

Removal of Phenolic Compounds from Aqueous Solutions using Poly(styrene-co-divinylbenzene) Functionalized with Aminophosphonic Acid

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Removal of aromatic pollutants from water by using polymeric adsorbents has been of great interest. In this paper, adsorption of 2,3-dimethylphenol and 2,4,6-trimethylphenol from aqueous solution onto a poly(styrene-co-divinylbenzene) functionalized with isopropyl-aminophosphonic acid group at temperatures of 20 °C, was studied.

Keywords: polymeric adsorbents, phenolic compounds (2,3-dimethylphenol and 2,4,6-trimethylphenol), removal

Water pollution by phenolic compounds has attracted many attentions in recent years. Phenols are pollutants of high priority concerns because of their toxicity and possible accumulation in the environment. Phenolic compounds exist in wastewaters from olive mill, oil refineries, plastics, leather, paint, pharmaceutical and steel industries, and must be removed to satisfy the actual environmental regulations [1].

These organic compounds are the common organic contaminants and can threaten both of human beings and wildlife [2]. Methods to remove aromatic pollutants from the contaminated waters are classified as recovery (e.g., adsorption, solvent extraction, and membrane separation) or destruction (e.g., chemical oxidation, electrolysis, and biodegradation) techniques [3-5].

Adsorption with easy and inexpensive regeneration is a desirable means to control the emissions of aromatic pollutants from industrial wastewaters as it allows for capture, recovery and reuse of those compounds [6].

Synthetic porous polymeric sorbents (i.e., resins) are excellent adsorbents for phenolic compounds and, due to their higher physicochemical stabilities and better regeneration properties have been commercialized as alternatives to activated carbon for adsorption-oriented applications [7].

In the present study, some polymeric adsorbents containing aminophosphonic groups were tested in batch experiments for phenolic compounds (2,3-dimethylphenol and 2,4,6-trimethylphenol) adsorption from aqueous solutions. The presence of functional groups (type aminophosphonic acid) on the surface of styrene-divinylbenzene copolymers results in a higher surface polarity and hydrophilicity and these features improve the sorption of phenolic compounds.

Experimental part

Reagents and instruments

Chloromethylated styrene-divinylbenzene copolymer was used as starting material and was supplied by Purolite Romania (St-6.7%DVB chloromethylated, %Cl= 14.22, $G_p = 4.01$ mmol Cl/g copolymer).

Concentration of phenolic compounds (2,3 dimethylphenol and 2,4,6 trimethylphenol) was determined using a Shimadzu UV mini 1240 UV-VIS spectrophotometer at the wavelength $\lambda = 267$ nm (2,3 dimethylphenol) and 270 nm (2,4,6 trimethylphenol) respectively.

Chemical modification of poly(styrene-co-divinylbenzene)

The synthesis of the S-DVB copolymers functionalized with aldehyde was performed by the method previously described [8-12].

5 g of styrene-divinylbenzene copolymer grafted with aldehyde (*CHO-3oxi*, *CHO-4oxi* and *CHO-2oxi* respectively), phosphorous acid, isopropylamine and 50 mL of dimethylformamide were added to a 100 mL round bottom flask equipped with a reflux condenser, mechanical stirrer and thermometer. The molar ratio S-DVB grafted with aldehyde (*CHO-3oxi*, *CHO-4oxi* and *CHO-2oxi* respectively) : isopropylamine : phosphorous acid was 1: 1: 1.5. The mixture was stirred for 24 h at 60°C. After cooling, the polymer beads were filtered washed with methanol (3 x 20mL), acetone (3 x 20mL, and diethyl ether (3x20mL) and dried at 50 °C for 24 h.

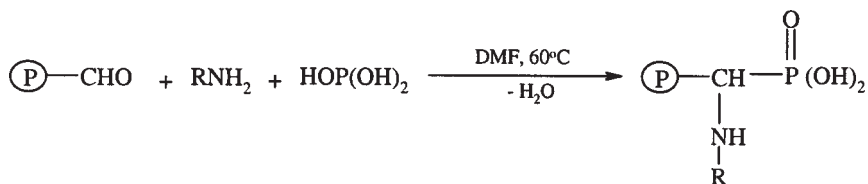
Procedure of the batch adsorption experiment

The procedure of the adsorption of phenolic compounds was performed by the method previously described [9, 10].

