

Adsorption of Phenol or Phenol Derivatives onto Styrene-1%(15%)divinylbenzene Polymeric Adsorbents Functionalized with Aminopropyl(benzyl)phosphonic Groups

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Removal of aromatic pollutants from water by means of adsorption has received great interest, being well known as an effective, efficient and economical method for water regeneration applications. So the elimination of phenol or phenol derivatives from industrial wastewater using adsorption techniques has been a focus for research in recent decades. In this paper, polymeric adsorbents based on styrene-1% (15%)divinylbenzene chemically modified with pendant aminophosphonic groups were prepared and tested in the removal process of phenol or phenol derivatives (2,3-dimethylphenol, and 2,4,6-trimethylphenol) from aqueous solutions.

Keywords: polymeric adsorbents, aminophosphonic groups, phenol, phenol derivatives (2,3-dimethylphenol, and 2,4,6-trimethylphenol)

Water pollution especially caused by industrial wastewater containing aromatic compounds is a major environmental problem. Phenol is a dangerous pollutant frequently found and its removal from water is important in environmental research [1]. Due to their toxicity and possible accumulation in the environment, the efficient removal of phenols has attracted significant attention. They are generally considered to be among the most dangerous organic pollutants discharged in the environment causing unpleasant taste and odor and toxicity problems in drinking water.

Phenol derivatives are difficult to process by conventional methods of treatment, such as activated sludge digestion, solvent extraction, chemical treatment, adsorption, etc [2].

Adsorption is well known as an effective, efficient and economical method in water regeneration applications and analytical separations. So the removal of phenol or phenol derivatives from industrial wastewater using adsorption processes has received important research interest in recent decades.

Polymeric adsorbents were used throughout for effective removal of specific organic compounds from contaminated water. To achieve a high adsorption capacity for specific organic compounds, chemical modification of polymeric adsorbents was often adopted by introducing specific functional groups as active centers on/in the adsorbent matrix [3-7].

In this paper, we describe some results obtained in the synthesis of polymeric adsorbents functionalized with aminophosphonic groups by one-pot Kabachnik-Fields reaction [8-10], their characterization and testing, for the first time, in order to achieve the removal of phenol derivatives (phenol, 2,3-dimethylphenol, and 2,4,6-trimethylphenol) from aqueous solutions.

Experimental part

Chemical reagents

Styrene-1% divinylbenzene copolymer with amino groups (Fluka, 2 mmoles amino groups/g polymer), phosphorus acid (Aldrich, 99%), benzaldehyde (Merck, p.a.), propionaldehyde (Merck, p.a.), methanol, acetone and diethyl ether (Chimreactiv, p.a) were used. Styrene-15%divinylbenzene copolymer with amino groups (N=2.7%; Cl_{residual}=4.05%) [11, 12] was used.

All chemicals used for experiments were of analytical reagent grade and were used without further purification. Distilled water was used in all experiments.

Styrene-1%(15%)divinylbenzene copolymers functionalized with aminophosphonic acid groups

The synthesis of styrene-divinylbenzene copolymer adsorbent functionalized with aminophosphonic groups, was performed by methods previously described [11-13].

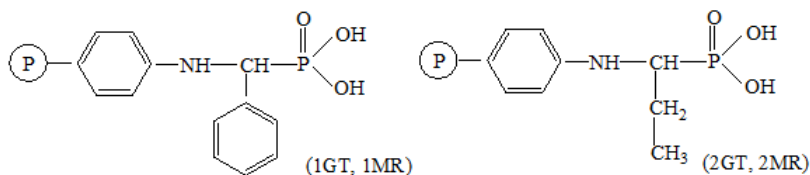
A mixture of 5 g of styrene-1%divinylbenzene gel-type copolymer bearing amino groups (GT) (or 5 g of styrene-15%divinylbenzene macroreticular, macroporous copolymer bearing amino groups (MR)), phosphorous acid, benzaldehyde (or propionaldehyde) and 50 mL tetrahydrofuran was maintained under stirring for 24 h at 55°C. The molar ratio of amino groups: phosphorous acid: benzaldehyde (or propionaldehyde) was 1 : 1.5 : 1.

After cooling, the polymer beads were separated by filtration, washed with methanol (3x20mL), acetone (3x20mL) and diethyl ether (3x20mL) and dried at 50°C for 24 h.

