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Phosphate binding polymeric hydrogels for aquaculture wastewater remediation

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Abstract

Methods that will remove conventional nutrient pollutants such as reactive phosphorus, even at extremely low concentrations, from wastewater effluents are a major need in the aquaculture industry. In this study, novel phosphate binding crosslinked poly(allylamine), PAA·HCl, polymeric hydrogel materials were developed, which efficiently bind phosphate anions in aquaculture wastewater effluents. The polymeric hydrogels were synthesized by chemically crosslinking linear PAA·HCl chains with epichlorohydrin. The phosphate binding capacity of the synthesized pH sensitive polymer gels was studied as a function of various gel processing parameters. Equilibrium orthophosphate (PO_4^{3-}) loadings of 47 mg g^{-1} polymer, were calculated from direct measurement of the decrease in phosphate concentration in aqueous solutions using UV spectroscopy. Experiments showed that pollutant concentrations in aquaculture wastewater effluents decreased with regard to by more than 99%. The ability of the gels to bind phosphates was not fouled by particulate or dissolved complex organics and inorganics, or counterions which are present in aquaculture wastewater effluents. The hydrogels can be regenerated by release of the bound phosphates upon washing with a 1 N NaOH solution. Results demonstrated that the novel crosslinked polymeric hydrogels are appropriate materials for treating aquaculture wastewater effluents, and reducing the phosphorus concentrations to levels, less than 0.01 ppm, suitable for discharge to natural surface waters. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aquaculture wastewater; Phosphates; Hydrogels; Poly(allylamine)

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1. Introduction

The discharge of wastewater containing phosphorus into natural waters causes concern over the effect phosphorus will have on water quality in the receiving body of water, since most natural waters are either phosphorus or nitrogen limited. Phosphorus concentrations are found in the discharge of flow-through and recirculating aquaculture production systems.

Phosphorus occurs as various types of phosphate in natural waters. The most common forms are organically bound phosphates, orthophosphates (H_2PO_4 , HPO_4^{2-} , PO_4^{3-}), and polyphosphates (polymers of phosphoric acid), (Hammer and MacKichan, 1981; Viessman and Hammer, 1985; Hammer and Hammer, 1996). Typical polyphosphates are sodium hexametaphosphate, $\text{Na}_3(\text{PO}_3)_6$, sodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$, and tetrasodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$. All polyphosphates gradually hydrolyze in aqueous solutions and revert to the ortho form. Bacterial decomposition of organic compounds also releases orthophosphates.

This research focuses on methods that will remove phosphorus even at extremely low concentrations from fish hatchery wastewater effluents. This is a major environmental need since the discharge of phosphorus into phosphorus limited waters often leads to algae blooms, (aquatic plant growth), that produce unsightly areas, and lower oxygen concentrations in the water that lead to fish kills. Productivity is the most conspicuous aspect of cultural eutrophication. It is accelerated by the run-off from agricultural land and municipal waste discharges, rich in phosphorus. Beveridge (1984), Enell (1987); Folke and Kautsky (1989), Ketola (1975) and Ketola et al. (1991) report numerous examples of pollution caused by phosphorus discharges from aquacultural facilities. For these reasons several states, within the USA, have adopted effluent standards for phosphorus. Effluent limits range from 0.10 to 2.00 mg l^{-1} as P, with many established as 1.00 mg l^{-1} (Hammer and Hammer, 1996). Phosphorus removal has been implemented at many wastewater treatment facilities in order to protect the lakes and surface waters of the Great Lakes and the Chesapeake Bay drainage basins (EPA, 1987). Of 526 plants in the Chesapeake Bay drainage basin (Maryland, Pennsylvania, and Virginia), 99 are removing phosphorus (EPA, 1987).

Phosphate removal from aquaculture production systems can be achieved using crosslinked polymeric hydrogel materials. Hydrogels are hydrophilic polymer networks that can absorb large amounts of water but remain insoluble because of the presence of crosslinks, entanglements, or crystalline regions. To be effective in removing phosphorus from wastewater effluents, the rate of transport of phosphate into the gels must be large enough so that efficient binding can be achieved. The transport process must also be reasonably insensitive to pH changes so that phosphates can be bound from aquaculture effluents of varying acidities. In addition, the ability of the gels to bind phosphorus should not be limited by the presence of particulates or organics which are common fouling constituents of aquaculture system effluents.

