ADSORPTION OF PHENOLIC COMPOUNDS FROM WATER ON POLYMERIC ADSORBENTS WITH OLEFIN GROUPS

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ABSTRACT

Removal and recovery of aromatic pollutants from water by solid adsorbents have been of considerable concern recently. In this paper, adsorption of phenolic compounds from aqueous solution onto a polymeric adsorbent with olefin groups at temperatures from 297 K was studied.

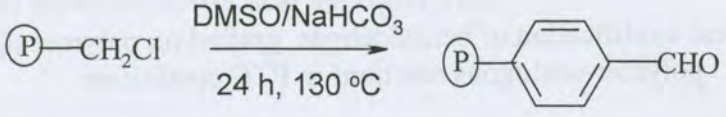
INTRODUCTION

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 [1, 2].
For phenolic compounds adsorption on a specific polymeric adsorbent, the solute–adsorbent interaction will play an important role in the adsorption capacity from aqueous solution [3].
In this preliminary study, a polymeric adsorbent P1n was prepared from benzaldehyde poly(styrene-co-divinylbenzene), and it was tested in batch experiments for phenol, 2,6-dimethylphenol and 2,4,6-trimethylphenol in aqueous solution.

EXPERIMENTAL PART

Synthesis of resin with benzaldehyde groups

The synthesis of the S-DVB copolymers functionalized with benzaldehyde groups were performed by the method previously described (Schema 1) [4]. 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 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 resin with benzaldehyde groups

General procedure for Wittig reactions in phase transfer catalysis conditions

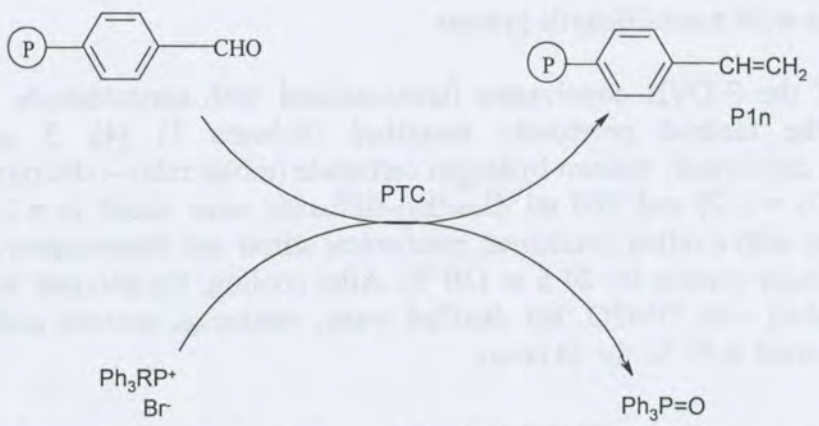
The synthesis of the S-6.7%DVB copolymers functionalized with olefin groups was performed by the method previously described [4].
A mixture of benzaldehyde (4.31 mmoles/g) grafted on styrene-divinylbenzene copolymer (1 g), tetraethylammonium iodide (0.05 g), solvent (THF/CH_3OH=1:1) (20 ml), K_2CO_3 (0.55 g) and a metyltriphenylphosphonium 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, methylenchloride, diethyl ether and then dried at 50 °C for 24 hours.

Determination of the adsorbtion capacity for P1n adsorbent

Batch adsorption experiments were carried out by allowing an accurately weighted amount of P1n adsorbent to reach equilibrium with phenolic compounds solution of an initial concentration of 0,300 mmoles/L at a temperature of 297 K. About 0.200 g of dry adsorbent was weighted and added into 100 mL of phenolic compounds aqueous solution, using a 200 mL Erlenmeyer flask. The mixture was continuously stirred for 24 hours, using a magnetic stirrer, to reach the adsorbtion eqiulibrium. 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 phenolic compounds concentration at equilibrium. The residual concentration of phenolic compounds was determined by UV spectrophotometry, measuring the absorbtion of phenol solutions at a wavelength of 270 nm, 2,6-dimethylphenol solutions at a wavelength of 269 nm and 2,4,6-trimethylphenol solutions at a wavelength of 270 nm. For UV measurements we used a UV-VIS Shimadzu UVmini 1240 spectrophotometer.

RESULTS

Wittig reaction on polymer support is presented in scheme 2:



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

The concentration of phenol in aqueous solution was analyzed by UV analysis performed on a Shimadzu UV-VIS spectrophotometer with the wavelength at 270 nm. The UV absorbtion spectra of the phenol in aqueous solution is presented in figure 1:

