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Characterization of anion diffusion in polymer hydrogels used for wastewater remediation

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Abstract

Ion exchange systems for the removal of nutrient pollutants, even at extremely low concentrations, from wastewater effluents are a major environmental need. This work reports on the features of batch sorption processes for the ultimate removal and recovery of reactive phosphorus, nitrogen, and sulfur anions from aquaculture production wastewater effluents. The sorbent used was a crosslinked polyamine (PAA·HCl) polymeric hydrogel. The PAA·HCl hydrogels were prepared by chemically crosslinking aqueous solutions of linear PAA·HCl chains with epichlorohydrin (EPI). The nutrient anion binding capacity of the gels was studied as a function of various processing parameters. Lab scale batch and experiments showed maximum anion removal, from aquaculture wastewater, with regard to PO_4^{3-} by 99%, NO_3^- by 70%, and SO_4^{2-} by 95%. PO_4^{3-} diffusivities of 16, 10, and 8×10^{-6} cm^2/s were measured at pH levels of 5.5, 7.0, and 8.5.

Keywords: Hydrogel; Phosphate; Wastewater

1. Introduction

Aquatic ecosystems are often limited in the availability of two nutrients; phosphorus (P) and nitrogen (N) [1–3]. Limited nutrient availability prevents the excessive growth of algae blooms that produce unsightly areas, lower dissolved oxygen (DO) concentrations in the water, and may lead to fish kills [1]. Sulfur (S) has enormous environmental significance because it complexes with many toxic agents, organic materials, and hydrogen in surface waters, and is the primary agent of acidification in many lakes and rivers [4]. Thus S limits the movement of such agents in the environment, so concomitant toxicologic effects are minimized. However, excess S ultimately leads to acidification of freshwaters, resulting in the mobilization of these same agents. Many thousands of lakes and rivers have been devastated by acidification, and the potential of adulteration of drinking water increases with acidification. Methods that will effectively remove nutrient anion pollutants even at extremely low concentrations from wastewater effluents are a major environmental need. This work describes an approach that introduces novel cross-linked cationic polymeric materials into the contaminated aqueous slurry. The polymer materials we have developed selectively bind the pollutant anions into the polymer matrix, permitting their subsequent removal from the contaminated system. The polymer containing the bound pollutant anion can either be regenerated or incinerated. The treated water system can then be safely discharged into natural waters or sent for further treatment for use as a municipal water supply.

Many aquaculture production facilities operate as ‘flow through’ or ‘open’ systems thus releasing large quantities of nutrient rich water into another receiving body of water. At sufficiently high concentration levels, nutrient anions can become toxic to fish or lead to the crash of a phytoplankton bloom resulting in the rapid growth of filamentous algae or undesirable macrophytes [5–7]. Productivity is the most conspicuous aspect of cultural eutrophication. It is accelerated by the runoff from aquaculture waste discharges, rich in nutrients.

The microstructure of a hydrogel can affect solute diffusion. Some of the factors affecting solute diffusion in hydrogels are chain entanglement, chain mobility,

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crosslinking density, equilibrium degree of swelling, degree of crosslinking, and the relaxational characteristics of the gel network. On a molecular level, the solute diffusion rate through swollen gels depends on the relative hydrodynamic radius of the solute, and the network mesh size formed by the macromolecular chains; a larger solute diffuses at a slower rate than a smaller one [10]. For homogeneous gels, the mesh openings are neither constant in size nor homogeneously distributed in location [11]. Generally, the diffusivity of a solute through the PAA·HCl gels decreases as crosslinking density increases, as solute hydrodynamic radius increases, and as volume fraction of the water inside the gel decreases.

Fabrication of polymeric materials, such as the homogeneous PAA·HCl hydrogels used in this study, which can bind quantities of ionic pollutants from wastewater in batch or continuous-flow processes requires careful analysis of the diffusive behavior of the ionic pollutant into the polymer network. A rapid anion diffusion into the hydrogel is essential for the development of a viable commercial product for agricultural, aquacultural, municipal, and industrial wastewater treatment. The objectives of this study are to measure the diffusion coefficient of these ion binding hydrogels at various effluent pHs, and relate the measured diffusion to hydrogel synthesis parameters.