2. Background

Several chemical and biological processes for removal of phosphate from wastewaters are currently applied in wastewater treatment plants. Chemical processes involve the addition of metal salts (aluminum, or iron) or lime to wastewater to form insoluble phosphate precipitates, removal of the precipitate from the wastewater, and disposal of the precipitate which becomes incorporated in the sludge by-product. The precipitation of calcium phosphate in a fluidized bed reactor, and chemical treatment following the coal-sand filtration with lime and manganese sulphate, or ferric chloride are such processes (Bruinsma et al., 1996; Goel and Chaudhuri, 1996; Van Leeuwen et al., 1996; Seckler et al., 1996). At optimal conditions these processes are only able to achieve phosphate removal of 50–60% (80–95% in the presence of carbonate and magnesium ions), 95, 79 and 92% for the calcium, lime-manganese, lime (alone), and ferric chloride processes, respectively. For example, a fluidized bed reactor operating at optimal conditions can reduce an influent concentration of around 0.5 ppm PO_4 down to 0.10–0.08 ppm PO_4 .

Biological phosphorous removal is based on the ability of some microorganisms to accumulate large amounts of phosphorous under aerobic conditions and store it in form of polyphosphate granules. Enhanced biological phosphorus removal (bio-P) is a process used in wastewater treatment plants for the removal of phosphorus. Experiments performed with phosphorus-rich (60–100 mg P l^{-1}) wastewater have shown effluent orthophosphate concentrations reaching as low as 5–10 mg P l^{-1} , i.e. a 90–92% removal was achieved with 18–48-h hydraulic retention times and 20 day sludge retention time for the effluents (Comeau et al., 1996). A combined anaerobic and aerobic process in a single reactor had percent removal efficiencies of 92% for total phosphorus and 90% for PO_4 , with 10-day sludge retention time (Choi et al., 1996).

We will demonstrate in the ensuing discussion that, in comparison to these phosphorus removal technologies, the crosslinked polymeric hydrogels we synthesized, are capable of removing more than 99% of orthophosphates present in the wastewater within 2 h. This capability makes the polymeric hydrogels a more attractive and promising technology than any of the currently available phosphorus removal methods.

3. Chemistry of hydrogels

A polymer network consists of initially linear polymer chains chemically connected to at least two other chains through a ‘bridge-forming’ reaction referred to as the ‘crosslinking reaction’. Poly(allylamine hydrochloride), $\text{PAA} \cdot \text{HCl}$ (Fig. 1), a water soluble linear polymer, has been used to synthesize the polymeric networks presented in this study. The randomly crosslinked polymeric networks which bind phosphate anions from wastewater have been obtained via chemical crosslinking. Chemical crosslinking involves the use of a compound, the ‘crosslinking agent’, bridging two or more linear polymer chains.

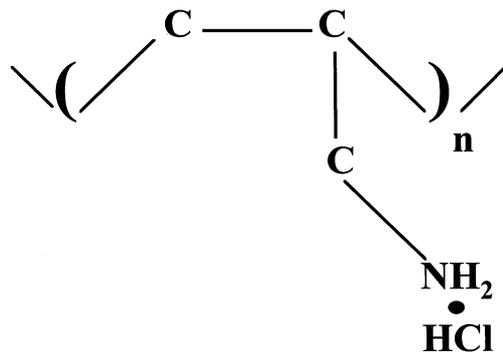


Fig. 1. Repeat unit of PAA · HCl.

Hydrogels were therefore prepared by the aqueous reaction of poly(allylamine) and epichlorohydrin (EPI), which serves as the crosslinking agent. Before reacting with EPI a portion of the HCl groups of PAA · HCl were neutralized with NaOH to provide free amine sites for the EPI crosslinking reaction. The chemical crosslinking reaction steps are shown in detail in Fig. 2.

The relative amounts of the materials used in the hydrogel synthesis steps were independently varied to determine their possible influence on the final structure and phosphate binding properties of the resulting gel. For example, the crosslink density, which affects both the mechanical properties and the solute transport through the hydrogel, was controlled via the amount of crosslink agent (EPI) added during the synthesis or via the number of free amine sites available for crosslinking to occur, i.e. varying the amount of NaOH (neutralizer) added.

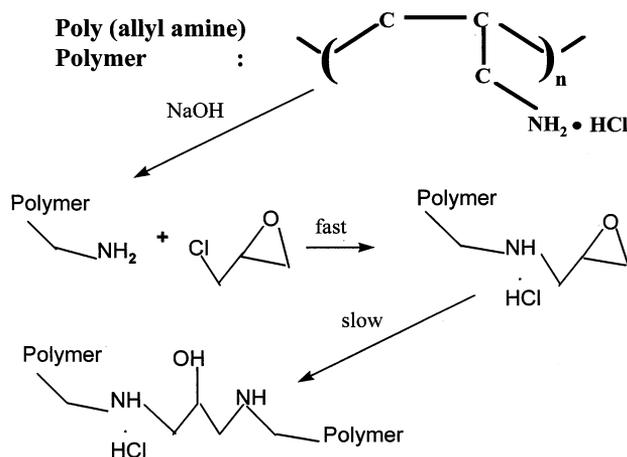


Fig. 2. Hydrogel synthesis by chemical crosslinking.

