

Adsorption of p-Nitrophenol from Water on Polymeric Adsorbents

R. Ardelean*, C.M. Davidescu* and A. Popa**

* University "Politehnica" Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Piata Victoriei no. 2, 300006 Timisoara, Romania, e-mail: radu.ardelean@chim.upt.ro

** Romanian Academy, Institute of Chemistry, 24 Mihai Viteazul Bul, 300223 Timisoara, Romania

Abstract: Water pollution, especially the industrial wastewater containing aromatic compounds, is one of the most urgent environmental problems. Phenolic compounds are pollutants of great concern because of the high toxicity and possible accumulation in the environment. Most of these compounds are recognized as organic contaminants in environmental systems. For p-nitrophenol adsorption on a specific polymeric adsorbent, the solute-adsorbent interaction will play an important role in the adsorption capacity from aqueous solution. In this preliminary study, a polymeric adsorbent P1n was prepared from benzaldehyde poly(styrene-co-divinylbenzene), and it together with amberlite, XAD-4 were thereafter tested in batch experiments for adsorption of p-nitrophenol from aqueous solutions. Amberlite XAD-4 with single π - π stacking or hydrogen bonding interaction, respectively, was selected as comparative resin.

Keywords: adsorption, p-nitrophenol, amberlite

1. Introduction

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. Different techniques have been applied to remove or eliminate phenolic compounds from polluted waters, including chemical oxidation, chemical coagulation, solvent extraction, membrane techniques and adsorption. Adsorption by uncharged polymeric resins has been widely studied as an effective technique for removing hydrocarbons from wastewater. The use of this technique depends on various factors such as temperature, pH and sorbent characteristics such as microporosity and chemical properties [6].

Phenolic compounds are pollutants of great concern because of the high toxicity and possible accumulation in the environment. Most of these compounds are recognized as organic contaminants in environmental systems [3,4].

For p-nitrophenol adsorption on a specific polymeric adsorbent, the solute-adsorbent interaction will play an important role in the adsorption capacity from aqueous solution.

For a commercially available polymeric adsorbent, such as amberlite XAD-4, it is generally known that van der Waals interaction is the main force to drive phenol molecules from bulk solution to adsorbent phase [5].

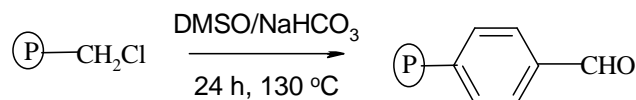
methanol (Chimopar), acetone (Chimopar). Chloromethylated styrene-divinylbenzene copolymer was used as starting materials and was supplied by Purolite Romania (St-6.7%DVB chloromethylated, %Cl= 14.22, $G_F = 4.01$ mmoles Cl/g. copolymer), Amberlite XAD-4 resin was purchased from Merck Company, (St-DVB, % Cl = 0, surface area: S, $m^2/g = 914$, Average pore diameter (nm) = 5.8, Particle size (mm) = 0.4-0.6.

Synthesis of chloromethylated styrene-divinylbenzene copolymer with benzaldehyde groups

The synthesis of the S-DVB copolymers functionalized with benzaldehyde groups was performed by the method previously described (Scheme 1) [1].

5 g sample of chloromethylated copolymer, sodium hydrogen carbonate (molar ratio – chloromethyl groups (CH_2Cl): $NaHCO_3 = 1:2$) and 100 ml dimethyl-sulfoxide were added to a 250 ml round bottom flask fitted with a reflux condenser, mechanical stirrer and thermometer. The mixture was maintained under stirring for 24 h at 130 °C.

After cooling, the polymer beads were separated by filtration, washed with DMSO, hot distilled water, methanol, acetone and finally with diethyl ether and dried at 50 °C for 24 hours.



