Sorption of 2-Chlorophenol from Aqueous Solutions by Functionalized Cross-linked Polymers

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Abstract: This manuscript describes the synthesis of three polymers based on styrene (STY), divinylbenzene (DVB) and two different vinyl monomers: methyl methacrylate (MMA) and acrylonitrile (AN). The STY-DVB, STY-DVB-MMA and STY-DVB-AN polymers were synthesized employing the aqueous suspension technique. Reaction yields were 73%, 81% and 75%, respectively. They were morphological and chemically characterized using different techniques. The extraction capacity of the polymers was evaluated using 2-chlorophenol. The polymer extraction capacities were evaluated varying contact time the (1 h, 3 h and 5 h), temperature (30 °C, 35 °C and 40 °C), and pH (3, 5.6 and 8). The STY-DVB-AN polymer was the most efficient; it removed around 95% of the analyte using a contact time 50 h.

Keywords: *2-chlorophenol, polymer, extraction.*

Introduction

The growth of the world population has motivated an increase in the demand for food, that has provoked the use of large quantities of herbicides to control different agricultural pests[1]. Acidic herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA) are widely used to control broad-leaved weeds in plantations[2].

The degradation of 2,4-D and MCPA in soil produces different phenol derivatives, such as: 2-chlorophenol (2-CP), 2-methylphenol, 4-chlorophenol, 2,4-dichlorophenol and 4-chloro-2-methylphenol[3]. These derivatives can reach and contaminate subsurface waters polluting the environment. Hence, the extraction of these compounds from water have been investigated[4,5].

These chlorinated organic compounds can be removed from aqueous solution using porous materials such as activated carbons[6] or polymers[7]. These latter material have already been employed successfully to extract pollutants from water[8,9].

Cross-linked polymers are of great importance due to their thermal stability and easy synthesis. These polymers may be produced using an aqueous suspension polymerization technique, which provides beads with spherical morphology. This procedure uses an initiator, which by decomposition produces free-radicals that initiate the polymerization and cross-linking reactions[10].

Surface polarity of these polymers can be modified inserting a polar group[11]. These functional groups are inserted into the polymeric structure either by functionalized monomer polymerization or by chemical modification of the original polymer[12]. Cross-linked polymers have a high specific surface area allowing different interactions (π-π, dipole-dipole or hydrogen bonding) between the aromatic sites and the analyte[13].

These modified polymers are more hydrophilic and are useful for numerous applications[14].

Literature has reported the use of these polymers for organic pollutant extraction[15,16], as well as for the treatment of water produced by the oil industry[17].

The aim of this manuscript was to compare the abilities of three cross-linked polymers to adsorb 2-chlorophenol from an aqueous solution. These polymers were based on styrene and divinylbenzene containing methyl methacrylate or acrylonitrile as the polar monomer.

Experimental

Materials

Styrene (STY) was provided by Petroflex; *p*-divinylbenzene (DVB) (commercial grade 45%, containing a mixture of DVB and *p*-ethylvinylbenzene), acrylonitrile (AN) and methyl methacrylate (MMA) were provided by Nitriflex; 2,2′-Azobis (2-methylbutanenitrile) or Vazo-67 and 2-hydroxyethylcelullose (HEC, Cellosize QP-100MH) were provided by Metacril and Union Carbide, respectively. Monomers and reagents presented commercial grade of purity and were used as received. The reagents gelatin, sodium chloride, propanone, heptane (HEP), toluene (TOL) (Vetec Química Fina Ltda., Brazil) and anisole (ANI) (Merck) were bought as P.A. grade and used as received. Aqueous solutions were prepared using Milli-Q water.

Polymer synthesis

Aqueous suspension polymerization was carried out in a 1-L, three-necked, round-bottomed flask fitted with a mechanical stirrer, and reflux condenser with a silicon

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oil seal at its top. The aqueous phase (AP) was composed of gelatin and HEC (both at 1 wt.% in relation to AP) and NaCl (5 wt.% in relation to AP). The organic phase (OP) was composed of a mixture of monomers with different compositions (total amount = 0.5 mol). HEP, TOL or ANI were used as diluents at 200 %-v/v in relation to the monomers[10]. This percentage was used to favor higher porosity. Vazo-67 was used as an initiator (1 mol% in relation to the monomers).

