

Adsorption Characteristics of Some Polymeric Materials with Olefin Groups used for Removal of Phenol and *p*-nitrophenol from Aqueous Solutions

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Removal and recovery of aromatic pollutants from water by solid adsorbents have been of considerable interest. In this paper, adsorption of phenol and p-nitrophenol from aqueous solution onto a polymeric adsorbent with olefin groups at temperatures of 24°C was studied. The weak interactions between p-nitrophenol molecules and the polymeric adsorbents in batch adsorption experiments were observed.

Keywords: polymeric adsorbents, phenol, p-nitrophenol, removal

Water pollution is indeed of great concern since it is a major carrier of both organic and inorganic contaminants [1].

Phenolic compounds are considered to be dangerous wastes, which are released into the aquatic environment by industries such as coke ovens in steel plants, petroleum refineries, petrochemical, phenolic resin, and pharmaceutical, chemical, and dye industries, etc. The discharge of phenolic waste into waterways may adversely affect human health as well as that of flora and fauna. Ingestion of a small amount of phenol by human beings may cause nausea, vomiting, paralysis, coma, greenish or smoky colored urine, and even death from respiratory failure or cardiac arrests [2 - 5].

Various processes such as oxidation, biodegradation, solvent extraction, incineration, reverse osmosis and adsorption have been proposed to remove phenolic compounds from contaminated waters, among which adsorption is one of the most effective techniques in either laboratory or industrial scale. As a widely used adsorbent, activated carbon always exhibits satisfactory performance for phenol removal, however, its wider application is restricted due to the high operation costs and relatively poor mechanical strength. In recent years, considerable attention has also been devoted to the study involving different types of low-cost materials. More recently, polymeric adsorbents have attracted increasing interest in this problem of removal of phenolic compounds from industrial effluents. Their excellent performances for phenol removal are tightly associated with their high capacity, satisfactory mechanical strength and feasible regeneration under mild conditions [6].

In the present study, some polymeric adsorbents with olefin groups were tested in batch experiments for phenol and *p*-nitrophenol adsorption from aqueous solutions. These functional groups introduced to the polymer matrix are able to modify the surface chemistry of the adsorbent allowing specific adsorbent-adsorbate interactions and then to improve adsorption behavior of organic compounds.

Experimental part

Materials

Methyltriphenylphosphonium bromide, tetraethylammonium iodide, dimethylformamide and tetrahydrofuran, 1,2-dichloromethane, ethanol, ethyl ether, methanol, acetone were used as received. Chloromethylated styrene-divinylbenzene copolymer was used as starting materials (St-6.7%DVB chloromethylated, %Cl=14.22, $G_F = 4.01$ mmols Cl/g. copolymer).

Apparatus

Phenol and *p*-nitrophenol concentrations were determined using a Shimadzu UV mini 1240 UV-VIS spectrophotometer at the wavelength $\lambda = 270$ nm (phenol) and 315 nm (*p*-nitrophenol) respectively.

Chemical modification of poly(styrene-co-divinylbenzene) Reactions with 4-Hydroxy and 2-Hydroxy-Benzaldehyde under PTC Conditions

The synthesis of the S-DVB copolymers functionalized with benzaldehyde was performed by the method previously described [7].

This modification starts by mixing of 5 g chloromethylated styrene-divinylbenzene copolymer for 24 h with 40 mL *N,N*-dimethylformamide. The swollen copolymer was treated with 4-hydroxybenzaldehyde (or 2-hydroxybenzaldehyde), 0.2 mmols of tetraethylammonium iodide and 100 mL aqueous K_2CO_3 (30%). The molar ratio of chloromethyl groups: 4-hydroxybenzaldehyde (or 2-hydroxybenzaldehyde) was 1:2. The mixture was maintained under stirring for 16 h at a temperature of 95°C. After cooling, the polymer beads were separated by filtration, washed with methanol, distilled water, acetone and finally with diethyl ether and dried at 50°C for 24 h.

Wittig Reaction for obtaining polymeric adsorbents with olefin groups

The synthesis of the S-DVB copolymers functionalized with olefin groups follows our method previously described [8].