2. Materials and methods

2.1. Materials used

Poly(allyl amine) hydrochloride (PAA·HCl) solid powder (25 g), sodium hydroxide (NaOH) (pellets, 97%), were purchased from Aldrich Chemical Company. The crosslinking agent purchased from Aldrich, epichlorohydrin 99+% solution (EPI), was used to produce the hydrogel network. All reagents were ACS grade and were used without further purification. Non-wastewater related experiments were performed at room temperature in aqueous solution, using water from an Elix water purification system by Millipore, model #ZLXS6003Y. The PhosVer3 reagents used to perform the UV–vis concentration measurements were purchased from the Hach Company.

2.2. Hydrogel preparation

The randomly crosslinked PAA·HCl networks were prepared by the aqueous post polymerization reaction of 20% w/v solution of linear PAA·HCl chains and EPI as the crosslinking agent. The PAA·HCl used in the synthesis of the gels had a weight average molecular weight of 15, 000 g/mol and a polydispersity, determined by gel permeation chromatography, of 2.7. A hydrochloric acid (HCl) group is ionically associated with amine (NH_2) groups on the polymer chain backbone. Before crosslinking the polymer chains, a portion of the HCl groups of PAA·HCl were neutralized with NaOH. This was done to provide ‘free’ NH_2 sites for the crosslinking reaction. Crosslinker was subsequently added to react with the resulting free NH_2 sites and form crosslinks (tie points) between neighboring PAA·HCl chains in the aqueous solution. The PAA·HCl, NaOH, EPI reaction mixture was stirred for 6–20 min depending on the amount of NaOH or EPI that was added. The reaction mixture was poured into a petri dish to set into a gel slab before the sol–gel transition point was reached. Upon curing for an additional 24 h, the gel slab was washed with deionized water to remove residual NaCl (produced from the neutralization of HCl by NaOH), unreacted PAA·HCl and EPI. The polymer gel was repeatedly washed with de-ionized water to remove any remaining NaOH. The de-ionized water washes were performed in 1–2 h intervals, 3–4 times per day, while monitoring the pH of the effluent wash. When the effluent wash water, after an overnight equilibration period with the gel, was no longer basic it was determined that the polymer was free of excess NaOH. Typically, 5 days of washing the gel as described were required to remove all of the NaOH. Finally, the completely washed gel was dried under air in a 50 °C oven. The final water content of the dry gels, as determined by thermogravimetric analysis, was 5–8 wt%. The dried gel slab was ground into small pieces for further experimentation using a mortar an pestle to a uniform powder. UV–vis spectrophotometry was used to measure anion concentrations in the various samples. Phosphate concentrations were determined using a Hach DR2010 spectrophotometer The quantity of phosphorus contained in the sample was then determined using Hach’s total phosphorus test, method 8190 [9]. Prior to testing, the wash water sample was diluted so that the expected phosphorus concentration lay in the measurable range of the Hach test.

2.3. Diffusion coefficient measurements

The reaction medium was stirred for 15 min in order not to reach the sol–gel transition point (approximately 20 min). The reaction mixture was then poured into a silicone molding containing spherical cavities of 1.8 cm diameter. The mixture was allowed to cure in the cavity for 48 h. When the cavities were cut open, a spherical gel particle of known diameter was obtained. The resultant gel sphere was removed and washed in distilled water to purge any residual reactants from the gel.

Diffusivity measurements were conducted at room temperature (25 °C) in 10 mL glass beakers containing 7–8 mL aquaculture wastewater solutions. The PO_4^{3-} diffusivity was measured at pH levels ranging from acidic to basic conditions (5.5–8.5). The wastewater solutions were well stirred by a Teflon bar on a magnetic stirrer. Before the experimental run, the swollen gel particle was removed from the wastewater solution and then placed on filter paper to remove excess wastewater. The diameter of the swollen gel bead (d_s) was measured prior to experimentation using a set of vernier calipers. At time $t=0$, the swollen gel sphere was placed in a 10 mL beaker containing aquaculture wastewater solution. The transient concentration change of PO_4^{3-} was monitored using standard UV–vis spectrophotometric methods. Samples (0.1 mL) were withdrawn at various timed intervals and placed in 25 mL Hach sample cells. An equal volume of sample solution was added to the beaker, from identical experimental set-ups running simultaneously at each sampling.