The OP was slowly added to the previously prepared AP, using the ratio AP/OP = 4/1. These two phases were maintained under constant stirring (300 rpm) at 25 °C for 20 min. Finally, the mixture was stirred for 24 h at 80 °C. Table 1 summarizes the synthesis parameters.

The polymer beads obtained were thoroughly washed with water and propanone in a Soxhlet extractor and dried at 80 °C overnight. The polymer beads were sieved and the 0.32-0.60 mm fraction was used in the sorption experiments.

Polymer characterization

The apparent density (AD) was determined in a graduated cylinder using an adapted procedure of ASTM D1895[18]. The swelling degree (Sd) was determined inserting 3 mL of synthesized polymer in a 10 mL graduated cylinder[18]. The beads was kept in solvent for 24 h.

The morphological features were observed using an optical microscopy (Nikon, Model SNZ 800). The FTIR spectra (range 4,000-600 cm^{-1} with a resolution of 4 cm^{-1} and scan rate of 8 scans/s) of the beads were taken in KBr pellets using a Perkin Elmer Precisely spectrometer. The surface area and pore volume in the dry state were determined by the BET or BJH methods from low-temperature nitrogen adsorption isotherms (ASAP Micromeritics 2010), which were obtained at 77 K using a high-vacuum volumetric apparatus. The samples were degassed at 100 °C / 1 mPa for 3 h.

Adsorption experiments

The extraction capacity of different polymers was evaluated using batch experiments, which were performed with 0.3 g of the polymer and 25 mL of 2-CP (50 mg/L). The solution was shaken (120 rpm) on an orbital shaker (Cientec CT172) varying the contact time (1, 3 and 5 h), temperature (30 °C, 35 °C and 40 °C) and pH (3, 5.6 and 8). Finally, an aliquot of 2-CP was separated and its concentration was determined by UV/ VIS spectrophotometer (VARIAN, CARY 50). Detection was realized using the wavelength of 274 nm. The 2-CP concentration in solution was determined using an analytical curve ($r^2 = 0.9997$).

Results and Discussion

Three different polymers - C1 (STY/DVB), C2 (MMA/STY/DVB) and C3 (AN/STY/DVB) - were synthesized using the aqueous suspension technique. These reactions presented yields of 73 %, 81 % and 75 %, respectively. All polymers were characterized by FTIR spectra (Figure 1).

All polymer showed absorptions around 1630 cm^{-1} (C=C) and 710-750 cm^{-1} (monosubstituted aromatic ring). C2 presented absorption bands characteristic of the ester group, such as: 1730 cm^{-1} (C=O) and 1150 cm^{-1} (C-O-C). These results indicated MMA incorporation into the polymer structure. The nitrile group in C3 was supported by absorption at 2240 cm^{-1}[19,20].

Swelling degree of polymers (Sd) (Table 2) varied according to the solvent used. This fact indicated that the interaction between solvent and polymeric structure was differentiated[18].
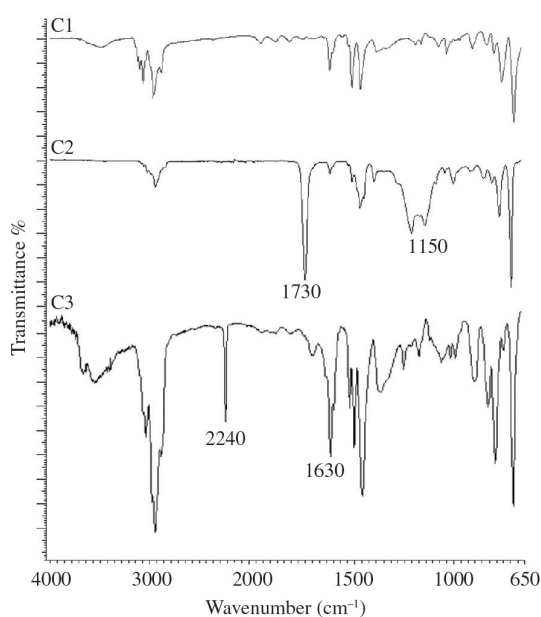

Figure 1. Infrared spectra of synthesized polymers (C1, C2, C3).

Table 1. Synthesis parameters of polymers[a].