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A mixture of 4-benzaldehyde (2.92 mmols/g) (1) or 2-benzaldehyde (2.77 mmols/g) (2) respectively grafted on styrene-6.7%-divinylbenzene copolymer (1 g), tetraethylammonium iodide (0.05 g), solvent (THF/CH₃OH = 1:1) (20 mL), K₂CO₃ (0.55 g) and a salt (methyltriphenylphosphonium bromide) were stirred 20 h at 60°C. The molar ratio 4-benzaldehyde (type 1), or 2-benzaldehyde (type 2) respectively, grafted on styrene-6.7% divinylbenzene copolymer : phosphonium salt was 1:2. The final product was separated by filtration, washed with ethanol, methylenechloride, diethyl ether, and then dried at 50°C for 24 h.

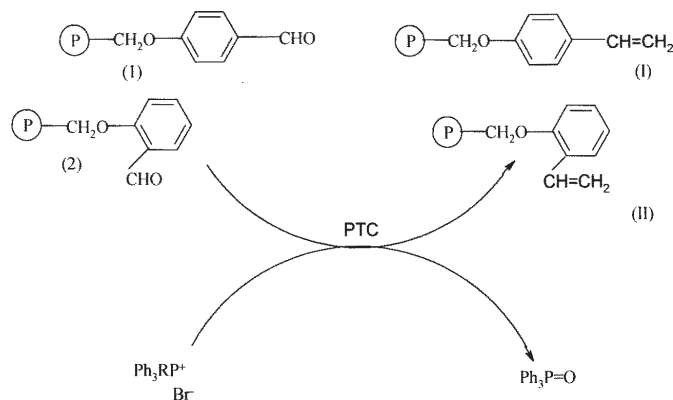
Sorbents characterization

Determination of the chlorine content:

A sample of the final reaction product, precisely weighted, was burnt out in an oxygen atmosphere; the gases were absorbed in an aqueous solution of H₂O₂ (0.15 %W) and the chloride ion was quantitatively determined by potentiometric titration with an aqueous solution of AgNO₃ 0.05M [8, 9].

Determination of the double bond content

To a sample of the final product, precisely weighted (~200 mg), 10 mL carbon tetrachloride, 10 mL distilled water, 40 mL 0.05N KBrO₃-KBr and 10 mL 10% H₂SO₄ were added. The mixture was kept under continuously stirring. After 2 h another 4 mL 0.05 N KBrO₃-KBr and 1 mL H₂SO₄ were added and this operation was repeated until the yellow-brown color persists 10 min. Then 10 mL 20% KI was added. The iodide was titrated with 0.1 N Na₂S₂O₃ until the color is changed in yellow then 0.5 mL 1% starch was added and the titration was continued until complete discoloring [7-9].



Scheme 1. Wittig reaction for obtaining polymeric adsorbents with olefin groups

Procedure of the batch adsorption experiment

Batch adsorption tests were carried out in 200-mL Erlenmeyer flasks. To start the experiment, 0.200 g of polymeric adsorbent (I and II respectively) were introduced in 25 mL phenol solution (S) with 4 mmols/L concentration, at a solution-adsorbent weight ratio, S:I/II=1:8 and temperature of 24 °C. The contents of the flask were mixed using a magnetic stirrer. The amount of 1 mL of phenol solution was sampled from the flask at various time intervals to analyze the phenol uptakes on the adsorbent until the adsorption equilibrium was reached.

A similar procedure was used for adsorption of *p*-nitrophenol from aqueous solutions. In this case, 100 mL pollutant solution with concentration of 0.275 mmols/L at a solution-adsorbent weight ratio S:I/II=1:2 and temperature of 24°C were used for batch adsorption tests.

Preliminary experiments showed that adsorption equilibrium was reached within 24 h. At the end of the equilibrium period the contents of the bottles were vacuum-filtered and the supernatant was subsequently analyzed for remanent concentration of phenol and *p*-nitrophenol respectively, using the UV spectrophotometry.

Results and discussions

Wittig reactions on polymer supports are presented in Scheme 1. The characteristics of the olefin grafted on polymeric supports are given in table 1.