Scheme 1. Obtaining of chloromethylated styrene-divinylbenzene copolymer with benzaldehyde groups

2. Experimental

Reagents

Methyltriphenylphosphonium bromide (Aldrich), tetraethylammonium iodide (Merck), dimethyl-sulfoxide (Fluka) and tetrahydrofurane (Fluka) 1,2-dichloromethane (Chimopar), ethanol (Chimopar), ethyl ether (Chimopar),

General procedure for Wittig reactions in phase transfer catalysis conditions

The synthesis of the S-6.7%DVB copolymers functionalized with olefin groups was performed by the method previously described [2].

A mixture of benzaldehyde (4.31 mmol/g) grafted on styrene-divinylbenzene copolymer (1 g), tetraethylammonium iodide (0.05 g), solvent (THF/CH₃OH=1:1) (20 ml), K₂CO₃ (0.55 g) and a methyltriphenylphosphonium bromide were stirred 20 hours at 60 °C. The molar ratio benzaldehyde grafted on styrene-divinylbenzene copolymer: phosphonate was 1:2. The final product was separated by filtration, washed with ethanol, methylenechloride, diethyl ether and then dried at 50 °C for 24 hours.

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 hours 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 minutes. 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 discoloration [2].

Determination of the adsorption capacity for XAD-4 resin and P1n adsorbent

Batch adsorption experiments were carried out by allowing an accurately weighted amount of P1n adsorbent and XAD-4 resin to reach equilibrium with p-nitrophenol solution of an initial concentration of 0,275 mmol/L at a temperature of 297 K.

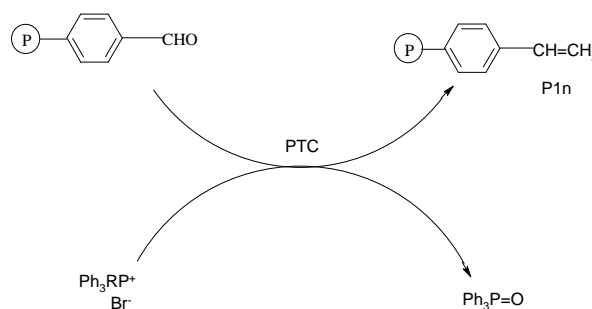
About 0.200 g of dry adsorbent was weighted and added into 100 mL of p-nitrophenol aqueous solution, using an 200 mL Erlenmeyer flask. The mixture was continuously stirred for 24 hours, using a magnetic stirrer, to reach the adsorption equilibrium. An amount of 1 mL solution was sampled from the flasks at various time intervals to determine adsorption kinetics. After 24 hours, the mixtures were vacuum-filtered in order to determine p-nitrophenol concentration at equilibrium. The residual concentration of p-nitrophenol was determined by UV spectrophotometry, measuring the absorption of p-nitrophenol solutions at a wavelength of 315 nm. For UV measurements we used a UV-VIS Shimadzu UVmini 1240 spectrophotometer.

3. Results and Discussion

Wittig reaction on polymer support is presented in scheme 2. The main characteristic of the olefin grafted on polymeric support is given in Table 1.

TABLE 1. Characterisation of copolymer obtained by Wittig reaction in PTC conditions.

No.	Olefin grafted on polymer	G _F (mmoles double bonds/g of copolymer)
1	P1n	1.74



Scheme 2. Chemical modification of benzaldehyde grafted on polymer through Wittig polymer-analogous reactions in PTC conditions

Adsorption of p-nitrophenol on resins

The UV absorption spectra of the p-nitrophenol in aqueous solution is presented in figure 1:

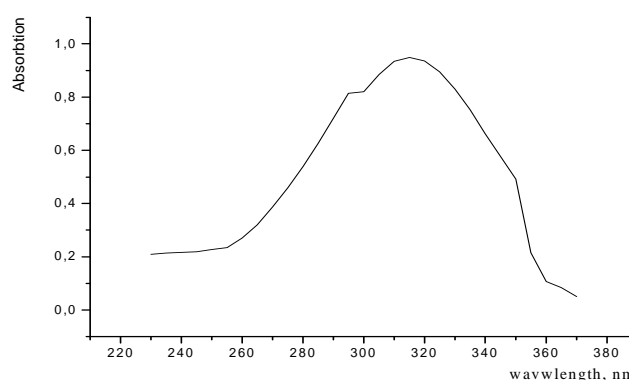


Figure 1. UV absorption spectra of p-nitrophenol in aqueous solution

The absorptions of p-nitrophenol solutions at 315 nm, the residual concentration of p-nitrophenol and the amount of p-nitrophenol adsorbed, at various time periods, are presented in table 2 for XAD-4 resin and table 3 for P1n adsorbent.

TABLE 2. Time variation of the absorptions of p-nitrophenol solutions at 315 nm, the residual concentration of p-nitrophenol and the amount of p-nitrophenol adsorbed for XAD-4 resin

Time (hrs)	Absorbion	Residual concentration (mmoles/L)	Amount of p-nitrophenol adsorbed (mmoles/L)
0	2,600	0,275	0,000
0.5	1,418	0,149	0,125
1	1,267	0,134	0,140
1.5	1,202	0,127	0,147
2	1,165	0,123	0,151
2.5	1,138	0,120	0,154
3	1,112	0,117	0,157
3.5	1,098	0,116	0,158
4	1,075	0,113	0,161
4.5	1,059	0,112	0,162
5	1,040	0,110	0,165
5.5	1,019	0,107	0,167
6	1,002	0,105	0,169
6.5	0,987	0,104	0,170
7	0,972	0,102	0,172
7.5	0,960	0,101	0,173
8	0,949	0,100	0,174
24	0,863	0,091	0,183

TABLE 3. Time variation of the absorptions of *p*-nitrophenol solutions at 315 nm, the residual concentration of *p*-nitrophenol and the amount of *p*-nitrophenol adsorbed for P1n adsorbent

Time (hrs)	Absorption	Residual concentration (mmoles/L)	Amount of <i>p</i> -nitrophenol adsorbed (mmoles/L)
0	2.600	0.275	0,000
0.5	1.614	0.170	0,104
1	1.351	0.142	0,132
1.5	1.069	0.113	0,161
2	0.915	0.096	0,178
2.5	0.812	0.085	0,189
3	0.732	0.077	0,197
3.5	0.678	0.071	0,203
4	0.625	0.066	0,208
4.5	0.588	0.062	0,212
5	0.552	0.058	0,216
5.5	0.523	0.055	0,219
6	0.498	0.052	0,222
6.5	0.480	0.050	0,224
7	0.465	0.049	0,225
7.5	0.452	0.047	0,227
8	0.439	0.046	0,228
24	0.233	0.024	0,250

Comparative *p*-nitrophenol adsorption from aqueous solution for XAD-4 resin and P1n adsorbent from 0 to 24 hours is presented in figures 2 and 3.

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

The *p*-nitrophenol adsorption capacity of the functionalized polymer P1n is greater than the adsorption capacity of the commercial resin Amberlite XAD-4.

After 6 hours, the *p*-nitrophenol removal efficiency of the XAD-4 resin was 61,50 % at the adsorbent concentration of 0,2 g/100mL, and the efficiency of the P1n adsorbent was 80,70 % when using the same initial concentration.

At equilibrium the *p*-nitrophenol removal efficiency of the XAD-4 resin was 66,50 % at the adsorbent concentration of 0,2 g/100mL, and the efficiency of the P1n adsorbent was 90,9 % in the same conditions.