Polymer	STY (mol%)	MMA (mol%)	AN (mol%)	Diluent system(vol%)
C1 - (STY/DVB)	80	-	-	60 HEP
				40 TOL
C2 - (MMA/STY/DVB)	40	40	-	60 HEP
				40 TOL
C3 - (AN/STY/DVB)	40	-	40	60 HEP
				40 ANI

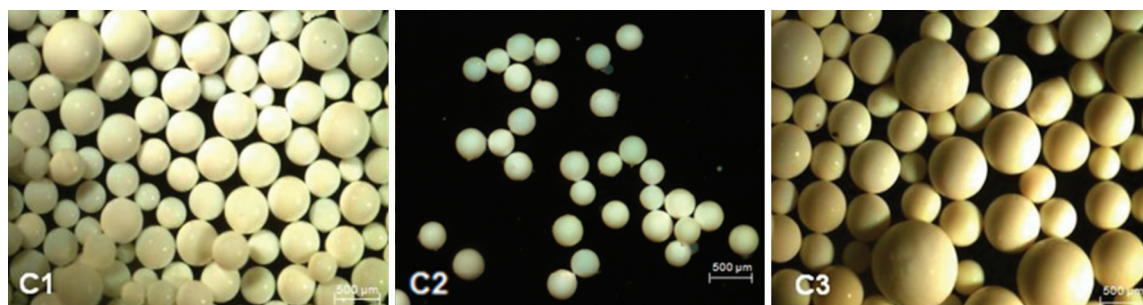[a] – all reactions used DVB (mol %) = 20.

Figure 2. Optical microscopy photomicrograph of synthesized polymers (C1, C2, and C3).

Table 2. Swelling degree of synthesized polymers.

Solvent	Swelling percentage		
	C1	C2	C3
Water	2	4	5
Heptane	26	28	29
nitrobenzene	77	157	130
o-dichlorobenzene	100	163	154

Table 3. Solubility parameters (δ)[24] of monomers and diluents.

Monomer	δ (MPa$^{1/2}$)[b]	Diluent	δ (MPa$^{1/2}$)[b]
STY	19.0	AN	24.8
DVB	18.2	HEP	15.3
MMA	18.0	ANI	19.4
		TOL	18.2
		HEP/TOL[a]	16.5[b]
		HEP/ANI[a]	16.9[b]

[a]Diluents (%v/v) – (60/40); [b]$\delta_{dil} = \sum_i \delta_i \Phi_i$; δ - solubility parameter; ϕ – molar fraction.

Table 4. Morphological characteristics of synthesized polymers.

Polymer	$D_p{}^a$ (nm)	$d_a{}^b$ (g/cm^3)	$S_a{}^c$ (m^2/g)	$V_p{}^d$ (cm^3/g)
C1	27	0.40	82	0.45
C2	83	0.39	49	0.40
C3	74	0.42	110	0.45

[a]Average pore diameter; [b]apparent density; [c]specific surface area; [d]pore volume.

The swelling degree results using water were not measurable considering an experimental uncertainly of around 10 %. The use of heptane produced a poor swelling. Higher percentages were obtained using aromatic solvents (Table 2) that indicated a good affinity between the solvents and polymeric structure[21]. The lowest swelling degree obtained with C1 using aromatic solvents may be related to its lower polarity compared to the others.

All polymers were evaluated using optical microscopy (Figure 2). This technique provided an indication of polymer porosity as a function of different degrees of opacity, such as: transparency, diaphanous and opaque[22].

According to the literature, opaque beads have a structural heterogeneity, which not allows the passage of light through the polymer structure, unlike transparent beads[22,23]. This fact is associated to greater refraction of the light passing through the beads. All the polymers reported in this manuscript presented opaque beads with spherical morphology[22,23].

The solubility parameter (δ) influences the porous nature of polymer. The Hildebrand solubility parameter[24] theory has in many cases proved effective in predicting the physical characteristics of reticulated polymers. Table 3 shows the values for this parameter of the monomers and diluents (pure and mixtures) used in the synthesis.

As the solubility parameter value for synthesized polymers was not found in the literature, the values of the acrylonitrile and methyl methacrylate homopolymers (δ_{polyAN} = 25.1 MPa$^{1/2}$; $\delta_{polyMMA}$ = 18.6 MPa$^{1/2}$) were used, as well the STY-DVB copolymer with a cross-linking of 10 % ($\delta_{polySTY-DVB}$ = 15.7 MPa$^{1/2}$)[24].

According to the Hildebrand theory[25], the solubility of a polymer in a solvent is favored when this difference ($\delta_1 - \delta_2$) is minimized. However, if ($\delta_1 - \delta_2$) > 3 a non solvent character is expected. In this case, the toluene and anisole acted as the solvent diluents and heptane as the non-solvent diluent.