The effective diffusion coefficient, D_e, for PO_4^{3-} diffusion into a PAA·HCl spherical gel particle was calculated using a simple and standard model [14]. A Fickian model can be used to determine the PO_4^{3-} diffusion coefficient under the assumptions that the gel sphere is swollen close to its equilibrium point and the PO_4^{3-} anion has no interaction with the matrix (since the ionic radius of PO_4^{3-} is orders of magnitude smaller than the mesh size of the gel). The experimental results are modeled as three-dimensional diffusion into a sphere, using the approximation of Fick's second law for the case of long times.

In our experimental set-up the swollen spherical gel bead initially free of PO_4^{3-} is suspended in a well-stirred solution with an initial PO_4^{3-} concentration C_{so}. When a sphere free of solute is suspended in a well-stirred solution with an initial solute concentration C_{so} and the external mass transfer resistance surrounding the sphere is negligible, the transient concentration change of the solute, C_s(t), is given by Crank [14] as follows:

$$C_s(t) = \frac{\alpha C_{so}}{1+\alpha}\left(1 + \sum_{n=1}^{\infty} \frac{6(1+\alpha)\exp(-D_e q_n^2 t/a^2)}{9 + 9\alpha + q_n^2\alpha^2}\right) \tag{1}$$

where a is the diameter of the sphere; t is the diffusion time; $\alpha=(3V)/(S4\pi a^3)$ is the ratio of the volume of the solution, excluding the volume occupied by the sphere (S is the partition coefficient of PO_4^{3-} in the polymer phase); n is the number of spheres (in our case $n=1$); D_e is the effective diffusivity; and q_n is the positive non-zero root of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \tag{2}$$

For diffusion time, $t=0$ at the instant the sphere is dropped into the solution. For a given set of a, α and C_{so} and C_s(t), the effective diffusivity D_e as a function of pH was easily calculated from Eqs. (1) and (2) using a computer.

2.4. Wastewater characteristics

Hybrid Striped Bass and Tilapia fish tank wastewater from the Department of Biological Resources Engineering at the University of Maryland was used. Wastewater samples were collected directly from inside the fish tanks. The fish were grown in a pilot-scale recirculating water system (with circular fiberglass tanks, filters for solids removal, and biofilters) and were being fed commercial fish feed containing approximately 38% crude protein, 8% crude fat, and 5% crude fiber. This aquaculture wastewater effluent has an average pH of 7.70 and contains high levels of dissolved and particulate complex organics as well as other compounds such as (NH_3), PO_4^{3-}, NO_3^-, NO_2^-, Cl^- (5 g/L), S^{2-}, SO_4^{2-}; $SO_4^{2-}/Cl^- = 0.017$. The average total ammonia nitrogen (TAN), total organic carbon (TOC), biological oxygen demand (BOD_5), alkalinity and dissolved oxygen (DO) content of the wastewater is 0.8, 21, 5.3, 110 and 6.2 mg/L, respectively. Proper sample collection, preservation and storage were critical for accurate testing. The aquaculture wastewater samples were filtered using Whatman qualitative filter circles (particle retention > 11 μm, porosity: medium) prior to the diffusion experiments. The initial target anion concentrations were measured before testing.

3. Results and discussion

3.1. Phosphate binding experiments

Experimental results indicated that within 3 h the polymeric amine gels were capable of binding more than 98% of the phosphates initially present in the aquaculture wastewater. Phosphate binding values up to 47 mg-PO_4/g-gel were obtained depending on the gel chemical composition.

The crosslinking density of the polymeric hydrogel is directly related to their EPI (crosslinker) content. Increasing the amount of EPI in the gel synthesis causes the resulting hydrogel to be more tightly crosslinked and, therefore, swell less in water. However, this had no effect on the rate of transport of phosphates into the polymer network. This was due to the fact that the mesh size of the network (the space between crosslinks) was orders of magnitude larger than the size of the phosphate anion.

A factor that must be considered when increasing the amount of NaOH is the duration of the gel forming reaction. Gels prepared using 0.28 g NaOH per g PAA·HCl reacted for 20 min before a solid gel was formed. Gels synthesized with 0.34 g NaOH per g PAA·HCl would typically react for an average of 6–7 min. This significant reduction in reaction time had an effect on the homogeneity of the crosslinking reaction. Gels synthesized with relatively small reaction times until gelation (higher NaOH and/or EPI contents) had an increasing amount of crosslink inhomogeneities present in the polymeric matrix, which ultimately had a negative effect on the phosphate binding capacities and mechanical integrity of the gel.