4. Materials and methods

4.1. Synthesis of hydrogels by chemical crosslinking

The PAA used in the synthesis of the phosphate binding gels had an average molecular weight ranging from 8500 to 65 000 g mol⁻¹, including a hydrochloric acid group ionically associated with each amine (PAA · HCl). A typical phosphate binding hydrogel is synthesized as follows: a 12.5–25% by volume solution of PAA · HCl is mixed with 0.23–0.34 g of sodium hydroxide (NaOH) per g of PAA · HCl until the NaOH dissolves. When the temperature of the solution drops below 27°C (the dissolution of NaOH is exothermic), the desired amount of EPI is added. EPI reacts with the free amine groups produced from the neutralization of HCl by NaOH. The PAA · HCl, NaOH, PAA reaction mixture is then stirred for 10–20 min. The reaction mixture is then poured into a Petri dish to set into a gel slab. Upon curing for an additional 18–24 h the gel is washed three times with deionized water, to remove residual NaCl produced from the NaOH neutralization of the HCl groups. Upon completion of the washing step the salt-free hydrogel slabs, now in their fully swollen state, are air-dried in an oven at 40–50°C. The final water content of the dry gels, as determined by thermogravimetric analysis, is 5–8 wt.%. The dried gel slabs are then ground into small pieces for further experimentation.

4.2. Parameters influencing the structure and phosphate binding capacities

The structure and phosphate binding capacity of the hydrogels can be influenced by parameters such as:

1. The amount of crosslinking agent (EPI).
2. The number of free amine sites per gram of gel available for phosphate binding.
3. The pH and temperature of the water.
4. The amount of sodium hydroxide, NaOH, used to neutralize HCl groups on the PAA · HCl chains.
5. The initial concentration, and the molecular weight of the PAA · HCl.

These potential influences on the gel's chemical structure, morphology and properties, raise the question of batch-to-batch reproducibility, which is an important issue for the commercialization of this product in the aquaculture industry. The following issues were therefore addressed: how sensitive is the gel morphology and its phosphate binding capacity to perturbations in any of these parameters? Is the structure uniform in every batch? The detailed elucidation of a gel's properties is an indirect, but effective way to document the influence of all the aforementioned parameters on the structure, mechanical integrity and phosphorus binding ability of the resulting gel.

4.2.1. Variation in PAA · HCl initial concentration and molecular weight

The effect of uncrosslinked polymer concentration and molecular weight on the final synthesized hydrogels was investigated by synthesizing hydrogels using a 12.5,

20, and 25% PAA · HCl initial concentration having molecular weights of 9750 and 57 500 g mol⁻¹ while keeping the amount of EPI and NaOH used in the crosslinking reaction constant.

4.2.2. Variation in NaOH content

The aqueous PAA · HCl solutions are partially neutralized using NaOH to cleave off HCl groups. After the addition of the NaOH, EPI is added to crosslink the free amines produced from the neutralization of the HCl groups. The pH of the gel formation reaction becomes more basic with increasing amount of NaOH added to the reaction medium. Gels were synthesized using 2.51×10^{-3} mol EPI and 0.23, 0.28, and 0.34 g NaOH per g PAA · HCl. The time to gelation, upon the addition of EPI, decreased with increasing amount of NaOH. The samples synthesized with 0.34 g NaOH per g PAA · HCl gelled within 6–7 min after addition of the crosslinker to the stirred solution of NaOH and PAA · HCl.

4.2.3. Variation in EPI content

The amount of EPI used for the chemical crosslinking reaction was also varied, keeping the amounts of NaOH and PAA · HCl unchanged, to produce gels having varying crosslink density. Gels were synthesized using 2.51, 3.13, and 3.76×10^{-3} mol EPI.

4.3. Reactive phosphorous concentration measurements

Phosphate levels were measured using Hach Company PhosVer 3 Method (Hach, 1997) on a Hach DR/2010 UV spectrophotometer. The detection procedure used by the spectrophotometer is equivalent to USEPA method 365.2 and Standard Method 4500-P-e for natural water and wastewater and is also known as the Ascorbic Acid method. The phosphate concentration of the sample was measured by diluting the sample with deionized water in 25 ml sample cells. Samples were diluted because the Ascorbic Acid method had a low detection range of 0.1–2.5 mg l⁻¹ PO₄, and the initial phosphate concentration in the wastewater samples was much higher (40–80 ppm) than this method could detect.

4.4. Phosphate binding in constant pH distilled water

The decrease in phosphate concentration at various pH's was measured in buffered potassium dihydrogen phosphate solutions. In this way it was possible to determine the total phosphate binding capacity of the poly(allylamine) gels at various pH's, which remained constant during the binding reactions.