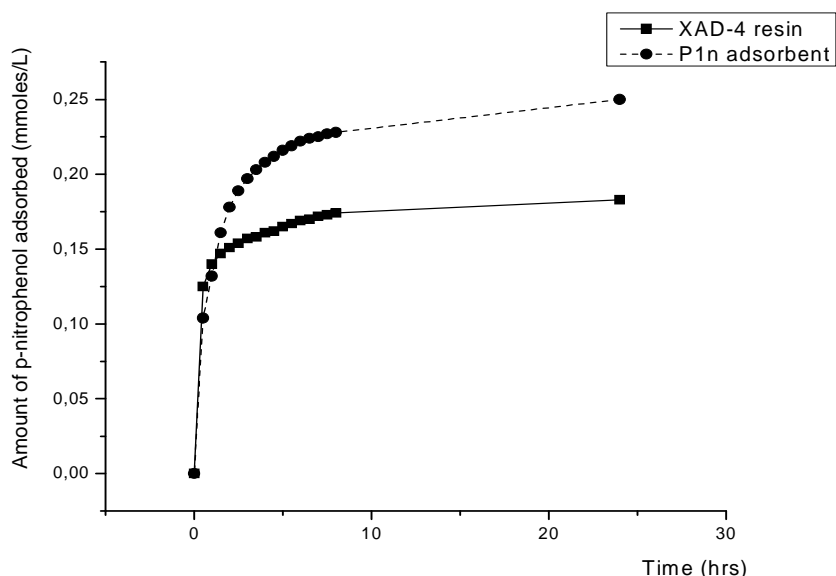


Figure 2. Comparative *p*-nitrophenol adsorption from aqueous solution for XAD-4 resin and P1n adsorbent

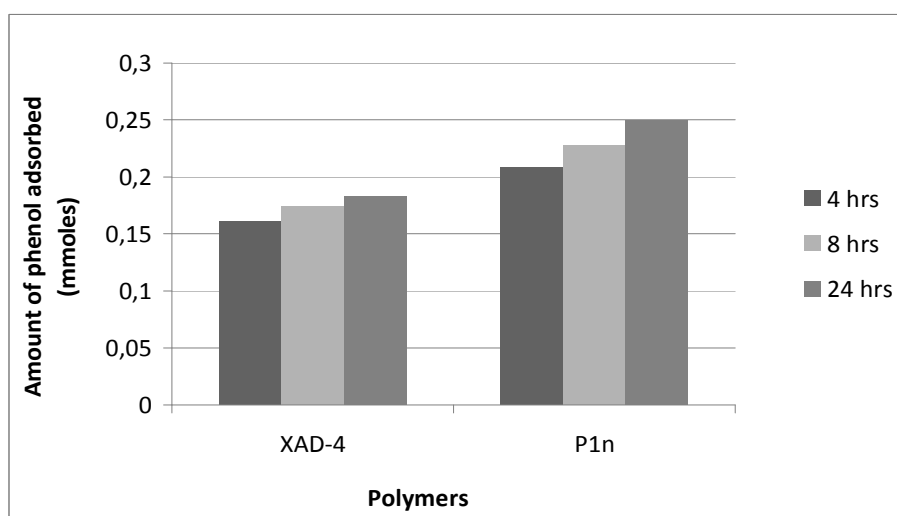


Figure 3. Representation of the amount of *p*-nitrophenol adsorbed by the XAD-4 resin and P1n adsorbent at 4, 8 and 24 hours

4. Conclusions

After 6 hours, the p-nitrophenol removal efficiency of the XAD-4 resin was 61,50% at the adsorbent concentration of 0,2 g/100mL, and the efficiency of the P1n adsorbent was 80,70% when using the same initial concentration.

At equilibrium the p-nitrophenol removal efficiency of the XAD-4 resin was 66,50% at the adsorbent concentration of 0,2 g/100mL, and the efficiency of the P1n adsorbent was 90,9% using the same conditions .

The preliminary experiments showed that the adsorption of 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.

The p-nitrophenol adsorption capacity of the functionalized polymer P1n is greater than the adsorption capacity of the commercial resin Amberlite XAD-4, recommending P1n for further detailed investigation.

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Received: 08 May 2010

Accepted: 18 November 2010