ARTICLE

Phenol removal from wastewater using eco-friendly hybrid hydrogels

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Abstract

The intent of this study was to evaluate the ability of low-cost polyacrylamide/starch hybrid hydrogels in removing organic pollutants from wastewater, using phenol as a model compound, besides of investigating the adsorption/desorption behavior as a function of hydrogels composition. The results indicated that the hydrogel with the lowest amount of starch and crosslinking agent exhibited the maximum phenol adsorption capacity, 21 mg g⁻¹. The adsorption isotherm data were described by Langmuir and Freundlich adsorption isotherm models. According to linear regression analysis, the Freundlich isotherm model was the best fit among the isotherm models for the adsorption process. Furthermore, desorption study revealed a minimum of about 60% of phenol release, indicating reusability to wastewater treatment.

KEYWORDS
adsorption, biopolymers and renewable polymers, polysaccharides

1 | INTRODUCTION

The aquatic environment has been increasingly targeted of chemical deposition produced by agricultural, industrial, and domestic activities. Phenolic compounds, for example, are a class of toxic organic compounds commonly disposed into aqueous media.1,2 These compounds are present in various industrial activities, such as in the petrochemical and pharmaceutical industry, in the manufacture of resins, plastics, paints, cellulose, paper, pesticides, among others. The improper waste disposal causes serious and harmful effects to animals and humans. For this reason, phenol was considered a priority pollutant by the United States Environmental Protection Agency (EPA) and by the National Pollutant Release Inventory (NPRI) in Canada. The EPA has established a water purity standard of less than 1 ppb for phenol in water. In addition, phenolic compounds are highly reactive with other compounds present in the environment, producing derivatives that can be even more dangerous.1–4

There are several methods for removing phenolic compounds from water, which include polymerization,5,6 photocatalytic degradation,7,8 ozonation,9,10 electrocoagulation,11 extraction,12,13 advanced oxidation,14–16 ion exchange,17–19 distillation,20 biological treatment,21 enzymatic treatment,22–24 Electro-Fenton method,25,26 and adsorption.27–30 Among them, adsorption is the most used due the simplicity of the process. The adsorption efficiency will depend on the properties of the adsorbent material, such as porosity, reaction composition, size and surface area, pore size distribution, concentration of adsorbate, in addition to competition to other residues for the surface area of the adsorbent.31 The adsorption is based on the migration of the adsorbate from the solution to the active sites of the adsorbent pore surface by diffusion.32,33 To observe the effectiveness of pollutant removal and to predict the type of mechanism involved in the adsorption process, mathematical models of adsorption can be used. Isotherms of adsorption are a good parameter to predict the type of mechanism involved and the contaminant removal efficiency.34–36
Different adsorbent materials, such as activated carbon,37 seaweeds,38–40 zeolites,41 and graphenes,42 have already been used in adsorption processes. However, the use of these adsorbent materials is expensive and can become infeasible to industries. Two recent studies of adsorption in the area of polymers have been developed using hydrogels to remove phenolic pollutants. Si et al (2019)43 synthesized hydrogels with thermoresponsive behavior based on N-isopropylacrylamide for application in the adsorption and release of phenolic contaminants. As expected, the adsorption process was controlled by temperature. Wang et al (2018)42 developed polymeric hydrogels composed of hydroxypropylcellulose and graphene oxide, which showed good phenol adsorption capacity from aqueous solutions.