All chemicals used for the experiments were A.C.S. grade, and aqueous solutions were prepared in deionized water. The constant pH buffer consists of *N,N*-bis(hydroxyethyl)-2-aminoethane sulfonic acid (BES), sodium chloride (NaCl), and potassium phosphate (KH₂PO₄). To make 400 ml of buffer having an initial PO₄ concentration of 11 mg l⁻¹, 8.5 g of BES, 1.88 g NaCl, and 0.006 g KH₂PO₄ were added to 200 ml of deionized water. The initial pH was measured and then adjusted

to the desired pH for the phosphate binding experiment using 1 N NaOH. Upon reaching the desired pH the buffer solution was further diluted with another 200 ml of deionized water. Buffer solutions at pH levels of 5.60, 7.00, 8.00, and 9.13 were prepared and the phosphate binding capacity of the gels was investigated at these pH levels. In all cases, phosphate binding reactions were allowed to run for 4 h and the decrease of PO_4 concentration in the buffered KH_2PO_4 solutions, which occurred when a slurry of PAA particles was added to the solutions, was measured every 30 min using the spectrophotometer. The experiment stopped when the hydrogel reached its saturation point and the phosphate concentration in the buffer sample remained constant. At the end of each experimental run, the final pH of the reaction medium was measured to determine whether the buffer was successful in maintaining conditions of constant pH throughout the experiment.

4.5. Wastewater characteristics

The aquaculture wastewater samples that were used in the phosphate binding experiments came from hybrid striped bass and tilapia fish tanks from the Department of Biological Resources Engineering at the University of Maryland. The fish were being fed commercial fish feed containing approximately 38% crude protein, 8% crude fat, and 5% crude fiber. This aquaculture water has an average pH of 7.70 and contains high concentrations of dissolved and particulate complex organics as well as other compounds such as ammonia (NH_3), nitrates (NO_3), and nitrites (NO_2). The average total ammonia nitrogen (TAN), total organic carbon (TOC), BOD_5 , and dissolved oxygen (DO) content of the wastewater is 0.8, 15, 5.3 and 6.2 ppm, respectively. The aquaculture water also has a salinity content of 5 ppt. Phosphate concentration in the fish tanks ranged from 40 to 80 mg l^{-1} .

Proper sample collection, preservation and storage were critical for accurate testing. The samples were filtered immediately upon collection, to remove the various particulates and solids, and stored at 4°C for up to 48 h if immediate analysis was not possible. If analysis was not possible within 48 h the aquaculture water pH was lowered to 2 by using 1 N sulfuric acid and the samples could then be stored for up to 28 days until they were used.

4.6. Phosphate binding in aquaculture water

Experiments in aquaculture wastewater effluent were designed to evaluate the effect the variety of inorganic and organic constituents present in aquaculture wastewater may have on the phosphate binding ability of the polymeric hydrogels. Once the initial concentration of phosphates was determined in the aquaculture wastewater the decrease in phosphate concentration of the wastewater that occurred when a slurry of hydrogel particles was added to the solution was recorded using the UV spectrophotometer. Concentration measurements were taken at 30 min intervals at first, and then every 15 min when the phosphate concentration dropped below 0.05 mg l^{-1} .

The experiment stopped when the hydrogel reached its saturation point and the phosphate concentration in the aquaculture wastewater sample remained constant.

Experiments to investigate the ability of the hydrogels to be regenerated, after use in aquaculture wastewater, were also performed. The regeneration capability of the hydrogels was demonstrated by release of all bound phosphates upon adding 1 N NaOH solution to the saturated gels and reusing the same gels to remove phosphates from new wastewater effluents.

Experiment were conducted to investigate how the phosphate binding capacity of the gels would change after several regeneration cycles. A regeneration cycle consisted of a phosphate removal experiment and a phosphate release experiment (1 N NaOH), followed by rewashing of the gel with distilled water to remove residual sodium phosphate, and sodium chloride (NaCl) formed after the addition of the NaOH.

5. Results

5.1. Experiments in phosphate buffer solution

The total phosphate binding capacity (mg-PO₄ bound per g-dry gel) of the PAA·HCl gel was calculated from the UV experimental data using the following equations:

$$\frac{\text{Amount of PO}_4 \text{ bound (mg)}}{\text{g - gel}} = \frac{(C_0 - C_f)V_s}{m_0}$$

$$\frac{\text{Amount of PO}_4 \text{ bound (mmol)}}{\text{g - gel}} = \frac{(C_0 - C_f)V_s}{m_0 M_w}$$

where C_0 = initial phosphate concentration (mg l⁻¹ PO₄); C_f = final phosphate concentration (mg l⁻¹ PO₄); V_s = volume of sample (l); m_0 = amount of dry xerogel used in the experiment (g); and M_w = molecular weight of phosphate ion (g mol⁻¹). The dependence of the total phosphate binding capacity of the polymeric hydrogels on pH, temperature, and gel chemical composition was determined.