Adsorption experiments

Batch adsorption studies were carried out in 200-mL Erlenmeyer flasks. To start the experiment, 0.200 g of polymeric adsorbent were added to 25 mL solution

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Scheme 1. Prepared polymeric adsorbent functionalized with aminophosphonic groups, where:
 P - copolymer styrene-1%divinylbenzene gel type (functionalized with aminobenzylphosphonic groups (1GT) or aminopropylphosphonic groups (2GT))
 P - copolymer styrene-15%divinylbenzene (functionalized with aminobenzylphosphonic groups (1MR) or aminopropylphosphonic groups (2MR))

containing 3 mmoles/L phenol or phenol derivative (2,3-dimethylphenol, 2,4,6-trimethylphenol) at 298 K. The content of the flask was mixed using a Julabo SW22 shaker. Samples of 1 mL of reaction mixture were taken at time intervals in order to determine the phenol uptake by the adsorbent until the adsorption equilibrium was reached.

The concentration of phenol derivatives was determined by non-destructive UV spectrophotometric analysis of the samples as they were taken. After analysis the samples were returned to the reaction mixture.

The experiments showed that adsorption equilibrium was reached after around 24 h.

Characterization

The phosphorus content was determined according to the modified Schöniger method [14-16].

The polymeric adsorbents were characterized by Fourier-transform infrared spectroscopy (FT-IR) on a Shimadzu Prestige-21 FT-IR spectrophotometer (4000-400 cm^{-1} , KBr pellets).

Energy dispersive X-ray analysis (EDX) was performed using an Inspec S Scanning Electron Microscope (SEM), which also provided imaging capabilities.

The residual concentrations of phenol compounds were determined using a Shimadzu UV mini 1240 UV-VIS spectrophotometer, measuring the absorption of phenol solutions at the wavelength of 270 nm, at 267 nm for 2,3-dimethylphenol and at 270 nm for 2,4,6-trimethylphenol solutions.

Results and discussions

Characterization polymeric adsorbents functionalized with aminophosphonic groups

The method for the preparation of styrene-1%(15%)divinylbenzene copolymers functionalized with aminophosphonic acid groups has been reported in previous papers [11-13].

Aminobenzylphosphonic groups or aminopropylphosphonic groups were introduced on styrene-1%divinylbenzene gel type or styrene-15%divinylbenzene, macroreticular, macroporous copolymers by use of polymer-analogous reactions. The products are presented in scheme 1.

The characteristics of the polymeric adsorbents are presented in table 1.

The functionalization degrees (G_f) are suitable for a polymeric adsorbent and correlated with the type of copolymer precursor used: gel-type, styrene-1%divinylbenzene or macroporous, macroreticular styrene-15%divinylbenzene (table 1).

The obtained polymeric resins were characterized by Fourier-transform infrared spectroscopy (FT-IR). The presence of the system of bands between 3200 and 3400 cm^{-1} and the decrease in the intensity of amino group adsorption band around at 1575 cm^{-1} confirmed the functionalization reaction took place at the amino group level. In addition, the bands around 1035 cm^{-1} and 1380 cm^{-1} are assigned to the P-OH and respectively P=O vibrations from the phosphonic groups, as previously described [11-13].

Table 1

CHARACTERISTIC DATA OF THE POLYMERIC ADSORBENTS FUNCTIONALIZED WITH AMINOPHOSPHONIC ACID GROUPS

Adsorbent code	Polymer precursor	P (% weight)	G_f , mmoles aminophosphonic acid groups /g of copolymer
1GT	S-1%DVB-NH ₂	4.10	1.40
2GT	S-1%DVB-NH ₂	3.98	1.48
1MR	S-15%DVB-NH ₂	4.04	1.57
2MR	S-15%DVB-NH ₂	4.80	1.66

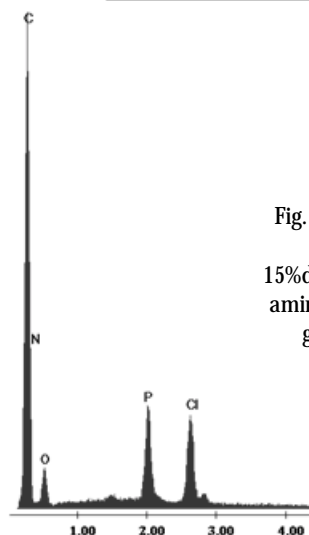


Fig. 1. The EDX spectrum of copolymer styrene-15%divinylbenzene containing aminopropylphosphonic acid groups (2MR) sample.