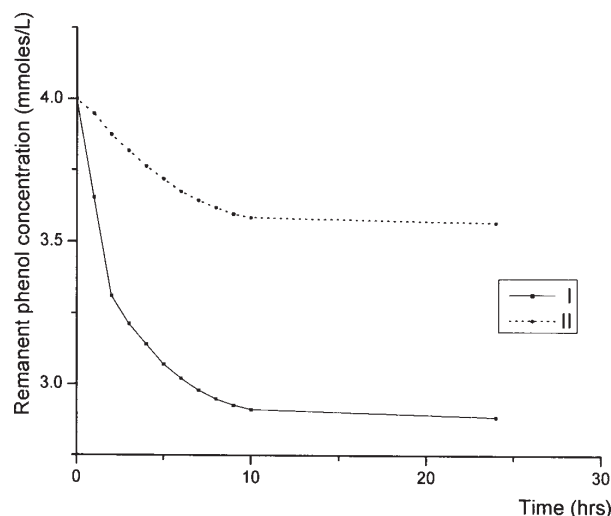


Fig. 1. Representation of the remanent concentration of phenol in aqueous solution for I and II functionalized polymers, previously described, I and II (0.2g), S:I/II=1:8, [phenol] = 4mmols/L

Table 1
CHARACTERISATION OF POLYMERIC ADSORBENTS WITH OLEFIN GROUPS

No.	olefin grafted on polymeric adsorbent	G _F (mmoles double bonds/g of poly(styrene-co-divinylbenzene))
1	I	2.15
2	II	2.05

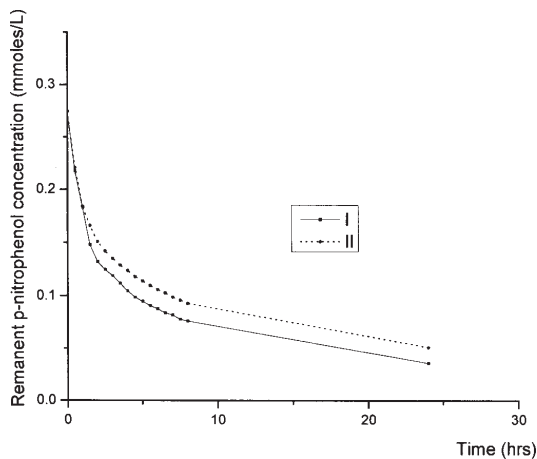


Fig. 2. Representation of the remanent concentration of *p*-nitrophenol in aqueous solution for I and II functionalized polymers, previously described, I and II (0.2g), S:I/II=1:2, [p-nitrophenol] = 0.275 mmols/L

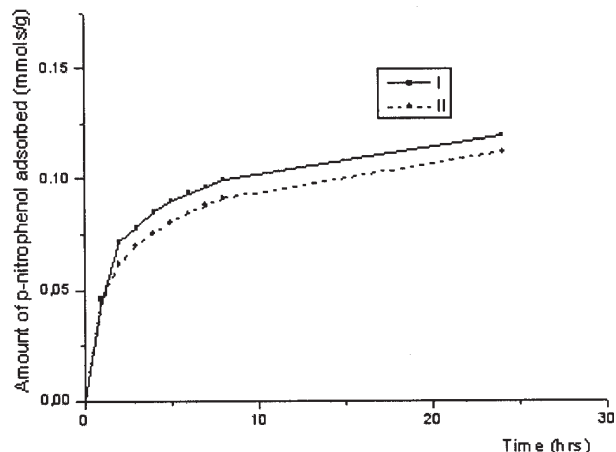


Fig. 4. Representation of the amount of *p*-nitrophenol adsorbed by the two functionalized polymers previously described, I and II (0.2g), S:I/II=1:2, [p-nitrophenol] = 0.275 mmols/L

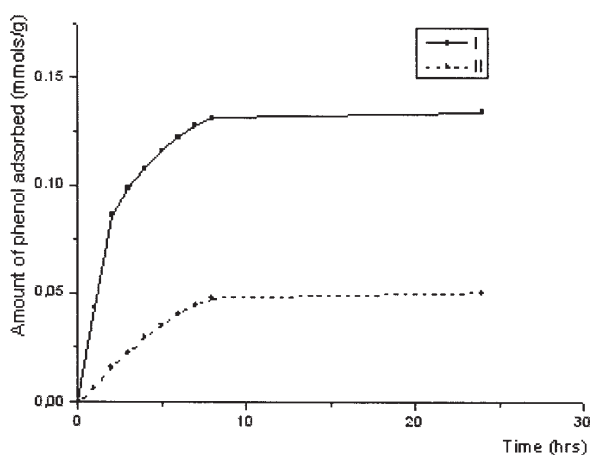


Fig. 3. Representation of the amount of phenol adsorbed by the two functionalized polymers previously described, I and II (0.2g), S:I/II=1:8, [phenol] = 4 mmols/L

The phenol adsorption dynamics from aqueous solution for I and II adsorbents from 0 to 24 h is presented in figure 3.