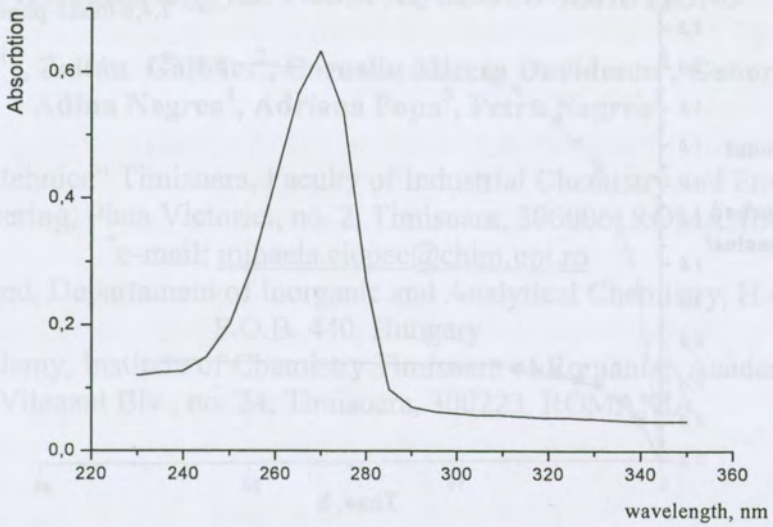


Figure 1. – UV absorbtion spectra of phenol in aqueous solution

Comparative phenolic compounds adsorbtion from aqueous solution for P1n adsorbent from 0 to 24 hours is presented in figures 2 and 3.

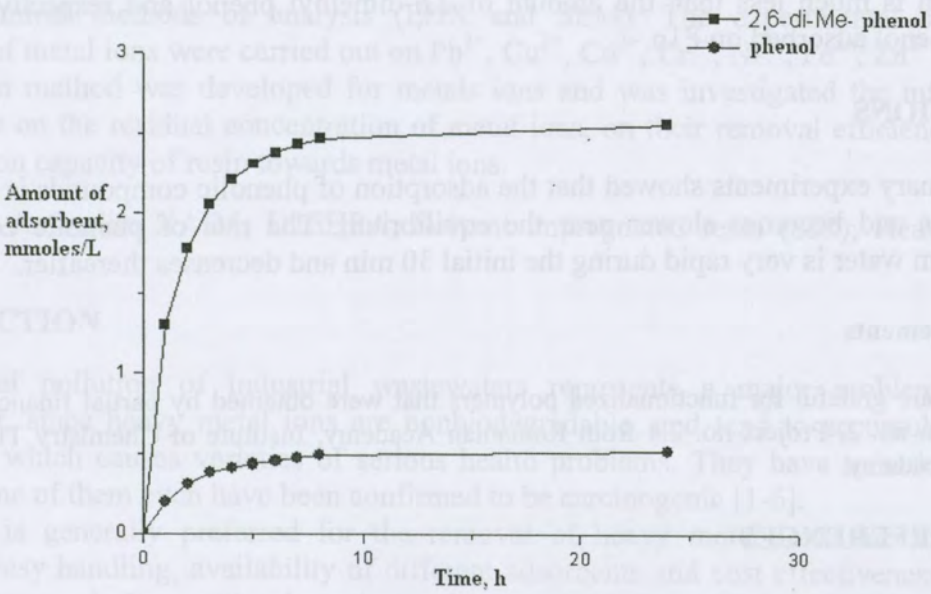


Figure 2. Comparative phenolic compounds adsorbtion from aqueous solution for P1n adsorbent.

Preliminary experiments showed that the adsorption of phenolic compounds is fast at the initial stages and becomes slower near the equilibrium.

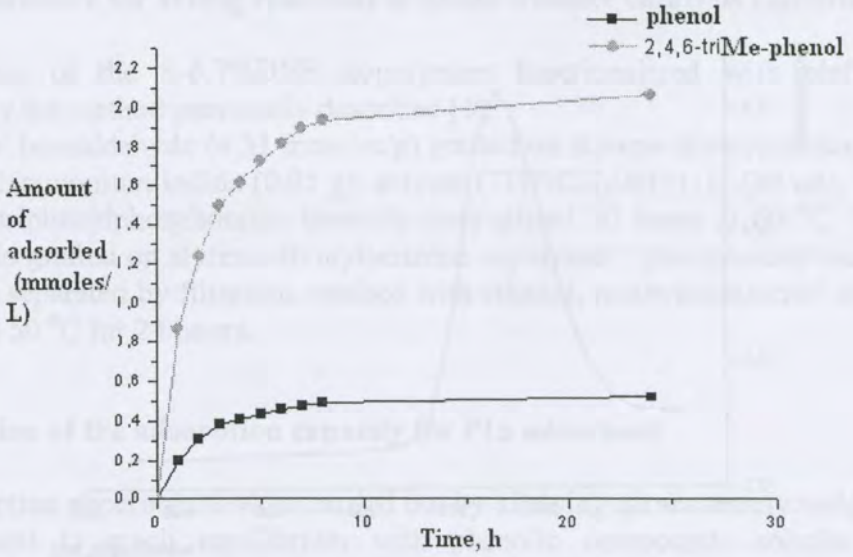


Figure 3. Comparative phenolic compounds adsorbtion from aqueous solution for P1n adsorbent.

The 2,6-dimethylphenol adsorption capacity on the functionalized polymer P1n is greater than the adsorption capacity of 2,4,6-trimethylphenol. The amount of phenol adsorbed on the polymer P1n is much less than the amount of 2,6-dimethyl phenol and respectively 2,4,6-trimethyl phenol adsorbed on P1n.

CONCLUSIONS

The preliminary experiments showed that the adsorption of phenolic compounds is fast at the initial stages and becomes slower near the equilibrium. The rate of phenolic compounds removal from water is very rapid during the initial 30 min and decreases thereafter.

Acknowledgements

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