Experiments were performed to determine whether the gels were capable of concurrently removing the PO_4^{3-}, SO_4^{2-}, and NO_3^- anions from the aquaculture wastewater effluents. Fig. 1 shows the decrease in anion concentration with time. More than 99% of PO_4^{3-}, 95% of SO_4^{2-}, and 70%

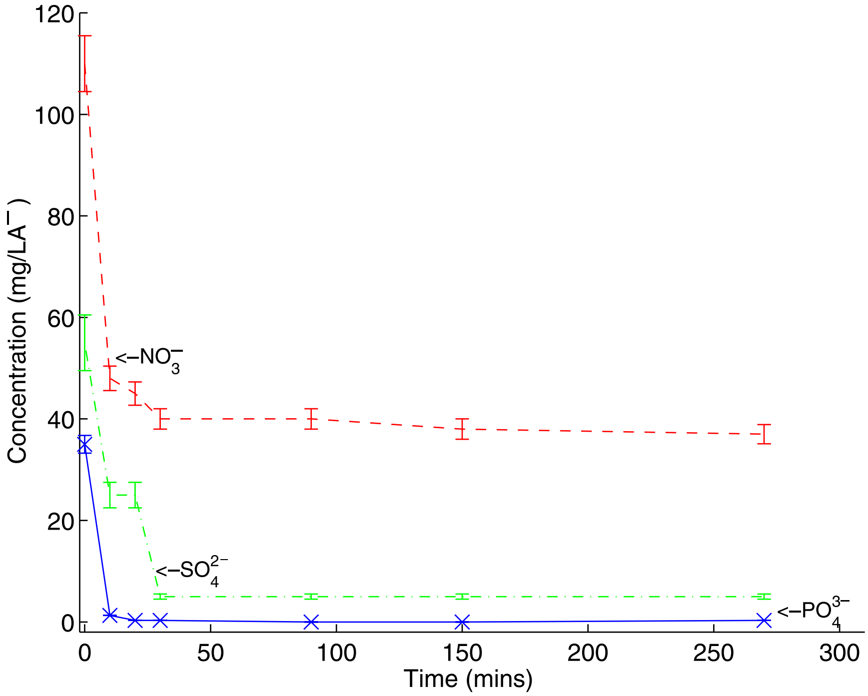

Fig. 1. Decrease in SO_4^{2-}, PO_4^{3-}, and NO_3^- concentration in aquaculture wastewater, pH = 7.50 ± 0.05. PAA·HCl concentration: 25% w/v, $M_n = 15{,}000$ g/mol, NaOH: 0.28 g/g PAA·HCl, EPI: 1.60×10^{-3} mol/g PAA·HCl.

of NO_3^- initially present were removed. The concentrations of NO_2^- (0.2 mg/L) and S^{2-} (0.01 mg/L) in the aquaculture were very low so their change with time was not followed. The gels selectively bound over PO_4^{3-} over SO_4^{2-}, NO_3^- and NO_2^-. The experimental results, demonstrated that the PAA·HCl gels are capable of concurrently removing these nutrient anions from aquaculture wastewater. After treating with the gel, the wastewater effluents can be safely discharged into natural waters or sent to a municipal wastewater treatment facility for further purification.

3.2. Diffusion coefficient determination

An issue characteristic of diffusion in gels is that the gel volume may not remain constant throughout the experiment [12]. This will occur if a gel has not reached its equilibrium degree of swelling before exposure to a solution from which solute diffusion takes place [12]. This effect can be eliminated by first equilibrating the gel in water for a prolonged period of time in order to avoid swelling during the experiment. In all our experiments, the PO_4^{3-} diffusion process into the PAA·HCl gel was investigated, after thermodynamic equilibrium between the network and the surrounding dissolution medium (water) was approached.

The PAA·HCl hydrogels contain pH-sensitive ionizable side chains that cause the network to swell extensively in aqueous media. The swelling behavior depends on the nature of the side groups as well as the pH of the medium [13]. From information on PO_4^{3-} concentration and known geometrical parameters (i.e. average diameter of gel particles) an effective diffusion coefficient for PO_4^{3-} in the gel was determined as a function of pH level.