The *p*-nitrophenol adsorption dynamics from aqueous solution for I and II adsorbents from 0 to 24 h is presented in figure 4.

Adsorption of phenol and *p*-nitrophenol onto polymeric adsorbents

The concentration of phenol and *p*-nitrophenol in aqueous solution was determined by UV analysis performed on a Shimadzu UV-Vis spectrophotometer. For phenol, the characteristic absorption wavelength is 270 nm. At 315 nm is the characteristic absorption wavelength for *p*-nitrophenol.

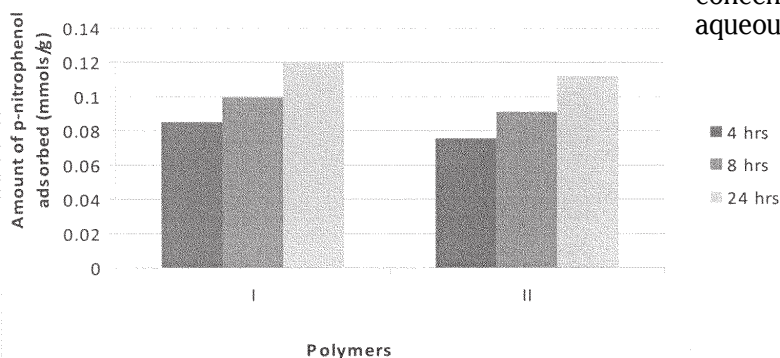


Fig. 6. Representation of the amount of *p*-nitrophenol adsorbed by the two functionalized polymers previously described, I and II at 4, 8 and 24 h

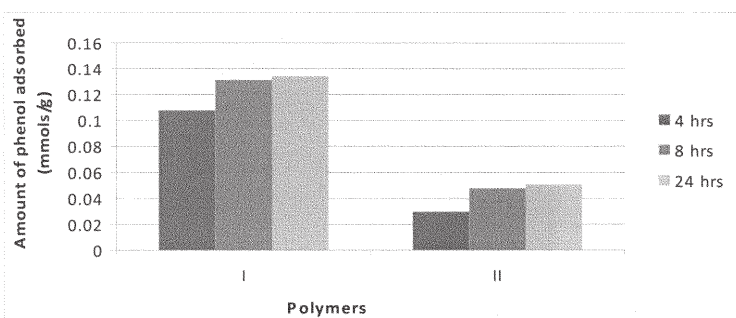


Fig. 5. Representation of the amount of phenol adsorbed by the two functionalized polymers previously described, I and II at 4, 8 and 24 h

The representation of the remanent concentration of phenol and *p*-nitrophenol in aqueous solution for I and II adsorbents from 0 to 24 h are presented in figures 1, 2.

Adsorption experiments presented in figures 5, 6 showed that the adsorption of phenol and *p*-nitrophenol is fast at the initial stages and become slower near the equilibrium.

The equilibrium concentrations of compounds were determined by spectrophotometric method. The recoveries (*R*, %) and equilibrium adsorption capacities (*Q_e*, mg/g) were calculated by the following equations:

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

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

where:

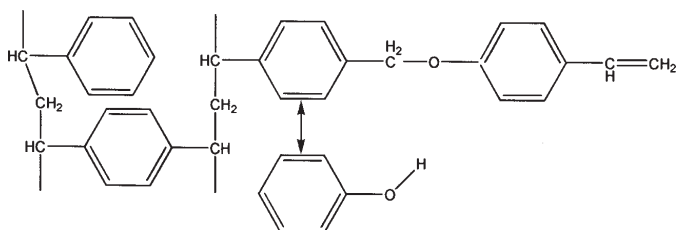
V₁ - the volume of solution (L),

W - the mass of dry adsorbent (g),

C₀ and *C_e* (mg/L) denote the initial and equilibrium concentration of phenol and *p*-nitrophenol (at 24 h) in aqueous solution, respectively.

