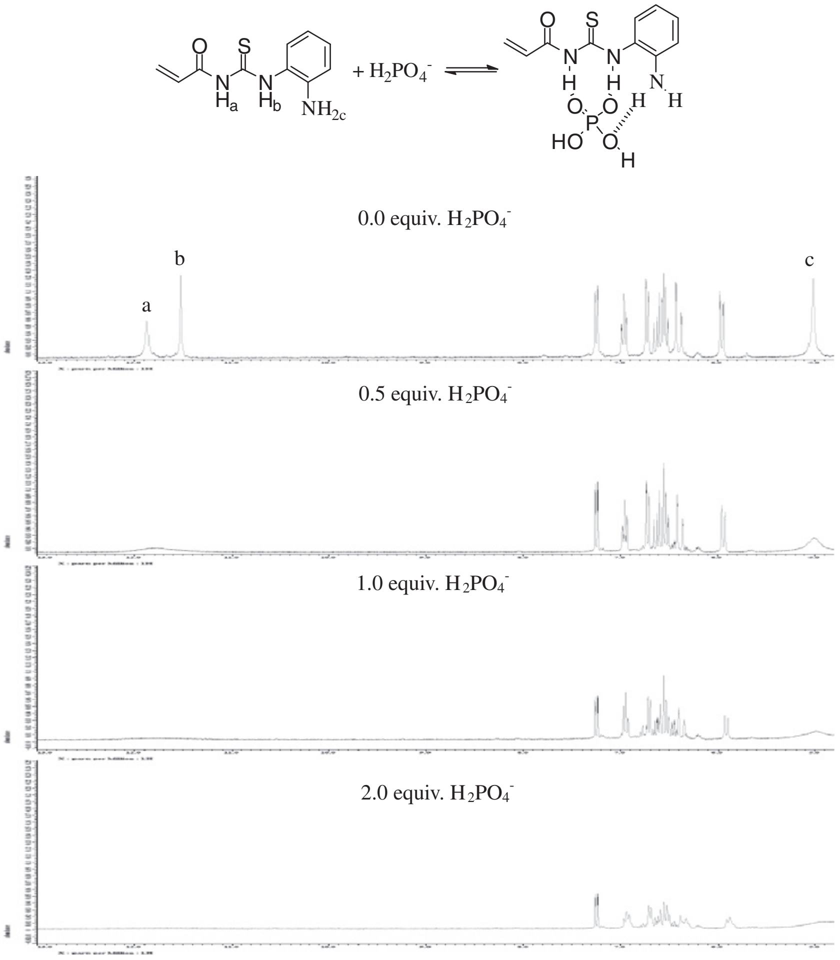
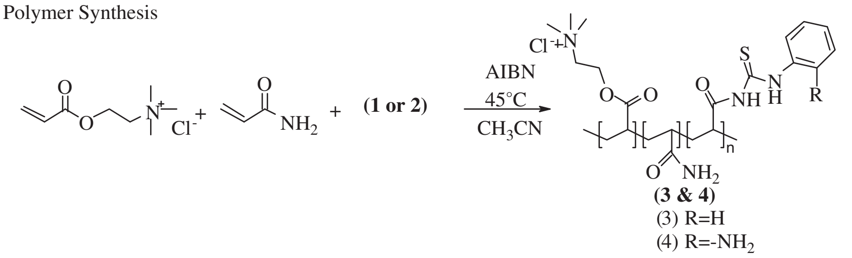


Figure 2. ^{1}H NMR (DMSO-d_6) of three-point thiourea monomer (2) and increasing concentrations of $H_2PO_4^-$. NMR's were run at 7.40×10^{-3} M concentration based on (2).



Scheme 2. Preparation of modified polymer flocculants.

Table 1
Mole percent of monomers for individual modified polymers

Monomer	C-40-00	C-40-20 (2-pt)	C-40-20 (3-pt)
Acrylamide	60	40	40
Trimethyl ammonium chloride	40	40	40
Thiourea (2-pt) (**1**)	N/A	20	N/A
Thiourea (3-pt) (**2**)	N/A	N/A	20

a known volume of water. NaH_2PO_4 was then added from an intermediate standard to create an aqueous suspension with a 5 mg/L phosphate concentration. The polymers tested were then added to the suspension and vortexed for 5 s. The suspension was left for 20 min to allow the flocs to form and settle out of solution. The resulting clear solution above the flocculated material was sampled and tested for phosphate using ion chromatography (IC).

