NJC

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. E. Villanueva, A. M. D. R. Diez, J. A. González, J. M. Lazaro Martinez, V. Campo Dall'Orto and G. J. Copello, *New J. Chem.*, 2017, DOI: 10.1039/C6NJ04031D.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Journal Name

ARTICLE

Phosphorus adsorption by a modified polyampholyte-diatomaceous earth material containing imidazole and carboxylic acid moieties: batch and dynamic studies. †

María Emilia Villanueva^{a,b}, Ana María del Rosario Diez^a, Joaquín Antonio González^{a,b}, Juan Manuel Lázaro-Martínez^{c,d}, Viviana Campo Dall'Orto^{*a,d} and Guillermo Javier Copello^{*a,b}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The aim of this study was to investigate phosphorus removal in water by using a polyampholyte obtained by the reaction of methacrylic acid, ethylene glycol diglycidyl ether and imidazole by a one step synthesis, mixed with diatomaceous earth. The material was characterized before and after phosphorus exposure by FT-IR, Raman and Solid State ³¹P-NMR and ¹³C-NMR spectroscopy concluding that the charged imidazole units were involved in the interaction between the phosphorus and the polyampholyte and that only H₂PO₄⁻ specie was adsorbed. The point of zero charge value was 5.09. Concomitantly, the optimal pH for P adsorption was 5.0. As pH raised, the polymer turned more negative, and the phosphate repulsion diminished the adsorption. In the batch experiments, the adsorption isotherms at pH 5.0 and 7.0 were studied. The effect of different flow rates, P influent concentration and the interference of nitrate and sulfate in the breakthrough curves were performed. The shorter breakthrough time occurred at a higher flow rate. The *q₀* not only increased from lower to higher influent levels but also showed a decrease with the presence of S and N as interferences demonstrating that there was a competition for the adsorption sites between those anions and the phosphate.

Introduction

Eutrophication is the ecosystem response to the nutrient enrichment. It involves excessive growth of aquatic plants and a reduction in the dissolved oxygen level which may cause death to aquatic animals.¹ Climate change is intensifying the symptoms of eutrophication in freshwaters and it is believed that eutrophication can concomitantly promote climate change.² Phosphorus is frequently the limiting nutrient for summer phytoplankton growth^{3–6} and sewage effluent is a major source of phosphorus in many lowland rivers. It is well known that the phosphorus concentration in receiving water above 0.02 mg/L can cause eutrophication.⁷ The reduction of the phosphorus concentration may reverse the

ecological effects of eutrophication rapidly.^{8–10} For this reason, treatment of waste water to decrease phosphate concentration and reach the discharge limit is imperative. Currently, several process for phosphorus removal can be found in literature such as chemical methods, including co-precipitation with iron, aluminum or lime, as well as biological methods involving different microorganisms like algae or bioretention.^{11–14} However, these techniques are either expensive or very difficult to implement. For example, chemical precipitation requires large amounts of chemical reagents when treating large volumes of contaminated water. On this subject, the application of adsorption or ion exchange on solids is advantageous.^{15,16} Recently, water remediation of charged pollutants, like metal ions, herbicides, colorants and persistent pharmaceuticals have been performed with different polyampholytes and polycationic polymers either by themselves in batch or attached to silica or clay in a column.^{17–21}

The aim of this study was to investigate P removal in water by using a polyampholyte obtained by the reaction of methacrylic acid (MAA), ethylene glycol diglycidyl ether (EGDE) and imidazole (IM) by a one step synthesis, mixed with diatomaceous earth (DE). In order to characterize the material, FT-IR, Raman and Solid State ³¹P-NMR and ¹³C-NMR spectroscopy were performed and the point of zero charge was investigated by executing a Drift test. In the batch experiments, the adsorption at different pH values ranging from 4.0

^a Universidad de Buenos Aires (UBA), Facultad de Farmacia y Bioquímica, Departamento de Química Analítica y Fisicoquímica, Junín 956, C1113AAD Buenos Aires, Argentina;
^b Instituto de Química y Metabolismo del Fármaco, Facultad de Farmacia y Bioquímica, (IQUIMEFA-UBA-CONICET);
^c Universidad de Buenos Aires (UBA), Facultad de Farmacia y Bioquímica, Departamento de Química Orgánica, Junín 956, C1113AAD Buenos Aires, Argentina;
^d IQUIFIB-CONICET. Junín, 956 (1113) CABA, Argentina

†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

ARTICLE

Journal Name

to 8.0 and the adsorption isotherms at pH 5.0 and 7.0 were studied. The polymer and the DE were packed in a column and the effect of different flow rates, P influent concentration and the interference of N and S in the breakthrough curves were performed. The role of DE was to minimize the column backpressure generated from the swelling of this polyampholyte.