Batch adsorption tests were carried out in 200-mL Erlenmeyer flasks. To start the experiment, 0.200 g of polymeric adsorbent (1E-*CHO-3oxi*, 2E-*CHO-4oxi* and 3E-*CHO-2oxi* respectively) were introduced in to 25 mL phenolic compounds solution (S) with 3 mmol/L concentration of (2,3 dimethylphenolic, 2,4,6-trimethylphenolic) compound, at a solution-adsorbent weight ratio, S: 1E/2E/3E = 1:8 and temperature of 20°C. The contents of the flask were mixed using a magnetic stirrer. The amount of 1 mL of phenolic compound solutions were sampled from the flask at various time intervals (from 1 h to 1h) to analyze the phenolic compounds uptakes on the adsorbent until the adsorption equilibrium was reached.

Preliminary experiments showed that adsorption equilibrium was reached within 24 h. At the end of the

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Scheme 1. Obtaining of aminophosphonic acid on polymeric support where: P- copolymer styrene-6,7%divinylbenzene (grafted with aldehyde group in *m*-, *p*-, *o*-); R-NH₂= izopropylamine; HOP(OH)₂

No.	Code	R-NH ₂	R-CHO	P (% w)	G _F (mmoles - P(O)(OH) ₂ /g copolymer)
1	1E	(CH ₃) ₂ CH-NH ₂	<i>para</i> -aldehyde polymer	1.36	1.79
2	2E	(CH ₃) ₂ CH-NH ₂	<i>orto</i> -aldehyde polymer	1.52	1.71
3	3E	(CH ₃) ₂ CH-NH ₂	<i>meta</i> -aldehyde polymer	1.49	1.84

Table 1
EXPERIMENTAL DATA OF S-6.7% DVB COPOLYMERS WITH AMINOPHOSPHONIC GROUPS

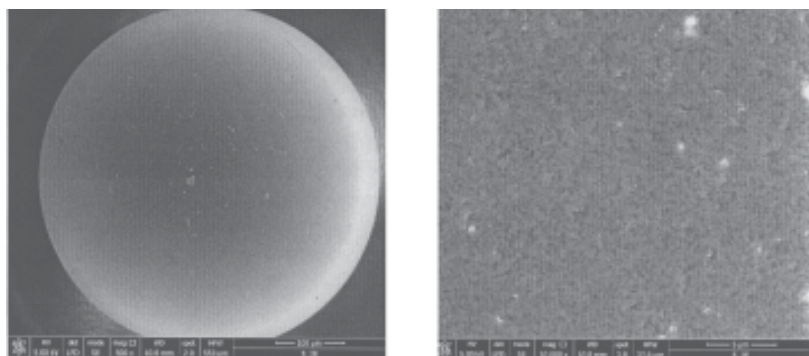


Fig. 1 SEM image for S-6.7%DVB copolymers with aminophosphonic groups (2E)

equilibrium period the contents of the bottles were vacuum-filtered and the supernatant was subsequently analyzed for remanent concentration of phenolic compounds (2,3-dimethylphenol and 2,4,6-trimethylphenol respectively), using the UV spectrophotometry.

Results and discussions

Characterization of aminophosphonic grafted on St-DVB copolymer

The polymer-analogous reaction for the obtaining of aminophosphonic acid groups grafted on styrene-divinylbenzene copolymer is presented above in scheme 1.

The characteristics of aminophosphonic acid groups grafted on polymeric support by polymer-analogous reactions are given in table 1.

The SEM micrographs of sample (2E) are presented in figure 1. The S-6.7% DVB copolymers functionalized with aminophosphonic particles can be regarded as macroporous polymer materials.

