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

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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 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− species 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 qe not only increased from lower to higher influent levels but also showed a decrease with the presence of S and N as interferents 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. Climate change is intensifying the symptoms of eutrophication in freshwaters and it is believed that eutrophication can concomitantly promote climate change.

Phosphorus is the frequently the limiting nutrient for summer phytoplankton growth 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. The reduction of the phosphorus concentration may reverse the ecological effects of eutrophication rapidly. For this reason, treatment of waste water to decrease phosphate concentration and reach the discharge limit is imperative. Currently, several processes 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. 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. Recently, water remediation of charged pollutants, like metals, 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.

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 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 to 10.0 was studied.
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. Benzoyl peroxide was obtained from Fluka. ATR-FTIR (diamond attenuated total reflectance) of DE, Poly(EGDE–MAA–IM) – DE mixture after the storage at 25, 37 and 45 ºC for 48 h were recorded using a Nicolet i550 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 after the storage at 25, 37 and 45 ºC for 48 h were recorded using a Nicolet i550 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 after the storage at 25, 37 and 45 ºC for 48 h were recorded using a Nicolet i550 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 after the storage at 25, 37 and 45 ºC for 48 h were recorded using a Nicolet i550 Advanced Spectrometer (Thermo Scientific). ATR-FTIR spectra were recorded with 32 scans and a resolution of 1 cm⁻¹.

Characterization

FT-IR and Raman spectroscopy

Desorption and regeneration were performed with 0.1 M NaOH. 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. Desorption and regeneration were performed with 0.1 M NaOH.

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. 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

High-resolution ³¹C solid-state spectra for the polymers were recorded using the ramp ¹H–³¹C 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 ³¹C spectra and to set the Hartmann-Hahn matching condition in the cross-polarization experiments in ³¹C 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¿ satisfying ω₁p/2π = νp, H¿ = 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.
Synthesis and characterization of the polyampholyte

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. 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) in the presence of phosphate. The bands corresponding to H₃PO₄ (1159 and 1077 cm⁻¹) are hidden by the signals of the polymer and the diatomaceous earth at that wavenumber. The bands at 990 cm⁻¹ of HPO₄²⁻ and 940 cm⁻¹ of H₂PO₄⁻ 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 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, ³¹P-MAS and ¹³C CP-MAS NMR spectra were performed and the results are shown in Figure 2A and 2B. Both single-pulse ³¹P-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 the presence of H₃PO₄⁻ species bound to the positive domains of the polymer matrix. These results indicate that the distribution of phosphorus entities was homogeneous at the different pH conditions.

Then, the adsorption process was analyzed through the ¹³C CP-MAS spectra of the modified - polyampholyte material. The unequivocal assignment of the different resonance signals was previously reported. 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 ¹³C-NMR signal of ordered structures produce an increment of the signal because in these...
regions the cross polarization transfer from $^1$H 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.](image)

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.](image)

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. 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 $\text{H}_3\text{PO}_4^+$, which should interact with positively charged sites from the polymer: monosubstituted and protonated N-heterocycle units (IMH$^-$), and dissubstituted 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 (-COO$^-$). These anionic neighbors could be either randomly distributed onto the network, or forming clusters

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 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 $\text{N}_4\text{N}_4$-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 entire polyampholyte matrix being at pH 7.0 more important. 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 entire polyampholyte matrix being at pH 7.0 more important.

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 carboxylic groups of the MAA segments are interacting particularly with the positive 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 entire polyampholyte matrix being at pH 7.0 more important. 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 groups. However, at pH 7.0 the carboxylic groups of the MAA segments are interacting particularly with the positive 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 entire polyampholyte matrix being at pH 7.0 more important.

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.

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

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(small chains of –(MAA)ₙ–) contributing to affect the binding energy of H₃PO₄ 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 ± 41 µg of phosphate bound per mg of polymer reached experimentally.

Table 1. Isotherm models parameters

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>pH 5</th>
<th>pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>qₘₐₓ (µg/mg)</td>
<td>120.3 ± 6.2</td>
<td>335 ± 37</td>
</tr>
<tr>
<td></td>
<td>Kₐ (mL/µg)</td>
<td>(9.2 ± 2.2) x 10⁴</td>
<td>(6.6 ± 1.4) x 10⁴</td>
</tr>
<tr>
<td>Freundlich</td>
<td>kᵣ</td>
<td>17.0 ± 6.0</td>
<td>6.62 x 10⁴</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>0.23 ± 0.05</td>
<td>0.598 ± 0.045</td>
</tr>
<tr>
<td>R-P</td>
<td>qₕ (µg/mg)</td>
<td>1.11 ± 0.30</td>
<td>0.222 ± 0.088</td>
</tr>
<tr>
<td></td>
<td>nₓ</td>
<td>(9.20 ± 9.37) x 10⁴</td>
<td>3.46 x 10⁹</td>
</tr>
<tr>
<td>Sips</td>
<td>qₘₐₓ (µg/mg)</td>
<td>109.6 ± 5.7</td>
<td>118.64</td>
</tr>
<tr>
<td></td>
<td>nₙ</td>
<td>1.17 ± 0.30 x 10⁴</td>
<td>4.0</td>
</tr>
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</table>

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/Cₒ or Cᵢ versus time (t), where Cᵢ is the phosphorus concentration of effluent and influent, respectively.

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 Ce was between 70 and 500 µg 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 between –COO⁻ and uptake HPO₄²⁻ would account for an additional network expansion.

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...
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 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.

Table 2. Thomas model parameters.

<table>
<thead>
<tr>
<th>Flow rate (mL/min)</th>
<th>Influen P concentration (µg/ml)</th>
<th>Interferent</th>
<th>( q_0 ) (µg/g)</th>
<th>( K_{th} ) (mL/min µg)</th>
<th>AICc</th>
</tr>
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<tbody>
<tr>
<td>1.0</td>
<td>4.7</td>
<td>----</td>
<td>234 ± 12</td>
<td>-32.09</td>
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<tr>
<td>0.5</td>
<td>4.5</td>
<td>----</td>
<td>195 ± 3</td>
<td>-54.50</td>
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</tr>
<tr>
<td>1.5</td>
<td>4.9</td>
<td>----</td>
<td>200 ± 12</td>
<td>-32.01</td>
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</tr>
<tr>
<td>1.0</td>
<td>4.3</td>
<td>NO\textsubscript{3}</td>
<td>176 ± 12</td>
<td>-11.89</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>4.5</td>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>191 ± 11</td>
<td>-17.79</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.72</td>
<td>----</td>
<td>56 ± 1</td>
<td>-45.44</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>10.0</td>
<td>----</td>
<td>470 ± 18</td>
<td>-40.64</td>
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</tr>
</tbody>
</table>

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. 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 groups 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 becomes residual repulsion due to the phosphate anion and the carboxylic groups present in polyampholytes. On the other hand, the $q_e$ 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–MMA-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 responsible for P adsorption. Also, ss-NMR results showed that the H$_2$PO$_4^-$ was the main species 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.

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Notes and references