Experimental

Reagents and Material

Diatomaceous earth (DE), Celite® 545 was obtained from Sintogran (Buenos Aires, Argentina), ethylene glycol diglycidyl ether (EGDE; 50wt% in ethylene glycol dimethyl ether; MW: 174.197; 12.1% oxirane oxygen; SW: 1.1891) was purchased from TCI America. Imidazole (IM; 99 wt%; MW: 68.077) and methacrylic acid (MAA; 99 wt%; MW: 86.09; SW: 1.015) were purchased from Sigma-Aldrich. Benzoyl peroxide was obtained from Fluka. Acetonitrile from Baxter was of HPLC grade. **Synthesis of Poly(EGDE-MAA-IM) and its mixture with DE** The polyampholyte was synthesized in agreement with previously published work.^{15,22} After its synthesis the polyampholyte was mixed with DE (80 % polymer: 20% DE) in order to obtain an even flow in the column.

Characterization

FT-IR and Raman spectroscopy

ATR-FTIR (diamond attenuated total reflectance) of DE, Poly(EGDE-MAA-IM), Poly(EGDE-MAA-IM) – DE mixture before and after the exposure to a 0.2 M phosphate solution at pH 5 and 7 and Poly(EGDE-MAA-IM) – DE mixture after the storage at 25, 37 and 45 °C for 48 h were recorded using a Nicolet iS50 Advanced Spectrometer (Thermo Scientific). ATR-FTIR spectra were recorded with 32 scans and a resolution of 1 cm⁻¹. FT-Raman spectra of Poly(EGDE-MAA-IM), DE and Poly(EGDE-MAA-IM) – DE mixture was acquired with an excitation laser beam of 1064 nm, 0.5 W laser power, resolution of 4 cm⁻¹, 500 scans. All samples were previously dried for 24 h at 60 °C to avoid water related bands interference.

Drift method

The point of zero charge (PZC values) of the polymer mixed with the diatomaceous earth was determined by the pH drift method.²³ A solution of 0.01 M NaCl was boiled to remove dissolved CO₂ and then cooled to room temperature. The pH was adjusted to a value between 1 and 10 using 0.1 M HCl or 0.1 M NaOH. Previously weighted polyampholyte - DE mixture (75.0 mg) was added into 25 mL of the pH - adjusted solution in a conical plastic vessel and equilibrated for 48 h. The final pH was measured and plotted against the initial pH. The pH at which the curves intersect the initial pH and final pH line is considered as PZC. All measurements were carried out in triplicate.

Solid-State NMR Studies

High-resolution ¹³C solid-state spectra for the polymers were recorded using the ramp ¹H-¹³C CP-MAS sequence (cross-polarization and magic angle spinning) with proton decoupling

during acquisition. All the solid-state NMR experiments were performed at room temperature in a Bruker Avance II-300 spectrometer equipped with a 4-mm MAS probe. The operating frequency for protons, carbons and phosphorus was 300.13, 75.46 and 121.49 MHz, respectively. Glycine was used as an external reference for the ¹³C spectra and to set the Hartmann-Hahn matching condition in the cross-polarization experiments in ¹³C spectra. The recycling time was 4 s. The contact time during CP was 1.5 ms for the different materials. The two-pulse phase modulation (TPPM) was used for heteronuclear decoupling during acquisition with a proton field H_{1H} satisfying $\omega_{1H}/2\pi = \gamma_H H_{1H} = 62$ kHz. Single-pulse ³¹P experiments were performed in the different P-adsorbed materials and 85% H₃PO₄ was used as an external reference for the ³¹P spectra. The spinning rate for all the samples was 10 kHz.