Adsorption studies

The concentration of 2,3-dimethylphenol and 2,4,6-trimethylphenol in aqueous solution was determined by UV analysis performed on a Shimadzu UV-VIS spectrophotometer at the wavelength $\lambda=267$ nm and $\lambda=270$ nm. The UV absorption spectra of the 2,3-dimethylphenol in aqueous solution and the spectra of 2,4,6-trimethylphenol are presented in figures 2, 3.

The adsorption performance is expressed as the adsorption capacity (mmoles/g) of the adsorbent. The effect of contact time on 2,3 dimethylphenol and 2,4,6-trimethylphenol adsorption on the studied aminophosphonic resins is presented in figures 4, 5. The contact time varied in the range 0-24 h, the initial concentration was fixed 3 mmoles/L. The adsorption capacities of all copolymers functionalized with chelating aminophosphonic acid groups increased as the contact time.

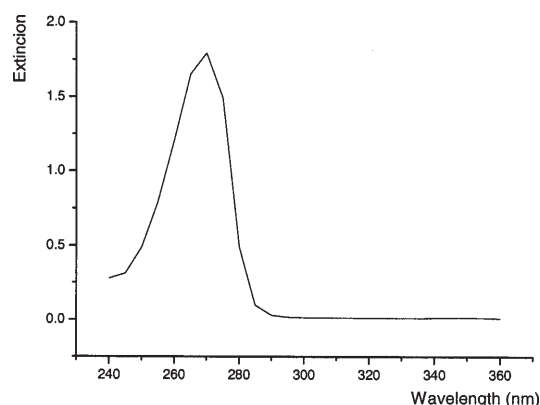


Fig. 2. UV absorption spectra of 2,3-dimethylphenol in aqueous solution

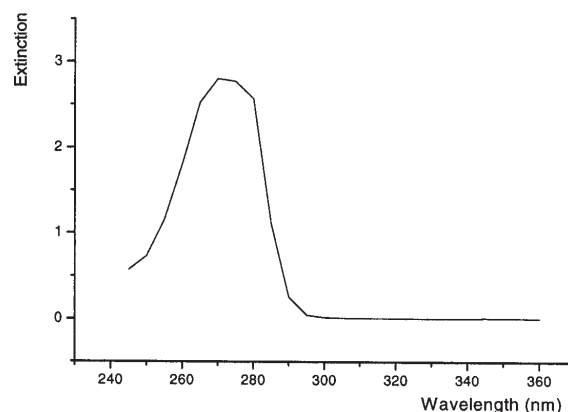


Fig. 3. UV absorption spectra of 2,4,6-trimethylphenol in aqueous solution

The adsorption process is very fast in the first five hours and becomes slower near the equilibrium. Equilibrium is reached after 24 h, at 20°C (fig. 4, 5).

The equilibrium concentrations of compounds were determined by spectrophotometric method. The

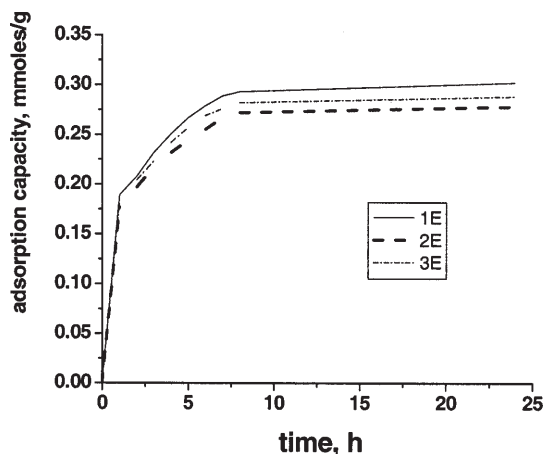


Fig. 4. Adsorption capacity of poly(styrene-co-divinylbenzene) functionalized with isopropylaminophosphonic acid (1E, 2E, 3E) with 2,3 dimethylphenol