Table 3 shows that the solubility parameter (δ) values for both diluent mixtures were near (16.5 MPa$^{1/2}$ and 16.9 MPa$^{1/2}$). The difference between the respective solubility parameter of the diluent mixtures and the homopolymer (MMA or AN) were 2.1 MPa$^{1/2}$ and 8.2 MPa$^{1/2}$, respectively. Therefore, the formation of a more porous polymer structure could be expected because of the low affinity of the diluent for the polymer, which is formed during the polymerization reaction.

On the other hand, the use of anisole as the diluent aimed to improve the degree of AN incorporation in synthesized polymers when compared to toluene[26]. This fact was attributed to the higher anisole dielectric constant (ε) value (ε = 4.3) compared to toluene (ε = 2.2). Hence, the acrylonitrile loss to the aqueous phase would be reduced[26].

Considering the pore diameter values reported in the literature[27] all synthesized polymers in this work can be classified as mesoporous structures (Table 4).

The lower C1 pore diameter value was a consequence of the small difference between the solubility parameter of the diluent mixture (16.5 MPa$^{1/2}$) and the copolymer STY-DVB containing a cross-linking degree of 10% (δ = 15.7 MPa$^{1/2}$). In this case, these results indicate a solvent character for the diluents.

Polymers based on MMA (C2) and AN (C3) presented higher pore diameters. This result indicated that the diluents presented a higher non solvating character for C2

and C3. This result confirms the expectation for C2 and C3 porosity according to the difference of the solubility parameters mentioned.

C2 showed the lowest specific area when compared to the others. This fact was justified by the increase of the phase separation, which occurred during the polymerization. On the other hand, C3 that was synthesized in the presence of a polar diluent (ANI) presented a higher specific area. Hence, it is possible to assume that ANI had higher affinity with a polymer compared to toluene. This better affinity can be consequence of a higher dielectric constant of anisole.

The first assays to evaluate the removal of 2-chlorophenol (2-CP) from aqueous solutions by synthesized polymers was performed at pH 5.6 and 30 °C using batch system and different contact times (Figure 3).
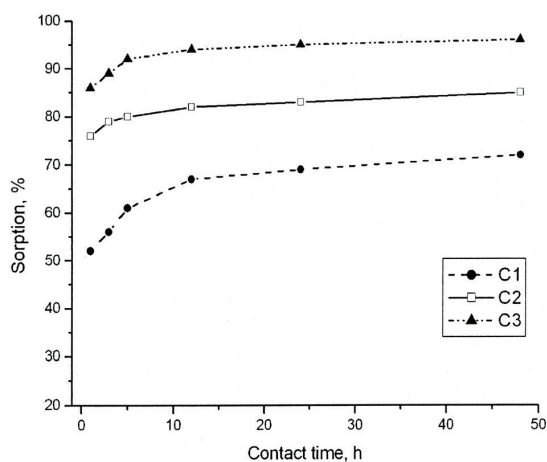

Figure 3. 2-Chlorophenol sorption by C1, C2 and C3 using different contact times.
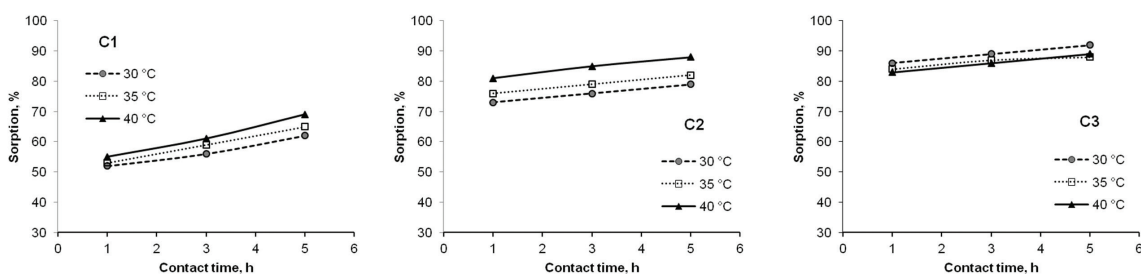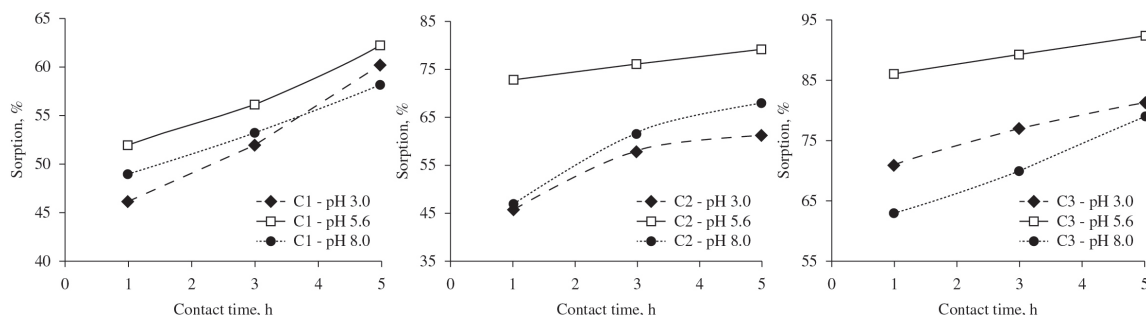
The lower sorption presented by C1 can be associated to its hydrophobicity, which hinders the diffusion process though the polymeric network.