Adsorption studies

The adsorption experiments were performed by a batch method with constant stirring (120 rpm) at 20 °C. The effect of the medium pH and adsorption isotherms were determined by sorbate decay in the solution supernatant. In the case of the isotherms analysis a weighted mass (5.0 mg precisely weighted) of the polyampholyte – DE mixture was added to an aqueous solution (5.00 mL) of phosphorus, ranging from 100 to 5000 mg/L at two different pH values: 5 and 7. These solutions were prepared from 6194 mg/L phosphate solutions at those pH values by weighting the corresponding amounts of Na₂HPO₄ and NaH₂PO₄. The P was quantified by Capillar Electrophoresis (Agilent technologies, capillary column 75 µm x 20cm, BGE: CrO₄K₂ (7.15 mM) TTAB (1.42 mM) pH= 10.0, Voltage -15 kV, injection 5 s, 10 mbar).

Breakthrough curves

The column adsorption tests were conducted in glass mini-columns of 10 cm height and 0.8 cm inner diameter. First, 0.300 g of the polyampholyte – DE mixture were stirred thoroughly with distilled water to enable the swelling and removing air bubbles. In the next step, it was packed into a column using the “slurry method”. The column was first filled with glass beads (~1 cm) at the bottom to produce an even flow. It was then packed with the wet mix of DE and polymer. The dynamic behavior of the polyampholyte - DE column was studied by analyzing the breakthrough curves obtained by varying flow rate, P influent concentration and sulfate and nitrate coexistence as interferents. Effluent samples were collected at definite intervals of time in 1 mL plastic tubes for determination of the phosphorus concentration. The phosphorus concentration determination was performed by the molybdenum method.²⁴ Desorption and regeneration were performed with 0.1 M NaOH.

Statistic

All quantitative results were obtained from triplicate samples. Data were expressed as means ± SD. Statistical analysis was carried out using a One-way ANOVA test and a Bonferroni post test. A value of $p < 0.05$ was considered to be statistically significant. The breakthrough curves were analyzed by non-linear regression.

Results and discussions

Synthesis and characterization of the polyampholyte

Scheme 1. Chemical structure of poly(EGDE-MAA-IM)

The material was synthesized via reaction of the selected monomers in the presence of benzoyl peroxide. Scheme 1 shows the representative chemical structure for Poly(EGDE-MAA-IM). The PZC of this synthetic batch mixed with the DE was 5.09, determined by the drift method (ESI 1 †). Figure 1 and ESI 2 † showed the results obtained after the FT-IR characterization. After the physical mixture of DE (20%) with polyampholyte (80%), the relative intensity of some bands of the polymer changed. The band at 1715 cm^{-1} corresponding to C=O symmetric stretching of carboxylic groups was more intense, and a decrease of the band at 1638 cm^{-1} (C=N stretching) was observed, indicating interaction with the functional groups of DE.²⁵ The addition of phosphate clearly reverted this interaction, and the mentioned bands from the polyampholyte recovered the former relative intensity. However, the relative intensity of these two bands was different in the mixture previously exposed at pH 5.0 than the one exposed at pH 7.0. At pH 7.0 the IM groups were partially protonated (IM^+), the interaction with the DE was less strong, and an increase in the intensity of the 1638 cm^{-1} band was observed. The band at 1370 cm^{-1} (presumably from νCH)²⁵ was split in two bands (1343 and 1400 cm^{-1}) in the presence of phosphate. The bands corresponding to H_2PO_4^- (1159 and 1077 cm^{-1})²⁶ are hidden by the signals of the polymer and the diatomaceous earth at that wavenumber. The bands at 990 cm^{-1} of HPO_4^{2-} and 940 cm^{-1} of H_2PO_4^- were not observed.

ESI 3 † showed the results obtained after the Raman characterization of the DE, the polyampholyte and the polyampholyte - DE mixture. In ESI 4 † a description of the band assignments can be found. In the mixture of the two components, the bands corresponding to the diatomaceous earth and the polyampholyte were present. ESI 5 † showed the FT-IR spectra after the storage at 25, 37 and 45 °C. By comparing those spectra it could be seen that no appreciable changes were observed in the different samples. However, the band that corresponded to the presence of O-H vibrations at 3305 cm^{-1} diminished its intensity as long as temperature increased. This was probably due to the amount of water present in the sample which was lower when the sample was treated at higher temperatures.