5.1.1. Effect of pH and EPI on phosphate removal

The PAA·HCl hydrogels proved to be very efficient in binding phosphates in experiments where constant pH phosphate buffer solutions, made with distilled deionized water, were used. The effect of the chemical crosslinker and the solution pH on the total phosphate binding capacity of the gels was investigated. By varying the amount of EPI, it was possible to prepare hydrogels with varying crosslink density, and hence networks that were either loosely crosslinked or more densely crosslinked. By experimenting with phosphate buffers of varying pH, the conditions of aquaculture wastewater effluent of varying acidities were simulated. Experimental data showed a pH dependence of the phosphate binding in the PAA·HCl hydrogels. The total phosphate binding capacity of the gels was maximized at pH 7.0. The

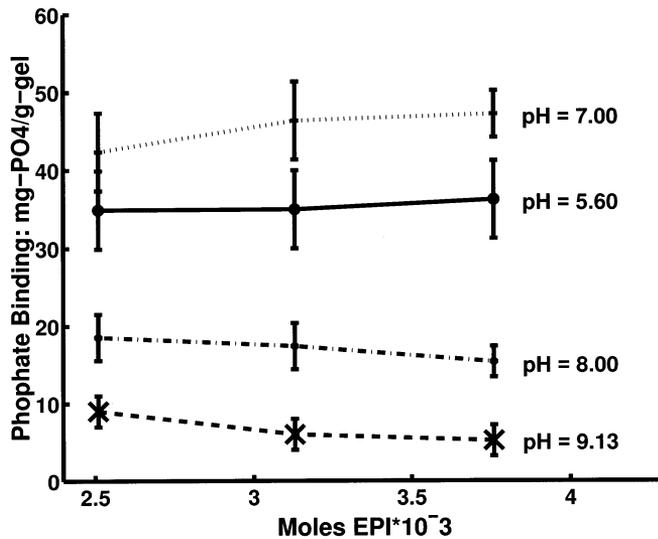


Fig. 3. Effect of EPI and solution pH on PO₄ binding capacity in distilled water. Initial concentration of PAA · HCl 25% b.v., $M_n = 57\,500\text{ g mol}^{-1}$.

average phosphate binding at pH 7.0 was 45 mg PO₄/g-gel. Binding decreased in the acidic pH range (5.6), with an average of 35 mg PO₄/g-gel. The phosphate binding showed a considerable drop in the alkaline pH range. There was nearly an 80% decrease of the total phosphate binding capacity upon varying the solution pH from 7.0 to 9.13. The phosphate binding capacity dropped from an average of 45 mg PO₄/g-gel at pH 7.0 to 7.0 mg PO₄/g-gel at pH 9.13. However, in the pH range of 6.0–8.2, which is the range of most aquaculture wastewaters, the binding capacity of the gels did not decrease significantly with increasing pH. The total phosphate binding capacity was found to remain constant with increasing EPI concentration at a given pH value in both the alkaline and the acidic pH range as shown in Fig. 3. However, a larger crosslinker (EPI) content in the hydrogel structure improved the mechanical integrity of the gels.

5.1.2. Hydrogel removal efficiency

Phosphate binding capacities calculated from the experimental data were used to estimate the amount of PAA · HCl gel required for the complete removal of phosphates initially present in the buffered samples. From the initial phosphate concentration, and the phosphate binding capacity value obtained from the experimental data (in buffer solution) for the particular gel variation, the theoretical amount of gel required for complete removal of phosphates from the buffered sample was calculated, and compared to experiments to determine the phosphate removal efficiency of the PAA · HCl gels. These results showed that the PAA · HCl gels are more than 98% efficient in removing phosphates initially present, as shown in Table 1.

Table 1

Determination of phosphate removal efficiency in pH 7.0 buffer solution^a

	Phosphate binding (mg-PO ₄ /g-gel)
Theoretical (calculated)	40.0
Experimental (measured)	39.2
% Efficiency	98

^a Initial PAA · HCl concentration of: 25% b.v., EPI: 2.51×10^{-3} mol.

5.2. Experiments in aquaculture wastewater

Experimental results indicated that within 3 h the polymeric amine gels were capable of binding more than 99% of the phosphates initially present in the aquaculture wastewater. Phosphate binding values up to 47 mg PO₄/g-gel were obtained depending on the gel chemical composition.