3.3. Diffusion experimental results

All measurements were conducted close to thermodynamic equilibrium between the gel network and the surrounding dissolution medium (water). At swelling equilibrium, the PAA·HCl gels contained 90–95% water as determined from equilibrium swelling studies. The PO_4^{3-} concentration was monitored at timed intervals in small batch reactors (10 mL) containing PO_4^{3-} buffer solutions. Normalized concentration versus time data for pH levels of 5.5, 7.0, and 8.5 are shown in Figs. 2–4, respectively. Calculated values for PO_4^{3-} diffusion coefficients through the PAA·HCl gels for the different pH's, using Eqs. (1) and (2), are presented in Table 1. The PO_4^{3-} anion was used as a probe to study the diffusion characteristics of the ionic pH-sensitive PAA·HCl gels. The PO_4^{3-} diffusion coefficient was found to decrease slightly with increasing pH level.

Table 1
PO_4^{3-} effective diffusion coefficients, D_e, through PAA·HCl hydrogels at 25 °C as a function of pH

pH	$D_e\times10^{-6}$ (cm^2/s)
5.5	16 ± 2
7.0	10 ± 3
8.5	8 ± 0.5

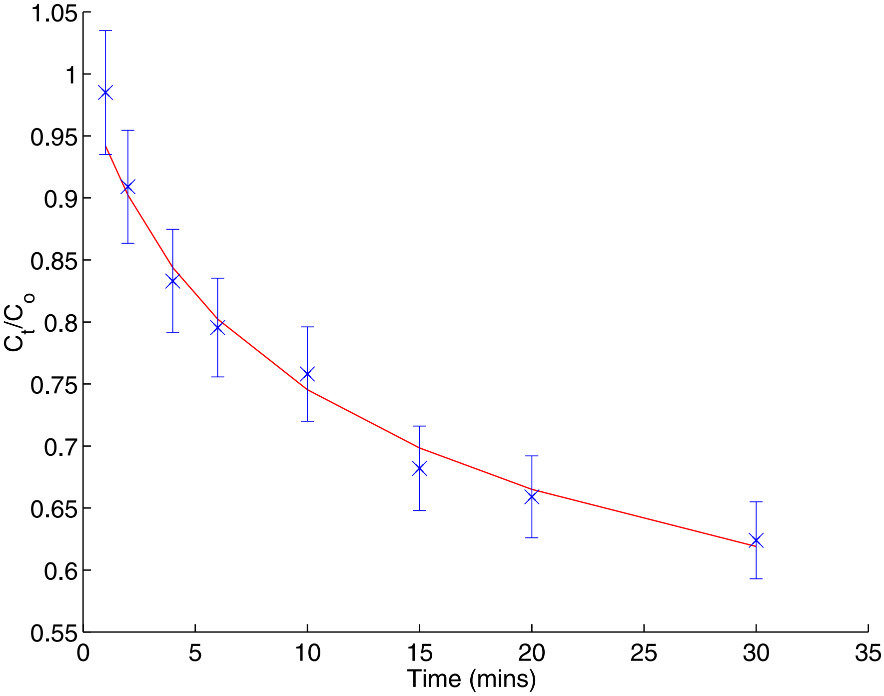

Fig. 2. Diffusion of PO_4^{3-} through PAA·HCl gel spheres ($d_s = 1.8$ cm) at pH 7.0: (×) experimental data and (–) diffusion model. Solid line: solution of Eq. (1).

At higher pH the gels have lower charge (ionic) density, thus decreasing the cationic gel's affinity toward the PO_4^{3-} anion.

There are various commercial ion exchange resins that remove nutrient anions from wastewaters; however, most of them cannot be easily regenerated, they suffer from bacterial growth (bio fouling), or they break down after extended use. Many exhibit selectivity problems, i.e. they might bind the specific anion very well in one medium, but not in another that contains specific counter-ions that decrease selectivity. The anion binding hydrogels of this work appear to be an improved technology that does not suffer from these disadvantages. This polymer hydrogel material does not exhibit selectivity problems in aquaculture