In order to analyze the adsorption process of phosphorus into the polyampholyte material, ^{31}P -MAS and ^{13}C CP-MAS NMR spectra were performed and the results are shown in Figure 2A and 2B. Both single-pulse ^{31}P -MAS spectra recorded for the samples at pH

values of 5.0 and 7.0 showed a unique and narrow signal (linewidth of 60 Hz / 0.5 ppm) with a chemical shift of 0.6 ppm associated to

Figure 1. FT-IR spectra of A: DE, B: polyampholyte, C: polyampholyte - DE mixture, D: polyampholyte - DE mixture after exposure to a P solution at pH 5 and E: polyampholyte - DE mixture after exposure to a P solution at pH 7

the presence of H_2PO_4^- species bound to the positive domains of the polymer matrix.²⁷ These results indicate that the distribution of phosphorus entities was homogeneous at the different pH conditions.

Then, the adsorption process was analyzed through the ^{13}C CP-MAS spectra of the modified - polyampholyte material. The unequivocal assignment of the different resonance signals was previously reported.²⁸ The incubation process was performed at different pH values. Thus, the polymeric material was placed at alkaline and acidic media as a control experiment with the aim to observe the changes produced due to the adsorption process and not related to the modification in the ionization state of the matrix. When the native polymeric material (Figure 2C) was treated with a 1 N HCl solution, a moderate increase in the carbon resonance signal coming from the hydrocarbon chain of the polymerized MAA segments at 56.3, 45.6 and 17.4 ppm was observed (Figure 2D). However, the treatment of the native polymer with 1 N NaOH solution only produced a slightly increase in the EGDE segments at 70.1 ppm (Figure 2E). On the other hand, the uptake of phosphorus produced complex changes in the relative intensity of all the resonance signals at both pH values (Figure 2F-G). The sample at a pH value of 5.0 clearly produced an increment of the signal associated to the IM and EGDE segment, together with the increment of the intensity of the methylene carbon bound to the nitrogen of the IM ring at 52.9 ppm. Meanwhile, in the adsorption at pH 7.0, an increment of all the signals from the polymerized MAA segments was observed. In general, the ^{13}C -NMR signal of ordered structures produce an increment of the signal because in these

ARTICLE

regions the cross polarization transfer from ^1H to ^{13}C is enhanced in comparison with disordered regions in polymer materials in the

Figure 2. Single-pulse ^{31}P NMR spectra for adsorbed phosphorus in polymer materials at pH value of 7.0 (A) or 5.0 (B). ^{13}C CP-MAS spectra for native polymer (C), polymer treated with 1N HCl solution (D) or 1 N NaOH solution (E) and for the adsorbed phosphorous in polymer materials at pH value of 5.0 (F) or 7.0 (G). The assignment corresponds to those in Scheme 1.

solid-state.²⁹ In that sense, the increment in the phosphorus content promoted a higher degree of order related to the IM and EGDE moieties at a pH 5.0 associated to the adsorption of phosphorus to the N_1, N_3 -disubstituted imidazole (IM^+) and protonated imidazole units (IMH^+). In contrast, at a pH 7.0 an increment of the NMR signals was observed for the MAA segments. The sorption process of phosphorus produced a reorganization of the entire polyampholyte matrix being at pH 7.0 more important the organization of the MAA segments while at pH 5.0 the organization of the EGDE-IM segments is more significant due to the uptake of P. In addition, an increment in the uptake of phosphorus was observed for the material at a pH value of 5.0, being possible to infer that the sorption process of P ordered the IM-EGDE segment with the concomitant disorder of the MAA groups. However, at pH 7.0 the carboxylate groups of the MAA segments are interacting particularly with the positive imidazole (IM^+ and IMH^+) segment bound to EGDE moieties. In this sense, the H_2PO_4^- species exchange with RCO_2^- groups (MAA segments) for the IM^+ or IMH^+ being more significant at pH 5.0 than at pH 7.0, which may explain the changes observed in the ^{13}C CP-MAS spectra. Besides, at pH 5 there was a prevalence of $-\text{CO}_2\text{H}$ over $-\text{CO}_2^-$ and at pH 7 only $-\text{CO}_2^-$ were present. Thus, the higher order of RCOO^- (MAA segments) at pH 7 could be driven by a more intense repulsion than at pH 5.

Effect of pH in batch adsorption

The effect of P adsorption at pH values 5.0, 6.0, 7.0 and 8.0 was evaluated in a batch system. In order to evidence differences in the adsorption capacities at different pHs, the Polyampholyte - DE mixture was incubated with a P concentration below the saturation point. The adsorption capacity was significantly higher at pH 5 (ESI 6 †). Since the polyampholyte PZC is 5.09, at pH 5 it is evenly charged with positive and negative groups. While the pH raised, the polymer turned more negative, and the phosphate repulsion diminished the adsorption capacity of this material.