In this scenario, hybrid hydrogels based on mango kernel starch and polyacrylamide were evaluated as adsorbent materials on wastewater purification contaminated with phenol. The use of starch from a solid waste beneficiation enables adding value to an industrial waste, besides of bringing to hydrogels the intrinsic character of polysaccharides, such as biocompatibility, hydrophilicity, biodegradability and non-toxicity.44,45

2 | EXPERIMENTAL

2.1 | Materials

Starch (M_w = 7.09 x 10^7 g mol^-1 and amylose/amylopectin content of 25/75 wt%) was extracted from mango (Mangifera indica L.) kernel (SISGEN: AD3DC70), according to the procedure reported by Cordeiro et al.46 Acrylamide (AAm), N,N'-methylenebisacrylamide (MBA), and cerium ammonium nitrate (CAN) were obtained from Sigma Aldrich. These chemicals were previously used to prepare the PAAm/Starch hybrid hydrogels, via free-radical polymerization in aqueous medium, as detailed described by our research group.47 The codes of the samples and the feed composition are presented in Table 1. Phenol was purchased from SYNTTH. Deionized water (≥18 MΩ cm^-1) was used throughout the work.

2.2 | Phenol calibration curve

The aqueous solutions of phenol were scanned from 190 to 500 nm on a UV-1800 Shimadzu Spectrometer. The maximum absorbance value (λ = 269 nm) was applied to construct the phenol calibration curve, as a function of the analyte concentration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Code of the hydrogels^a</th>
<th>Acrylamide/starch/MBA/CAN (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>AAm20/Starch1/MBA0.1</td>
<td>400/20/2/0.25</td>
</tr>
<tr>
<td>(II)</td>
<td>AAm20/Starch1/MBA0.2</td>
<td>400/20/4/0.25</td>
</tr>
<tr>
<td>(III)</td>
<td>AAm20/Starch1/MBA0.5</td>
<td>400/20/10/0.25</td>
</tr>
<tr>
<td>(IV)</td>
<td>AAm20/Starch2/MBA0.1</td>
<td>400/40/2/0.25</td>
</tr>
<tr>
<td>(V)</td>
<td>AAm20/Starch2/MBA0.2</td>
<td>400/40/4/0.25</td>
</tr>
<tr>
<td>(VI)</td>
<td>AAm20/Starch2/MBA0.5</td>
<td>400/40/10/0.25</td>
</tr>
</tbody>
</table>

Abbreviations: AAm, acrylamide; CAN, cerium ammonium nitrate; MBA, N,N'-methylenebisacrylamide. ^aThe numbers on the codes represent the molar amount of each reactant divided by 20.

2.3 | Adsorption of phenol within PAAm/starch hydrogels matrix

The adsorption study of the phenolic compound within the hydrogel matrix was carried out by inserting a known amount of hydrogel into 50 ml aqueous solution of phenol, which had initial concentrations (C_0) ranging from 10 to 200 mg L^-1. The studies were carried out as a function of time. Phenol concentration in the supernatant was determined by UV–VIS measurements, from the calibration curve obtained in the previous item (Section 2.2). The adsorption capacity (Q_eq, mg g^-1) of PAAm/Starch hybrid hydrogels was calculated according to Equation (1).

\[
Q_{eq} = \frac{(C_0 - C_t)xV}{w}
\]

where Q_eq (mg g^-1) is the equilibrium adsorption capacity of the adsorbent (PAAm/Starch hydrogels), C_0 (mg L^-1) and C_t (mg L^-1) represent the initial and the equilibrium phenol concentrations in the supernatant, respectively, V (ml) is the solution volume and w (mg) is the dry weight of the copolymers obtained after lyophilization of the swelled hydrogels.

2.4 | Isotherms of adsorption

In order to evaluate the type of adsorption, adsorption isotherms were constructed using two mathematical models,
the Langmuir and Freundlich isotherms. The Langmuir isotherm can be represented according to Equation (2).

\[
\frac{C_{eq}}{q_{eq}} = \frac{1}{Q_m K_L} + \frac{1}{K_L} C_{eq}
\]  

(2)

where \( K_L \) is the Langmuir constant, which provides the theoretical adsorptive capacity in the monolayer (L g\(^{-1}\)), \( Q_m \) represents the constant related to the adsorption energy (L mg\(^{-1}\)), \( C_{eq} \) is the concentration of the adsorbate (phenol) solution in equilibrium (mg L\(^{-1}\)) and \( q_{eq} \) is the adsorbed amount of adsorbate per gram of adsorbent (mg g\(^{-1}\)). Using this equation, it was possible to plot the graph of \( \frac{C_{eq}}{q_{eq}} \) as a function of \( C_{eq} \), obtaining \( \frac{1}{Q_m K_L} \) as the linear coefficient and \( \frac{1}{K_L} \) as the slope.