Controls containing phosphate and clay were tested to check the level of sorption of phosphate to clay (Clay, Fig. 3). Several different polymers were tested for an interaction with phosphate. Magnifloc 494C was tested as a control with 10% positive charge density and 90% acrylamide (Mag C, Fig. 3). The polymer C40-00 was made according to the U.S. patent 5,945,494 as a control with 40% positive charge density and 60% acrylamide, C40-20(2-pt) was made modifying the same patent (appendix) with 40% positive charge density, 20% two-point thiourea (**1**), and 40% acrylamide. C40-20(3-pt) (**2**) was made with 40% positive charge density, 20% three-point thiourea, and 40% acrylamide.

The results from the polymer sequestration experiment (Fig. 3A) show that kaolinite was able to sorb 30% of the phosphate

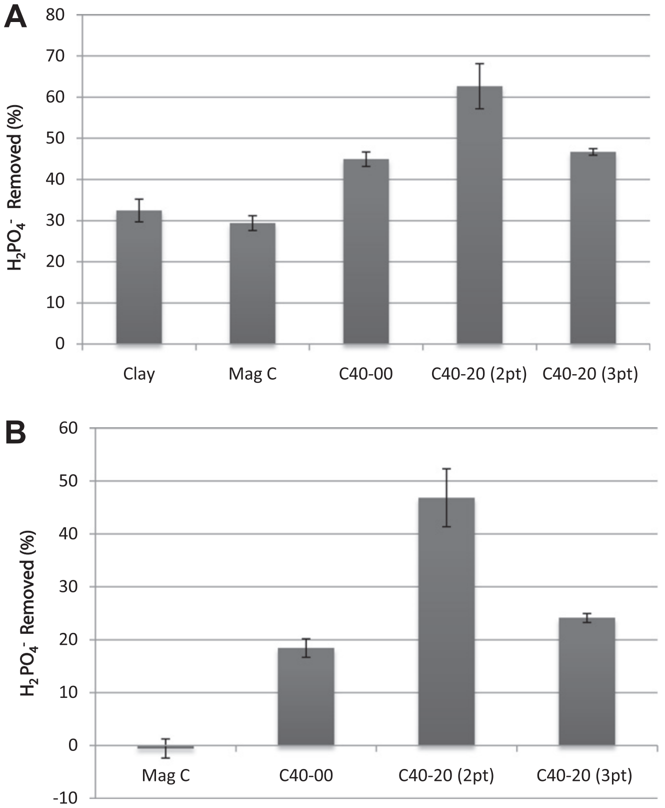


Figure 3. (A) Phosphate ($H_2PO_4^-$) removed by polymers with an initial phosphate concentration of 5 mg/L, and (B) the same results with the phosphate removed by kaolinite partitioned to examine the portion removed by the polymers.

from the solution. To further examine the results from the polymer treatment in this experiment the amount of phosphate removed by kaolinite was partitioned and removed to look at what portion of the phosphate left in solution bound to the polymers (Fig. 3B). Figure 3B suggests that the addition of Magnifloc 494C did not decrease the amount of phosphate in the solution. Comparing the results from Magnifloc 494C and C40-00 shows a decrease in phosphate concentration related to increasing the positive charge density on the polymer from 10% to 40%, suggesting that a positively charged quaternary ammonium group is interacting with the phosphate in the solution. Comparing the amount of phosphate removed from the solution when C40-00 was added to the addition of C40-20(2-pt) suggests that the addition of the thiourea group increased the polymers' sorption of phosphate. C40-20(3-pt) showed little improvement over the control C40-00.

While the monomers of the two-point and three-point thioureas displayed similar bonding to phosphate in the NMR studies, the polymer studies showed a difference in the amount of phosphate removed from the solution (2-pt vs 3-pt). The difference likely lies in the interaction of the thiourea (2-pt or 3-pt) portion of the polymer with the solid material present (kaolinite). The two-point thiourea polymer would likely not interact with the negatively charged clay surface as strongly as the three-point thiourea. The three-point thiourea polymer has an additional site (free amine) for interaction with the solid material thus decreasing the availability of the trapping group for the phosphate in the solution. Due to the higher affinity of the three-point thiourea polymer with the surface, the amount of phosphate removed through the flocculation event is decreased. These experiments are currently under investigation and will be reported in due course.

Conclusion

It has been discovered that substituted thiourea with two- and three-points of hydrogen bonding displays a high affinity for inorganic phosphate. ^{1}H NMR studies indicate that not only can derivatized thiourea molecules bind phosphate, but also the addition of neighboring amino moiety can induce a three point hydrogen bonding interaction.

Based on the high affinity of derivatized thiourea for inorganic phosphate, polymer flocculants were substituted with a thiourea-trapping group and sequestration studies discovered that up to 60% of inorganic phosphate could be removed from the solution. The polymer flocculants were able to remove the phosphate sorbed to the kaolinite through the flocculation event as well as remove an additional portion from the solution. These newly derived thiourea polymer flocculants worked up to 45% better than currently available commercial products in the removal of inorganic phosphate from water.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.07.130.

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