Table 2
RECOVERIES (R, %) OF PHENOL AND *p*-NITROPHENOL FROM AQUEOUS SOLUTIONS BY POLYMERIC ADSORBENTS WITH OLEFIN GROUPS

polymeric adsorbents with olefin groups / aromatic pollutant	R, %
I / phenol	27.85
II / phenol	10.82
I / <i>p</i> -nitrophenol	86.91
II / <i>p</i> -nitrophenol	81.45



All of the synthesized polymeric adsorbents were examined for the recoveries of phenol and *p*-nitrophenol from aqueous solutions and the results are presented in table 2.

At equilibrium, *p*-nitrophenol is recovered 86.91% from aqueous solution by I polymeric adsorbent and 81.41% by II polymeric adsorbent and values are higher than those values obtained at the recovery of phenol from aqueous solution by polymeric adsorbents I and II.

The adsorption capacity of phenol and *p*-nitrophenol on polymeric adsorbents with olefin groups are shown in figure 7.

The adsorption capacity of aromatic pollutant (*p*-nitrophenol) adsorbed per mass unit of copolymer is higher for polymeric adsorbent I with olefin groups in *para* than the adsorption capacity of II adsorbent with olefin groups in *orto*.

The adsorption capacity of the aromatic ring on phenol molecule by π - π interaction [10] was proposed (fig. 8).

The weak interaction between the phenol and *p*-nitrophenol molecules and the polymeric adsorbents in batch adsorption experiments was observed.

Conclusions

The preliminary experiments showed that the adsorption of both phenol and *p*-nitrophenol is fast at the initial stages and becomes slower near the equilibrium. The rate of *p*-nitrophenol removal from water is very rapid during the initial 30 min and decreases thereafter.

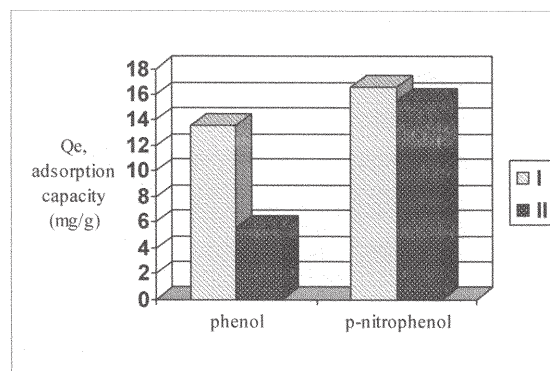


Fig. 7. The phenol and *p*-nitrophenol adsorbed from aqueous solution for polymers: I and II, at 24 h and 24 °C.

Fig. 8. The chemical structure of adsorbents and interactions between adsorbents and phenol.

The phenol and *p*-nitrophenol adsorption capacity of the functionalized polymer II with the olefin group in *orto* position is lower than the adsorption capacity of the functionalized polymer I with the olefin group in *para* position.

The best results were obtained for polymer I in the recovery of *p*-nitrophenol (R= 86.91 %) and its adsorption capacity ($Q_e=16.60$ mg/g).

References

- STEFAN D.S., BELCU M., STEFAN M., MARINESCU A., Rev.Chim. (Bucharest) **61**, no. 1, 2010, p. 31
- ZUMRIYE A., YENER J., Waste Manage., **21**, 2001, p. 695
- BASSO M.C., CERRELLA E.G., CUKIERMAN A.L., Ind. Eng. Chem. Res., **41**, 2001, p. 180
- PATTERSON J.W., Industrial Waste Water Treatment Technology, Ann Arbor Science Publication Inc, Ann Arbor, MI, 1985
- TERTIS M.C., JITARU M., SILAGHI-DUMITRESCU L., Rev.Chim. (Bucharest) **61**, no. 4, 2010, p. 360
- PAN B., PAN B., ZHANG W., ZHANG Q., ZHANG Q., ZHENG S., Journal of Hazardous Materials, **157**, 2008, p. 293
- POPA A., ILIA G., PASCARIU A., ILIESCU S., PLESU N., Chinese Journal of Polymer Science, **23(6)**, 2005, p.1
- POPA A., ILIA G., DAVIDESCU C.-M., ILIESCU S., MACARIE L., MARANESCU B., Mat. Plast., **43**, no. 1, 2006, p. 62
- POPA A., ILIA G., DAVIDESCU C.-M., ILIESCU S., PLESU N., PASCARIU A., ZHANG W., Polymer Bulletin, **57**, 2006, p. 189
- ZHANG W., DU Q., PAN B., LV L., HONG C., JIANG Z.G., KONG D., Colloids and Surfaces A: Physicochem. Eng. Aspects, **346**, 2009, p. 34

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