The Freundlich isotherm can be represented by the linearized Equation (3).

\[
\log Q_{eq} = \log K_F + \frac{1}{n} \log C_{eq}
\]  

(3)

where \( K_F \) is the Freundlich constant, which is related to the adsorption capacity (mg g\(^{-1}\)), and \( n \) is an empirical parameter, which is related to the adsorption intensity. Thus, through the graph of \( \log Q_{eq} \) as a function of \( \log C_{eq} \), \( \log K_F \) could be obtained as the linear coefficient and \( \frac{1}{n} \) as the slope.

2.5 | Desorption procedure

The hydrogels adsorbed with phenol from Section 2.3 were removed from the phenol solution, superficially washed and placed into 50 mL of deionized water to release of phenol in water. The amounts of phenol released from hydrogels for the period of 24 h were obtained with a UV–vis spectrophotometer, from the calibration curve obtained at Section 2.2.

3 | RESULTS AND DISCUSSION

3.1 | Adsorption capacity of phenol

The PAAm/Starch hybrid hydrogels ability to adsorb phenol was investigated and the curves of adsorption capacity as a function of time, from different initial
TABLE 2  The regression parameters obtained for Langmuir and Freundlich isotherms

<table>
<thead>
<tr>
<th>PAAm/starch hydrogels</th>
<th><strong>Langmuir constants</strong></th>
<th></th>
<th><strong>Freundlich constants</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$Q_m$ (mg.g$^{-1}$)</td>
<td>$K$ (L.mg$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>AAm20/Starch1/MBA0.1</td>
<td>0.8328</td>
<td>39.7</td>
<td>$5.6 \times 10^{-3}$</td>
<td>0.966</td>
</tr>
<tr>
<td>AAm20/Starch1/MBA0.2</td>
<td>0.5985</td>
<td>19.1</td>
<td>$8.47 \times 10^{-3}$</td>
<td>0.9764</td>
</tr>
<tr>
<td>AAm20/Starch1/MBA0.5</td>
<td>0.528</td>
<td>9.17</td>
<td>0.011</td>
<td>0.9226</td>
</tr>
<tr>
<td>AAm20/Starch2/MBA0.1</td>
<td>0.8202</td>
<td>16.7</td>
<td>$9.98 \times 10^{-3}$</td>
<td>0.9498</td>
</tr>
<tr>
<td>AAm20/Starch2/MBA0.2</td>
<td>0.3818</td>
<td>17.4</td>
<td>$6.18 \times 10^{-3}$</td>
<td>0.9343</td>
</tr>
<tr>
<td>AAm20/Starch2/MBA0.5</td>
<td>0.6368</td>
<td>11.32</td>
<td>$8.21 \times 10^{-3}$</td>
<td>0.9482</td>
</tr>
</tbody>
</table>

Abbreviations: AAm, acrylamide; MBA, $N,N'$-methylenebisacrylamide.
concentrations of phenol, are presented in Figure 1. Higher adsorption rates were obtained at the highest phenol concentration studied, 200 mg L\(^{-1}\), usually with the maximum adsorption observed within 8–24 h. The adsorption of phenol was quite slower for concentrations of 150, 100, 50 and 10 mg L\(^{-1}\). In general, the equilibrium adsorption capacity (\(q_{\text{eq}}\)) was in the order of 200 > 150 > 100 > 50 > 10 mg L\(^{-1}\). This behavior may be attributed to the high driving force from the difference in phenol concentration between the liquid phase and the adsorbent.