The C3 extraction was more effective followed by C2 for all contact times. These results can be related to the higher specific surface area and hydrophilicity of C3. The C3 hydrophilicity was influenced by the higher dielectric constant value of AN (33.0) compared with MMA (6.32)[28].

As extraction efficiency after 5 h was little modified (Figure 3) the next assays investigated the influence of temperature and pH (Figure 4) using three different contact times (1, 3, and 5 h).

These assays were performed using temperatures of 30 °C, 35 °C and 40 °C and pH values of 3, 5.6 and 8. In general, C3 showed the highest efficiency for all temperatures used. The assays realized at 40 ºC showed a small increase in efficiency (Figure 4), except for C3.

Probably, this result indicates that the C3 adsorption process occurred predominantly on the surface area. So, the analyte diffusion into porous structure did not have any measurable influence.

Another 2-CP extraction set was performed (Figure 5) using three different pH values (3, 5.6 and 8). As 2-CP acts as a weak acid[29] in aqueous solutions, the hydrogen ion dissociation is influenced by the solution pH. The assays using different pH showed that extraction efficiency was C3>C2>C1 (Figure 5) for all pH evaluated.

In these assays, the highest efficiency (92 %) was obtained by C3 at pH 5.6 using 5 h of contact time. This result was favored by the higher surface area and the hydrophilicity[30] of C3 compared to C1 and C2, which presented efficiencies of 62 % and 80 %, respectively.

The best C3 result at pH 5.6 was associated to the contributions of the hydrogen bond[30]. This interaction

Figure 4. 2-Chlorophenol sorption by polymers (C1, C2 and C3) using different temperatures.

Figure 5. 2-Chlorophenol sorption by polymers (C1, C2 and C3) using different pH values.

was influenced by the pH values (3 and 8). This fact was a consequence of the protonation (pH 3) of free electrons at the functional group in the polymer, as well the analyte deprotonation (pH 8).

The small difference between the analyte pKa (8.2) and basic pH (8) values favored the presence of two different compounds simultaneously: the phenolate ion and phenol. Under these conditions both intermediates had almost the same concentration. So, pH 8 presented a lower concentration of the phenol derivative capable of forming hydrogen bonds compared to pH 5.6[31]. This can be seen in Figure 5 considering the extraction results of C2 and C3 using pH 8 and 5.6.

C2 and C3 extraction efficiencies using pH 3 were lower than pH 5.6. This fact was attributed to the differentiated influence of the functional group in the polymer to form hydrogen bond[31]. The lower efficiency to C2 compared to C3 at pH 3 was related to more effective ester protonation compared to nitrile. So, C2 had lower quantities of the free functional group to interact with the analyte.

The lower efficiency observed for C1 was a consequence of its hydrophobic structure. This polymer provides only π-π interactions[31], so the influence from pH was not measurable.

Conclusions

The results obtained showed that polymers based on acrylonitrile or methyl methacrylate are potential sorbents capable of removing 2-CP. The surface area and hydrophilicity were important parameters for the sorption efficiency. The best of 2-CP extraction percentage (~95 %) was obtained by the C3 polymer using a contact time 5 h and pH 5.6. Temperature range investigated did not influence significantly the extraction process. All polymers showed the best efficiency using pH 5.6. C1 polymer presented the lowest efficiency for all pH used.

Acknowledgements

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