5.2.1. Effect of PAA concentration on phosphate removal

The initial PAA concentration effect on the phosphate binding capacity was studied in the aquaculture wastewaters from tilapia and hybrid striped bass fish tanks. Various initial PAA · HCl concentrations were used in the gel synthesis (all other synthetic steps remained the same). Due to the complex nature of the wastewater, definite conclusions as to the trends of the phosphate binding with gel composition could not be accurately drawn. However, it was observed that within experimental error, the phosphate binding remains constant, as can be seen in Fig.

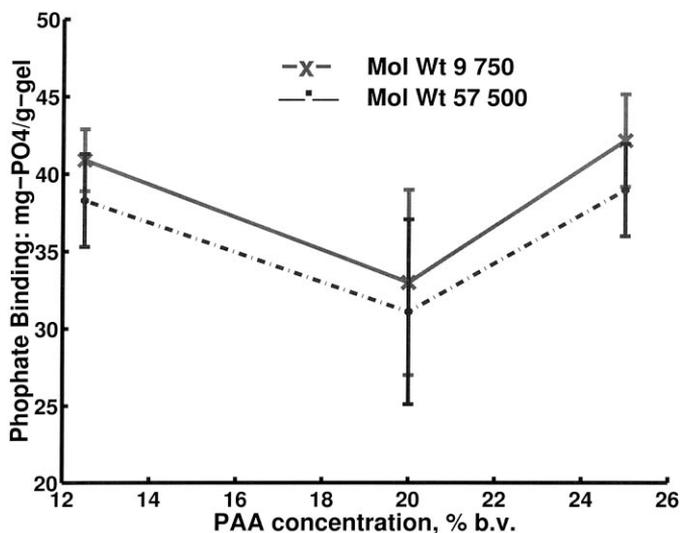


Fig. 4. Effect of PAA · HCl molecular weight and initial concentration on PO₄ binding capacity. Aquaculture wastewater pH 7.67 ± 0.50 ; NaOH: 0.28 g per g PAA · HCl; EPI: 2.51×10^{-3} mol.

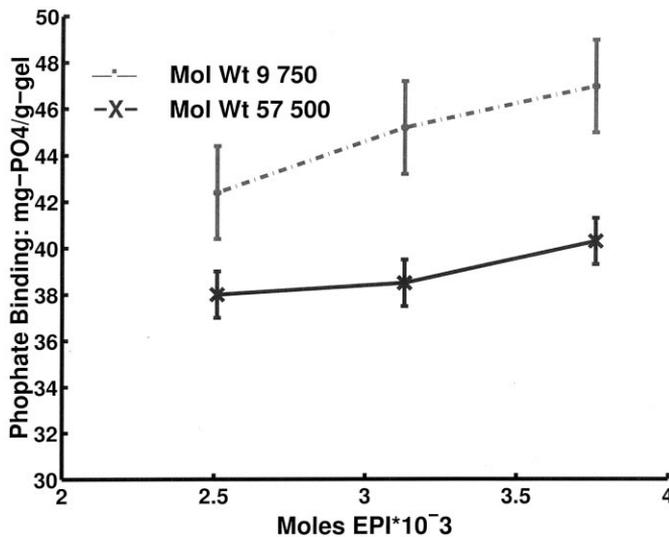


Fig. 5. Effect of EPI on PO₄ binding capacity. Aquaculture wastewater average pH 7.55 ± 0.50. Initial PAA · HCl concentration: 25% b.v.; NaOH: 0.28 g per g PAA · HCl.

4. The gels synthesized with 12.5 and 25% b.v. PAA · HCl had nearly similar binding capacity values. Contrary to our studies in controlled pH phosphate buffer solutions, where the high molecular weight gels showed higher binding capacities over the low molecular weight gels, in aquaculture wastewater the low molecular weight gels displayed improved phosphate binding as compared to the higher molecular weight gels. The initial PAA · HCl concentration was observed to have an effect on the mechanical integrity of the polymeric hydrogels. The 12.5% b.v. PAA · HCl hydrogels would break up into smaller pieces during the binding reaction due to insufficient mechanical strength.

5.2.2. Effect of neutralizer and EPI on phosphate removal

Experiments to determine the effect of crosslink density on the hydrogel phosphate binding capacity in aquaculture wastewater effluent were performed. Gels were synthesised using a 25% b.v., 57 500 and 9750 g mol⁻¹ solution of PAA · HCl, 0.23 g NaOH per g PAA · HCl, and varying amounts of EPI. From the experimental data the phosphate binding capacity was found to increase slightly with the EPI content in the polymeric hydrogels. The phosphate binding of the high molecular weight gels, as shown in Fig. 5, ranged between 38 and 40 mg-PO₄/g-gel upon increasing the number of moles of EPI used in the crosslinking reaction by 50%. The low molecular weight hydrogels showed similar trends as the higher molecular weight gels in the aquaculture wastewater. However, the average phosphate binding capacity of the low molecular weight gels was higher.