Equilibrium studies

In this study, the pH had a remarkable effect on the performance of the polymeric material as sorbent, due to the influence of the

Figure 3. Adsorption isotherms at pH 5 and 7. Only the best fitted models are represented.

ionization degree of both involved compounds. For this reason, the ion uptake had to be evaluated under carefully controlled conditions. Two pH values, 5.0 and 7.0, were selected, taking into account the pH of potential samples and the conditions that could maximize the interaction between ionic species.

The mechanism of phosphate uptake was explored analyzing the results of the uptake isotherm for the polyampholyte at 20 °C. Four adsorption isotherm models (Langmuir, Freundlich, Sips and Redlich–Peterson (R-P)) were used to fit the experimental binding data by non-linear regression (Table 1). The mathematical models are presented in ESI †.

At pH 5.0 the best fit of experimental data was obtained with the Sips, Langmuir and R-P isotherms (Figure 3), according to the evidence ratio based on the Akaike criterion.³⁰ The Freundlich model had no statistical support due to its significantly larger residual sum of squares. In this experimental case at pH 5.0, the assumption of a monolayer adsorption on a surface with finite number of binding sites had statistical support. A saturation value was reached, beyond which no further uptake was observed. Nevertheless, some features of Freundlich model (expressed in Sips and R-P expressions) could contribute to describe the interaction. In this particular polymeric material tested as sorbent, we must consider some heterogeneity in the nature of binding sites. At pH 5.0 the predominant ionic species is H_2PO_4^- , which should interact with positively charged sites from the polymer: monosubstituted and protonated N-heterocycle units (IMH^+), and disubstituted N-heterocycle units (IM^+). In addition to that, the PZC of this polyampholyte was equal to 5.09, indicating that these positive sites were counter - balanced by a fraction of carboxylic groups ionized at this pH value ($-\text{COO}^-$). These anionic neighbors could be either randomly distributed onto the network, or forming clusters

(small chains of $-(\text{MAA})_n-$) contributing to affect the binding energy of H_2PO_4^- to the hydrogel. The equilibrium results from studies at pH 7.0 exhibited a remarkable difference with the results at pH 5.0,

exposing positive sites otherwise involved in intra-chain and/or inter-chain binding events. These formerly hidden IM^+ (and IMH^+) were now available to ion exchange with the external medium, being responsible for $212 \pm 41 \mu\text{g}$ of phosphate bound per mg of

Model	Parameter	pH 5		pH 7	
		AICc	ER	AICc	ER
Langmuir	$q_m(\mu\text{g}/\text{mg})$	120.3 ± 6.2		335 ± 37	
	$K_{sp}(\text{mL}/\mu\text{g})$	$(9.2 \pm 2.2) \times 10^{-3}$		$(6.6 \pm 1.4) \times 10^{-4}$	
	k_F	17.0 ± 6.0		1.96 ± 0.66	
Freundlich	n	0.23 ± 0.05		0.598 ± 0.045	
	$K_{RP}(\mu\text{g}/\text{mg})$	1.11 ± 0.38		0.222 ± 0.088	
	$\alpha_{RP}(\text{mL}/\mu\text{g})^{\text{aRP}}$	$(9.20 \pm 9.37) \times 10^{-3}$		$6.62 \times 10^{-4} \pm 3.46 \times 10^{-3}$	
R-P	n_{RP}	1.000 ± 0.099		1.00 ± 0.59	
	$Q_{ms}(\mu\text{g}/\text{mg})$	109.6 ± 5.2		$(3.5 \pm 1.3) \times 10^2$	
	$K_S(\text{L}/\mu\text{g})$	$(1.17 \pm 0.203) \times 10^{-2}$		$(6.1 \pm 4.9) \times 10^{-4}$	
Sips	n_s	1.65 ± 0.43		0.97 ± 0.24	

Table 1. Isotherm models parameters

polymer reached experimentally.