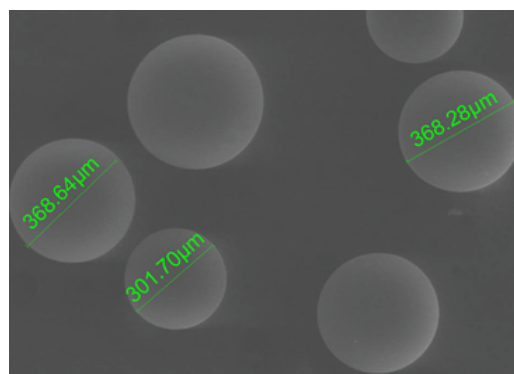


Fig. 2. SEM image for the copolymer styrene-15%divinylbenzene containing aminopropylphosphonic acid groups 2MR

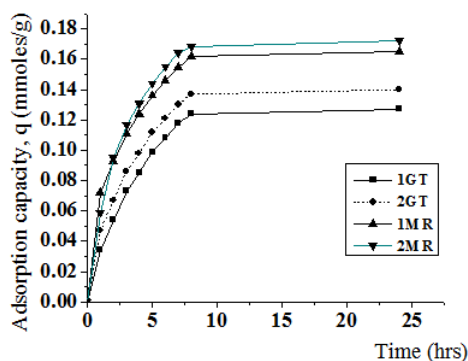


Fig. 3 Adsorption capacities towards phenol in aqueous solution for 1GT, 2GT, 1MR and 2MR polymeric adsorbents; (0.2 g adsorbent; adsorbate initial concentration 3.0 mmoles/L, 298 K)

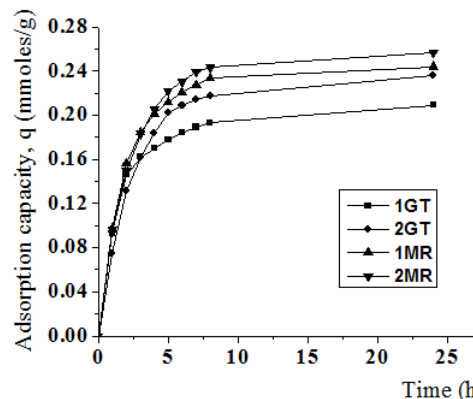


Fig. 5 Adsorption capacities towards 2,4,6-trimethylphenol in aqueous solution for 1GT, 2GT, 1MR and 2MR polymeric adsorbents; (0.2 g adsorbent; adsorbate initial concentration 3.0 mmoles/L, 298 K)

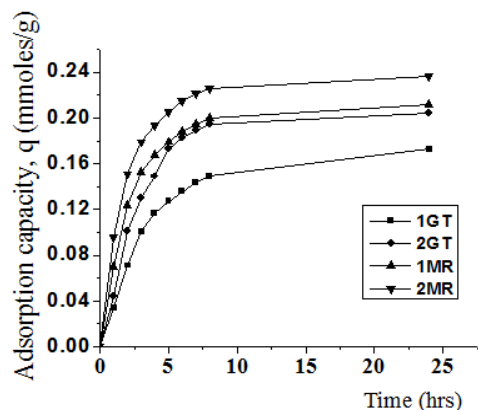


Fig. 4 Adsorption capacities towards 2,3-dimethylphenol in aqueous solution for 1GT, 2GT, 1MR and 2MR polymeric adsorbents; (0.2 g adsorbent; adsorbate initial concentration 3.0 mmoles/L, 298 K)

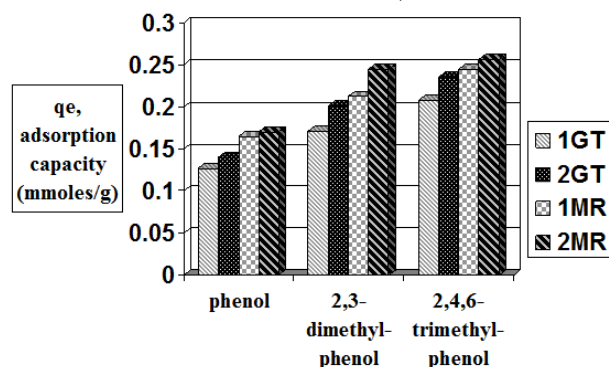


Fig. 6 The adsorption capacity of polymeric adsorbents: 1GT, 2GT, 1MR and 2MR towards phenol, 2,3-dimethylphenol or 2,4,6-trimethylphenol, after 24h, at 298K

The EDX spectrum of the polymeric adsorbent 2MR containing aminopropylphosphonic acid groups is presented in figure 1. The signal assigned to phosphorous proves the presence of aminophosphonic acid groups in the polymer matrix. Similar EDX spectra were obtained also for the other polymeric adsorbents (1GT, 2GT or 1MR).

The Scanning Electronic Microscopy (SEM) image (fig. 2) of the polymeric adsorbent 2MR containing aminopropylphosphonic acid groups indicates particle size in the range of 300 to 370 μm .