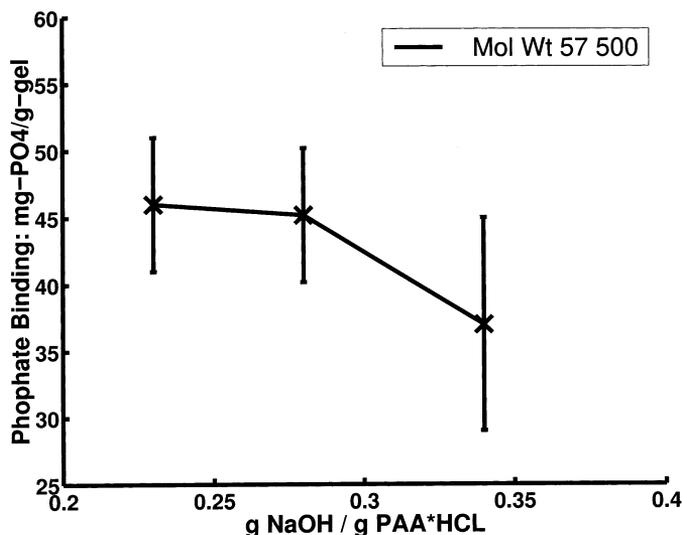


Fig. 6. Effect of NaOH amount on PO₄ binding capacity (mg-PO₄ gel/g-gel). Aquaculture water pH 7.42 ± 0.50 . Initial PAA · HCl concentration of: 25% b.v.; EPI: 2.51×10^{-3} mol.

The effect of the amount of neutralizer (NaOH) on the phosphate binding capacity was investigated in the aquaculture wastewater effluent. High molecular weight hydrogels were prepared with varying amounts of NaOH used in the synthesis, 2.51×10^{-3} mol EPI, and a 25% b.v. PAA · HCl initial concentration. From the UV data it was determined that the total phosphate binding capacity was found to decrease upon increasing the NaOH concentration of the hydrogels in the synthesis as shown in Fig. 6.

5.3. Phosphate regeneration experiments

Experimental results from the regeneration studies performed on several gels showed the ability of the gels to be reused for phosphate removal from wastewater successfully. The binding capacity of the gels investigated was found to increase by as much as 15% after being reused. This was because the addition of NaOH caused the release of PO₄ as well as neutralizing even more HCl groups, thus increasing the number of binding sites available for PO₄ removal.

Experimental data in Fig. 7 showed that the hydrogel regeneration efficiency was retained for at least five cycles. These binding capacity values are not indicative of the actual PO₄ removal ability of the gels since the binding experiments were stopped well before the gels reached their saturation point. The purpose of the experiment was to determine the change in the PO₄ binding capacity and not its maximum value. The increasing trend seen in Fig. 7 after each cycle is due to the addition of more NaOH.

6. Discussion

From studies undertaken in controlled environment (phosphate/buffer solutions), it was possible to determine the pH range where the hydrogels showed efficient phosphate binding characteristics. The polymeric hydrogels showed efficient phosphate binding capacities in the range of pH 5.00–9.00. Larger binding capacities were achieved at acidic pH's where the amine group was in the state. At more alkaline pH's, in excess of pH 8.00, the amine group loses a hydrogen (becomes deprotonated) and exists in the NH_2 form. This causes the decrease in phosphate binding into the polymer matrix. However, the wastewater effluent pH of aquaculture production systems is typically in the range of 6.00–8.20 where the polymeric hydrogels exhibit phosphate binding capacities in the range of 30–45 $\text{mg-PO}_4/\text{g-gel}$. The polymeric hydrogels have the ability to lower the effluent phosphate concentration to less than 0.01 mg l^{-1} .

The NaOH is used to partially neutralize amine groups of the $\text{PAA} \cdot \text{HCl}$, by cleaving off HCl groups, to enable crosslinking. By varying this parameter, the number of neutralized amines per PAA chain available for crosslinking was altered. As the pH of the reaction is increased by neutralizing more hydrochloric acid groups with NaOH, more free amine sites are produced. For example, for gels prepared using low molecular weight $\text{PAA} \cdot \text{HCl}$ the calculated average number of neutralized amines available for crosslinking per $\text{PAA} \cdot \text{HCl}$ chain increased from 55 to 83 upon increasing the amount of NaOH from 0.23 to 0.34 g NaOH per g $\text{PAA} \cdot \text{HCl}$. The increase in the number of free amine sites after the neutralization step, increases the number of crosslinks in the polymeric network structure. By