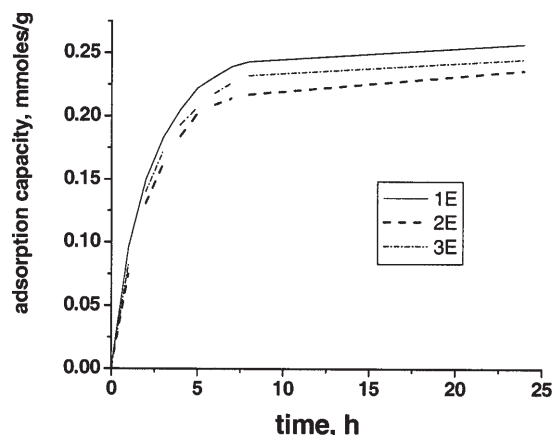


Fig. 5. Adsorption capacity of poly(styrene-co-divinylbenzene) functionalized with isopropylaminophosphonic acid (1E, 2E, 3E) with 2,4,6-trimethylphenol

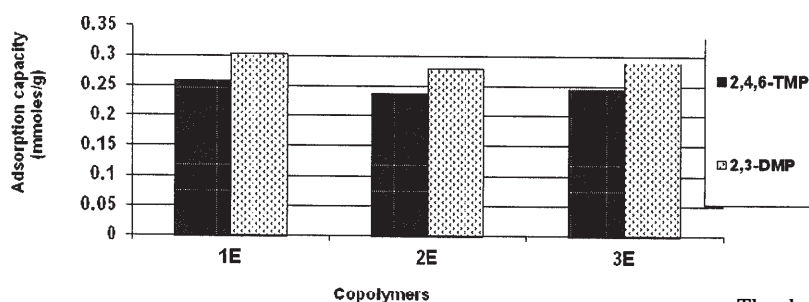


Fig. 6. Equilibrium adsorption capacities (Q_e , mmoles/g) of poly(styrene-co-divinylbenzene) functionalized with isopropylaminophosphonic acid (1E, 2E, 3E) with 2,3 dimethylphenol and 2,4,6-trimethylphenol after 24 h

equilibrium adsorption capacities (Q_e , mmoles/g) were calculated by the following equations:

$$Q_e = \frac{V_1(C_0 - C_e)}{W} \quad (1)$$

where V_1 is the volume of solution (L), W is the mass of dry adsorbent (g), C_0 and C_e (mmoles/L) denote the initial and equilibrium concentration of 2,4,6-trimethylphenol and 2,3-dimethylphenol (at 24 h) in aqueous solution, respectively.

The equilibrium adsorption capacity of 2,4,6-trimethylphenol and 2,3-dimethylphenol (at 24 h) on polymeric adsorbents with S-6.7% DVB copolymers grafted with aminophosphonic groups are shown in figure 6.

At equilibrium, 2,3-dimethylphenol is recovered on polymeric adsorbents with aminophosphonic groups (1E, 2E and 3E) and values are higher than those obtained at the recovery of 2,4,6-trimethylphenol from aqueous solution by the same polymeric adsorbents.

The adsorption capacity of the functionalized polymers 2E with the aminophosphonic group in *ortho* position is lower than adsorption capacity of the functionalized polymers 1E and 3E with the aminophosphonic group in *para* and *meta* position.

The best results were obtained for polymer 1E in the adsorption of 2,3 dimethylphenol ($Q_e = 0.302$ mmoles/g) and 2,4,6-trimethylphenol ($Q_e = 0.257$ mmoles/g).

The results obtained in this study showed that the polymeric adsorbents 1E, 2E and 3E can be used for the removal of phenolic compounds from aqueous solutions.

Conclusions

The experiments showed that the adsorption of both 2,3 dimethylphenol and 2,4,6-trimethylphenol is fast at the initial stages and becomes slower near the equilibrium.

Equilibrium is reached after 24 h, at 20 °C.

The best results were obtained for polymer 1E in the adsorption of 2,3 dimethylphenol ($Q_e = 0.302$ mmoles/g) and 2,4,6-trimethylphenol ($Q_e = 0.257$ mmoles/g).

The results obtained in this study showed that the adsorbent polymers 1E, 2E and 3E can be used for the removal of 2,3 dimethylphenol and 2,4,6-trimethylphenol from aqueous solutions.

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Manuscript received: 5.12.2013