in terms of maximal uptake capacity and affinity. At neutral pH, all the models described the uptake equilibrium, with both Sips and R-P closely approaching to Langmuir isotherm. The visual inspection of the results in Figure 3 indicated that the saturation of the material at pH 7.0 was not reached experimentally. In addition, the q_{max} at pH 7.0 estimated from Langmuir expression was 2.79 times higher than q_{max} at pH 5.0. On the other hand, the affinity between the interacting species resulted higher at pH 5.0. This different behavior at neutral pH is probably related to the ionization degree of the interacting entities. Regarding phosphate, the two predominant ionized species (instead of one) were H_2PO_4^- and HPO_4^{2-} , capable of electrostatic binding to positive sites onto the network. However, ss-NMR experiments showed that only H_2PO_4^- was adsorbed. The increase in negative charge on the inorganic ion should enhance its interaction with the positive chains but, at the same time, the net charge of the polyampholyte at pH 7.0 was negative (2 units beyond the PZC). The carboxylic neighbors from the MAA units were now completely ionized, interacting either with the positive sites (IMH^+ and IM^+) or free counterions (Na^+). Besides, the protonation degree of monosubstituted IM should be close to 0.5, reducing the number of available binding sites for phosphate. From the sum of all the mentioned effects, the electrostatic repulsion between $-\text{COO}^-$ and H_2PO_4^- seemed to determine the resulting lower affinity between oppositely charged species at pH 7.0.

Regarding the uptake capacity, the visual inspection of Figure 3 indicated a lack of dependence on pH value at the lowest phosphate concentration tested. When C_e was between 70 and 500 $\mu\text{g mL}^{-1}$, the uptake was higher at pH 5.0, which was consistent with a higher number of available positive sites from IMH^+ units in acid medium. Then, the saturation situation was sharply reached at pH 5.0, whereas significantly higher ion uptake values could be observed for higher phosphate concentration at neutral pH. Here, the electrostatic repulsion established between $-\text{COO}^-$ and uptaked HPO_4^{2-} would account for an additional network expansion,

Effect of column design parameters

Effect of flow rate.

The effect of different flow rates (0.5, 1.0 and 1.5 mL/min) on phosphorus adsorption by the polyampholyte - DE mixture was analyzed at a constant bed height (1 cm), with an initial phosphorus concentration of 5.0 mg/L. The breakthrough curves for the column were determined by plotting the C_t/C_o (C_t and C_o are the phosphorus concentration of effluent and influent, respectively) against the time and depicted in Figure 4A. As it was illustrated, the shorter breakthrough time occurred at higher flow rate. This can be explained by the fact that a larger volume of water elapsed through the bed at higher flow rate. As a consequence, more phosphate ions contacted the binding sites of the polymer, making them get saturated more quickly. Similarly, higher adsorption capacity was attained at lower flow rate. It is possible that the lower flow rate resulted in a higher residence time of the phosphorus ions in the column. Since phosphate ions had longer contact with poly(EGDE-MAA-IM), equilibrium can be reached before phosphate ions moved out of the column. These findings agree with the previous studies.³¹⁻³³ interestingly, neither the q_0 nor the k_{th} varied significantly with flow rate.

Effect of influent phosphorus concentration.

It is reported that influent phosphorus concentration can also affect the breakthrough curve. Figure 4B show the breakthrough curves for varying feed phosphorus concentrations (0.75, 5.0 and 10.0 mg/L), at a bed height of 1 cm and flow rate of 1 mL/min. The breakthrough times varied in the different situations. As expected the exhaustion time was higher when the initial concentration was

ARTICLE

Journal Name

the lowest influent concentration. In this case, the highest the influent phosphorus concentration was, the fastest the breakthrough and exhaustion took place. Higher retention rate and thus, earlier saturation might result from greater concentration gradient and smaller mass transfer resistance at higher phosphate concentration. Surprisingly, the exhaustion time did not varied

Figure 4. Breakthrough curves in different conditions: A: different flow rate B: different influent phosphorus concentrations C: presence of interferents.

significantly when the initial concentration was 10 mg/L compared to the situation when the initial concentration was 5 mg/L.

Nevertheless, the breakthrough curve was steeper and the q_0 increased from lower to higher influent levels. This result may have been due to the polyampholyte chain expansion with high sorbate concentrations. The polyampholyte charges interacts with themselves in the absence of other electrolytes in order to achieve electronic neutrality. Upon adsorption of groups present in the polyampholyte.^{15,22,34} When the phosphate concentration was

Table 2. Thomas model parameters.