In general, higher concentrations of starch and crosslinker caused a decrease in the adsorption efficiency. This result was attributed to the less effective interactions between OH of phenol and NH/OH of the polymeric structure, due to the smaller size of pores in the polymer network (Figure S1). It can be seen from Figure 1 that the AAm20/Starch1/MBA0.1 hydrogel (I) showed the best adsorptive capacity (21 mg g\(^{-1}\)) among the others.

<table>
<thead>
<tr>
<th>Phenol (mg.L(^{-1}))</th>
<th>Release (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>200</td>
<td>73.8</td>
</tr>
<tr>
<td>150</td>
<td>61.2</td>
</tr>
<tr>
<td>50</td>
<td>76.1</td>
</tr>
<tr>
<td>10</td>
<td>72.2</td>
</tr>
</tbody>
</table>
The equilibrium adsorption capacity of the PAAm/Starch hybrid hydrogels is comparable to other polymer-based hydrogels and carbon activated adsorbents founded at literature.37,43,49

3.2 Adsorption isotherms study

The isothermal models can provide correlation of the adsorption data with the surface properties of the PAAm/Starch hybrid hydrogels. The Langmuir and Freundlich isotherm models are the most used to describe the distribution and transport of adsorbate from a liquid phase to the adsorbent, targeted by thermodynamic aspects.50 Isotherm equations include constants that indicate the affinity and the surface properties of the adsorbent. The model’s applicability is expressed by the correlation coefficient R². The linear plots of Freundlich and Langmuir equations for adsorption of phenol on the hybrid hydrogels are showed in Figure 2 and the respective constants and correlation coefficients are summarized in Table 2.

The correlation coefficients obtained for Freundlich isotherms were more suitable, with higher R² values, than the ones for Langmuir isotherms. Then, it was suggested a multilayer adsorption of phenol at the surface of the PAAm/Starch hybrid hydrogels. The energy distribution points for the adsorption sites are non-uniform. Meanwhile, the Langmuir model would assume a monolayer and homogeneous surface adsorption.

The constants of the Freundlich adsorption isotherms, K_f and n, for each hydrogel, are show in Table 2. The K_f parameter is related to adsorption capacity. The hydrogels exhibited a decrease on the K_f with the increase of MBA concentration, which means a lower adsorption capacity. This is consistent with the q_eq results showed in Figure 1. In addition, the K_f showed a tendency to decreasing values with the increase of starch concentration, also in agreement with Figure 1. In addition, the 1/n value between 0 and 1 indicates a favorable adsorption for all hydrogels studied. The AAm20/Starch1/MBA0.1 hydrogel obtained the 1/n value closer to 1, indicating the maximum of the adsorption process, which is also in agreement with Figure 1. Similar results were obtained by Wang et al (2018), in which the Freundlich model fit better in the adsorption capacities.42

3.3 Desorption study

The desorption performance of the hydrogels is shown in Figure 3. The results revealed that phenol release increased with increasing MBA concentration, contrary to the adsorption behavior. Probably, the weaker the interaction with the adsorbent, the easier the releasing process. The release of phenol reached 86.4% to the AAm20/Starch1/MBA0.5. Ultimately, the PAAm/Starch hydrogels had a minimum release of around 60%, indicating a good reusability capacity.

4 CONCLUSION

In this study PAAm/Starch hybrids hydrogels were applied to removal of phenol from synthetic wastewater. The adsorption process of phenol was influenced by the amount of starch and crosslinker in the hydrogels matrix. The optimum adsorption capacity of phenol from aqueous solutions occurred for the AAm20/Starch1/MBA0.1 hybrid hydrogel. In addition, the adsorption isotherms study showed that phenol adsorption efficiency for the hybrid hydrogels followed the Freundlich model. Lastly, the study of phenol desorption performance from the AAm/Starch hybrids hydrogels indicated their reusability in the wastewater treatment. These results improved the understanding of the sorption behavior of organic pollutants as phenol in hybrid hydrogels.

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