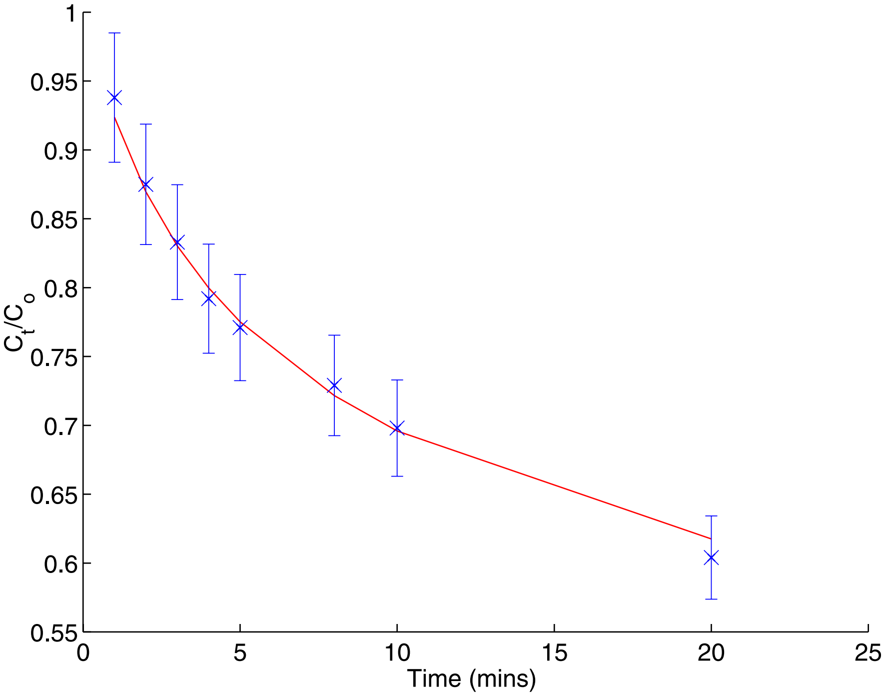

Fig. 3. Diffusion of PO_4^{3-} through PAA·HCl gel spheres ($d_s = 1.8$ cm) at pH 5.5: (×) experimental data and (–) diffusion model. Solid line: solution of Eq. (1).

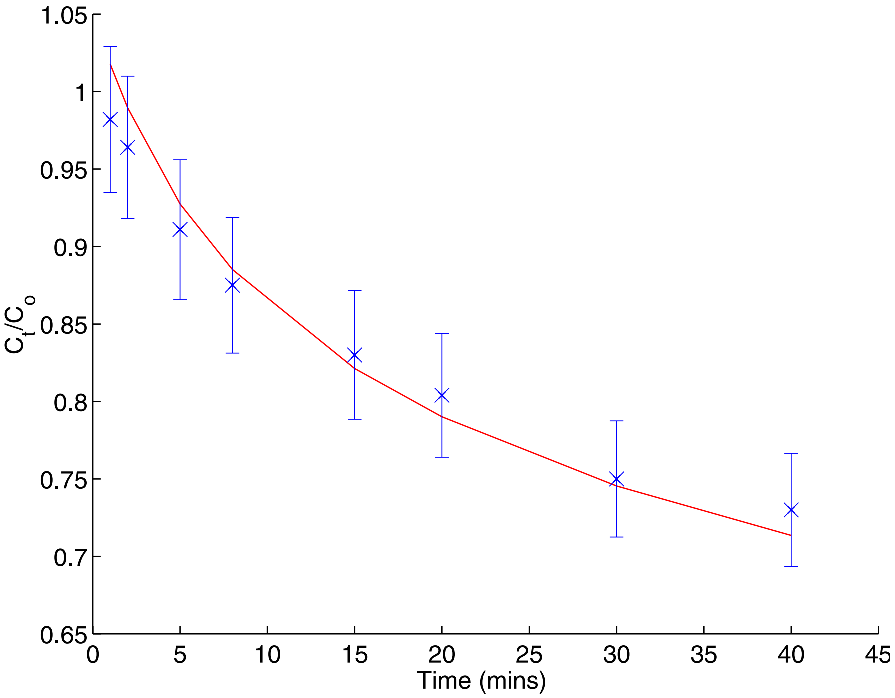

Fig. 4. Diffusion of PO_4^{3-} through PAA·HCl gel spheres ($d_s = 1.8$ cm) at pH 8.5: (×) experimental data and (–) diffusion model. Solid line: solution of Eq. (1).

wastewater, can bind multiple nutrient anions, does maintain its mechanical integrity after repeated use, and can be easily regenerated [15].

The diffusion and anion binding results will be correlated with atomic force microscopy experiments currently in progress, to characterize the microstructure of these hydrogels. These experiments will be used to determine the optimum hydrogel microstructure, with adequate mechanical integrity to withstand the flowrates and pressure drop experienced in commercial batch and packed-bed processes, but without significantly affecting the gel's anion binding capacity.

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