Flow rate (mL/min)	Influen P concentration ($\mu\text{g}/\text{ml}$)	Interferent	q_0 ($\mu\text{g}/\text{g}$)	K_{th} (mL/min μg)	AlCc
1.0	4.7	---	234 ± 12		-32.09
0.5	4.5	---	195 ± 3		-54.50
1.5	4.9	---	200 ± 12		-32.01
1.0	4.3	NO_3^-	176 ± 12		-11.89
1.0	4.5	SO_4^{2-}	191 ± 11		-17.79
1.0	0.72	---	56 ± 1		-45.44
1.0	10.0	---	470 ± 18		-40.64

higher, the internal repulsion was higher and internal sites of the polymer were exposed, allowing their interaction and resulting in higher capacity.

Effect of interferents

The effect of coexisting anions was studied by adding S or N at the same level as P (0.16 mM). The effect of interferents was shown in Figure 4C. As could be seen, sulfate and nitrate anions interfered very little in the phosphate uptake. These results agree with previous studies.^{35,36} Surprisingly, the interference presence delayed the breakthrough time. This result may be in concordance with those related to phosphorus influent concentration. The differences in the influent ionic strength induced a conformational change in the polyampholyte. As it had been described before, the polyampholyte charges interacted with phosphate by the positive

charges, the interaction would become in chain repulsion due to the phosphate anion and the carboxylic themselves in the absence of other electrolytes in order to achieve electronic neutralization. Upon adsorption of phosphate or other anions by the positive charges the interaction become in chain repulsion due to the phosphate anion and the carboxylic groups present in the polyampholyte. On the other hand, the q_0 decrease with the presence of both interferents demonstrating that there is a competition for the adsorption sites between those anions and the phosphate.

Conclusions

The efficiency of the polyampholyte Poly(EGDE-MAA-IM) for phosphorus removal from water was studied in batch and dynamic conditions. The ss-NMR and FT-IR spectroscopy and the batch adsorption experiments at different pH values showed that the electrostatic interaction between the anion and the positively charged imidazole units was the responsible for P adsorption. Also, ss-NMR results showed that the H_2PO_4^- was the main specie involved in the interaction. The P adsorption performance was influenced by pH, concentration, flow rate and the presence of interferents. Langmuir, R-P and Sips models fitted well experimental data in batch experiments. The reuse of the material was demonstrated in the dynamic studies. Thomas model was analyzed confirming the differences in capacity and affinity in the different situations.

Acknowledgements

M.E.V. is grateful for her posdoctoral fellowship granted by Consejo Nacional de Investigaciones Científicas y Técnicas. J.A.G. is grateful for his doctoral fellowship granted by Consejo Nacional de Investigaciones Científicas y Técnicas. This work was supported with grants from Universidad de Buenos Aires (UBACYT 20020130100780BA and 13-16/021), Consejo Nacional de Investigaciones Científicas y Técnicas (PIP 11220120100657CO and 10-12/PIP 076) and Agencia Nacional de Promoción Científica y Tecnológica (PICT 2012 071(UBACYT 20020130100780BA and 13-16/021), Consejo Nacional de Investigaciones Científicas y Técnicas (PIP 11220120100657CO and 10-12/PIP 076) and Agencia Nacional de Promoción Científica y Tecnológica (PICT 2012 0716).

Notes and references

- H. W. Paerl, H. Xu, N. S. Hall, K. L. Rossignol, A. R. Joyner, G. Zhu and B. Qin, *J. Freshw. Ecol.*, 2015, **30**, 5–24.
- B. Moss, S. Kosten, M. Meerhof, R. Battarbee, E. Jeppesen, N. Mazzeo, K. Havens, G. Lacerot, Z. Liu and L. De Meester, *Inland Waters*, 2011, **1**, 101–105.
- R. Q. Alam, B. C. Benson, J. M. Visser and D. D. Gang, *Ecol. Inform.*, 2016, **32**, 79–90.
- M. C. L. Abbate, J. C. Molinero, V. A. Guinder, M. S. Dutto, M. S. B. de Cao, L. A. R. Etcheverry, R. E. Pettigrosso, M. C. Carcedo and M. S. Hoffmeyer, *Mar. Pollut. Bull.*, 2015, **95**, 305–314.
- K. Sukačová, M. Trtílek and T. Rataj, *Water Res.*, 2015, **71**, 55–63.