Adsorption of phenol compounds onto polymeric adsorbents

The residual concentration of phenol or phenol derivatives in aqueous solutions was determined by UV analysis performed on a Shimadzu UV mini 1240 UV-Vis spectrophotometer.

Adsorption capacities presented in figures 3-5 showed that the adsorption of phenol or phenol derivatives is fast in the initial stages, (4-5 h) and then tend to saturation near the equilibrium.

The equilibrium concentration of the adsorbate was determined by spectrophotometric method. The recovery

degree (R , %) and equilibrium adsorption capacities (q_e , mmoles/g) were calculated with the following equations [17-19]:

$$R = (C_0 - C_e) / C_0 \times 100 \quad (1)$$

$$q_e = \frac{V_1(C_0 - C_e)}{W} \quad (2)$$

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 respectively equilibrium concentration of the adsorbate in aqueous solution.

A comparison of the adsorption capacities for phenol or phenol derivatives on the polymeric adsorbent chemically modified by polymer-analogous reactions with aminophosphonic acid groups as active centers is presented in figure 6.

All the polymeric adsorbents functionalized with aminopropylphosphonic or aminobenzylphosphonic acid groups were examined for the recovery degree of phenol or phenol derivatives from aqueous solutions. The results are presented in table 2.

We have observed that all the functionalized copolymers studied are effective in the removal phenol derivatives from

Table 2
RECOVERY DEGREE (R , %) OF PHENOL OR PHENOL DERIVATIVES FROM AQUEOUS SOLUTIONS USING POLYMERIC ADSORBENTS

Phenol derivative	Recovery degree, R%			
	1GT	2GT	1MR	2MR
Phenol	33.97	37.43	44.20	45.43
2,3-dimethylphenol	45.90	53.96	56.70	63.10
2,4,6-trimethylphenol	55.53	63.00	65.23	68.60

aqueous solutions. The efficiency is higher for substituted phenol derivatives (2,3-dimethylphenol and 2,4,6-trimethylphenol) in comparison with phenol.

At equilibrium, the recovery degree for 2,4,6-trimethylphenol is 55.53% using 1GT polymeric adsorbent, 63.00% with 2GT, 65.23% with 1MR and 68.60% with 2MR and the values are higher than those obtained in the removal of 2,3-dimethylphenol or phenol.

Polymeric adsorbents with aminoalkylphosphonic acid active centers are more effective in comparison with the counterparts bearing aminoarylphosphonic acid groups. Styrene-15%divinylbenzene, macroreticular, macroporous copolymers chemically modified with aminophosphonic groups were proved to be more effective in comparison with the styrene-1%divinylbenzene gel type chemically modified with aminophosphonic groups.

Functionalized copolymers that have been most effective in removing phenol derivatives were 1MR (macroreticular, macroporous, styrene-15%divinylbenzene copolymer containing aminobenzylphosphonic acid groups) and 2MR (macroreticular, macroporous, styrene-15%divinylbenzene copolymer containing aminopropylphosphonic acid groups).

The adsorption process speed is high in the first 4-5 h. In this time interval over 70% of the adsorbate is removed. Therefore the polymeric materials designed, prepared, characterized and tested are suitable for use as macromolecular adsorbents for phenol or phenol derivatives from aqueous solution.

The best results were obtained with the macroreticular, macroporous copolymer styrene-15%divinylbenzene containing aminopropylphosphonic acid groups (2MR) when used for removal of 2,4,6-trimethylphenol at room temperature. The adsorption capacity in this case was 0.257 mmoles adsorbate/g of copolymer.

Conclusions

Styrene-1%(15%)divinylbenzene copolymers functionalized with aminopropyl-phosphonic or aminobenzylphosphonic acid groups were obtained with good functionalized degrees.

Adsorption experiments showed that the adsorption of phenol or phenol derivatives is fast in the initial stages and shows saturation near equilibrium.

Functionalized copolymers proved to be most efficient in removing phenol or phenol derivatives were 1MR, macroporous, macroreticular styrene-15%divinylbenzene copolymer containing aminobenzylphosphonic acid groups as active centers and 2MR, macroporous, macroreticular styrene-15%divinylbenzene copolymer containing aminopropylphosphonic acid groups as active centers.

The best results were obtained with the styrene-15%divinylbenzene adsorbent containing aminopropyl-

phosphonic acid groups (2MR) when used for removal of 2,4,6-trimethylphenol at room temperature. The adsorption capacity was in this case 0.257 mmoles adsorbate/g of adsorbent.

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