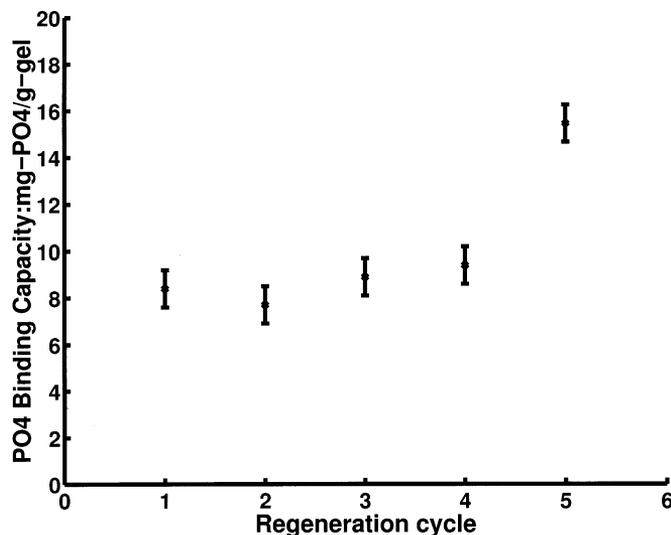


Fig. 7. Hydrogel regeneration in aquaculture wastewater. Initial $\text{PAA} \cdot \text{HCl}$ concentration of: 25% b.v.; EPI: $3.13 \times 10^{-3} \text{ mol}$.

Table 2
Effect of NaOH amount on PO₄ binding capacity (mg PO₄/g-gel)^a

PAA · HCl, M_n (g mol ⁻¹)	Phosphate binding (mg-PO ₄ /g-gel)		
	g NaOH per g PAA·HCl		
	0.23	0.28	0.34
57 500	46	45	37

^a Aquaculture water pH 7.42 ± 0.50 . Initial PAA · HCl concentration of: 25% b.v., EPI: 2.51×10^{-3} mol.

increasing the number of free amine sites per PAA · HCl chain available for crosslinking, the probability of occurrence of neighboring free amine sites on the PAA · HCl chains increases, which in turn may cause the EPI to react once or react with two amine groups on the same chain forming loops instead of crosslinks (Kofinas and Cohen, 1997). This will have an influence on the gel structure and its phosphate binding characteristics, since the gel will have less crosslinks and thus not have the expected mechanical integrity of a fully crosslinked network. Experimental data summarized in Table 2 shows the effect of NaOH on the phosphate removal properties of the gels.

A factor that must be considered when increasing the amount of NaOH during the gel forming reaction is the duration of this reaction. Gels prepared using 0.28 g NaOH per g PAA · HCl reacted for 20 min before attaining the gel point. Gels synthesized with 0.34 g NaOH per g PAA · HCl would typically react for an average of 8–10 min. This significant reduction in reaction time had an effect on the homogeneity of the crosslinked end-product. In contrast to model networks, with constant length of network chains between crosslinks, real networks exhibit a wide distribution of chain lengths between network junction points (Lindemann et al., 1997). A variety of network defects, such as dangling ends, elastically ineffective loops, and crosslink agglomerations, are also known to occur. These defects change the effective crosslinking density and morphology of the networks and thus influence their swelling behavior and elastic properties. Therefore, 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.

The EPI content of the gels was determined to have no effect on the rate of transport of phosphates into the polymer network and therefore did not influence their phosphate binding capacity. 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. However, the crosslinking density of the gels is directly related to their EPI 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, thus improving its mechanical integrity.

7. Conclusions

The aquaculture wastewater originating from recirculating aquacultural production systems had large amounts of particulate and dissolved complex organics, and inorganics. Upon comparing the experimental results for phosphate binding from the buffer solutions and aquaculture wastewater effluents, it is evident that the hydrogels were not fouled by organic and inorganic constituents, or counterions (Cl^- , NO_3^- , and NO_2^-) present in the aquaculture wastewater. The polymeric hydrogels selectively bind phosphates from aquaculture wastewater effluents without being affected by the many soluble and insoluble components present in the hybrid stripped bass and tilapia aquaculture wastewater effluents. Thus the novel crosslinked polymeric hydrogels are appropriate materials for treating aquaculture wastewater effluents, resulting in the reduction of phosphorus concentrations to levels suitable for discharge to natural surface waters.

An economic evaluation was undertaken to estimate the cost of producing bulk quantities of the chemically crosslinked phosphate binding polymeric hydrogels. Specialty polymer supplier gave a production cost for the PAA · HCl of approximately US\$400 per 10 kg. Costs of US\$8.90 per kg and US\$18.00 per kg for the NaOH and EPI respectively, were used to determine the production cost of the polymeric hydrogel. It was estimated that 1 kg of hydrogel costs US\$10.60 to manufacture. These costs, however, are based on a price quote for the PAA · HCl given by a specialty manufacturer. A specialty manufacturer will supply polymer of high purity which is not necessarily required for the synthesis of the polymeric hydrogels used in this application, thus further reducing the costs of manufacture by using reagents of lower purity.

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