- A. Tofik, A. M. Tadesse, K. Tesfahun and G. Girma, *J. Environ. Chem. Eng.*, 2016, **4**, 2458–2468.
- T. Nguyen, H. Ngo, W. Guo, T. Pham, F. Li, T. Nguyen and X. Bui, *Sci. Total Environ.*, 2015, **523**, 40–49.
- D. Copetti, K. Finsterle, L. Marziali, F. Stefani, G. Tartari, G. Douglas, K. Reitzel, B. M. Spears, I. J. Winfield and G. Crosa, *Water Res.*, 2016, **97**, 162–174.
- C. Neal, H. P. Jarvie, S. M. Howarth, P. G. Whitehead, R. J. Williams, M. Neal, M. Harrow and H. Wickham, *Sci. Total Environ.*, 2000, **251**, 477–495.
- H. Yin, M. Han and W. Tang, *Chem. Eng. J.*, 2016, **285**, 671–678.
- R. P. Kralchevska, R. Prucek, J. Kolařík, J. Tuček, L. Machala, J. Filip, V. K. Sharma and R. Zbořil, *Water Res.*, 2016, **103**, 83–91.
- J. Li and A. P. Davis, *Water Res.*, 2016, **90**, 141–155.
- V. Singh, A. Tiwari and M. Das, *Fuel*, 2016, **173**, 90–97.
- R. Whitton, A. Le Mével, M. Pidou, F. Ometto, R. Villa and B. Jefferson, *Water Res.*, 2016, **91**, 371–378.
- G. J. Copello, L. E. Diaz and V. C. Dall'Orto, *J. Hazard. Mater.*, 2012, **217**, 374–381.
- M. L. P. Ramos, J. A. González, S. G. Albornoz, C. J. Pérez, M. E. Villanueva, S. A. Giorgieri and G. J. Copello, *Chem. Eng. J.*, 2016, **285**, 581–587.
- M. Arkas and D. Tsiourvas, *J. Hazard. Mater.*, 2009, **170**, 35–42.
- H. Kohay, A. Izbicki and Y. G. Mishael, *Environ. Sci. Technol.*, 2015, **49**, 9280–9288.
- L. V. Lombardo Lupano, J. M. Lázaro-Martínez, N. M. Vizioli, D. I. Torres and V. Campo Dall'Orto, *Macromol. Mater. Eng.*, 2016, **301**, 167–181.
- D. Zadaka, S. Nir, A. Radian and Y. G. Mishael, *Water Res.*, 2009, **43**, 677–683.
- J. M. L. Martínez, M. F. L. Denis, V. C. Dall'Orto and G. Y. Buldain, *Eur. Polym. J.*, 2008, **44**, 392–407.
- Y. Yang, Y. Chun, G. Sheng and M. Huang, *Langmuir*, 2004, **20**, 6736–6741.
- B. B. Johnson, A. V. Ivanov, O. N. Antzutkin and W. Forsling, *Langmuir*, 2002, **18**, 1104–1111.
- J. M. L. Martínez, A. K. Chattah, R. M. T. Sánchez, G. Y. Buldain and V. C. Dall'Orto, *Polymer*, 2012, **53**, 1288–1297.
- J. M. Lázaro-Martínez, E. Rodríguez-Castellón, D. Vega, G. A. Monti and A. K. Chattah, *Macromolecules*, 2015, **48**, 1115–1125.
- F. H. A. Rodrigues, C. Spagnol, A. G. B. Pereira, A. F. Martins, A. R. Fajardo, A. F. Rubira and E. C. Muniz, *J. Appl. Polym. Sci.*, 2014, **131**, n/a–n/a.
- T. Textor, M. M. G. Fouda and B. Mahltig, *Appl. Surf. Sci.*, 2010, **256**, 2337–2342.
- Standard SNV 195920-1992, .
- W. D. Schindler, P. J. Hauser and E. Textile Institute (Manchester, *Chemical Finishing of Textiles*, CRC, 2004.
- I. Cerkez, H. B. Kocer, S. D. Worley, R. M. Broughton and T. S. Huang, *J. Appl. Polym. Sci.*, 2012, **124**, 4230–4238.
- Y.-S. Ho and G. McKay, *Water Res.*, 2000, **34**, 735–742.
- S. Suen, *J. Chem. Technol. Biotechnol.*, 1996, **65**, 249–257.
- D. Kumar, L. K. Pandey and J. Gaur, *Colloids Surf. B Biointerfaces*, 2010, **81**, 476–485.
- Z. Xu, J. Cai and B. Pan, *J. Zhejiang Univ. Sci. A*, 2013, **14**, 155–176.