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ORIGINAL PAPER

Resins containing α-hydroxyphosphonic acid groups used for adsorption of dyes from wastewater

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Abstract The synthesis of styrene–divinylbenzene copolymers functionalized with α-hydroxyphosphonic acid groups is presented. The phosphorus content was determined in order to calculate the degree of functionalization with pendant α-hydroxyphosphonic group, with values of 0.66 for St–1%DVB$_{\mathrm{HOPHOS}}$ and 3.14 for St–6.7%DVB$_{\mathrm{HOPHOS}}$. Their characterization by IR, thermogravimetry is reported. The kinetics of adsorption of three dyes on St–6.7%DVB$_{\mathrm{HOPHOS}}$ polymer was studied.

Keywords α-Hydroxyphosphonic acids · Styrene–divinylbenzene microbeads · Sorbent · Dye

List of symbols

Ff	α-hydroxyphosphonic acid groups
Fi	CHO groups
r	fraction of divinylbenzen (DVB) units
x–y	fraction of styrene units bearing pendant − CH_2Cl remaining groups
y–z	fraction of styrene units bearing pendant − CHO remaining groups (Fi)
z	fraction of styrene units bearing pendant − α-hydroxyphosphonic acid groups (Ff)
%P	phosphorus percentage in the final copolymer
A_{P}	atomic weight of phosphorus
n_{P}	number of phosphorus atoms in the pendant groups

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M_{mi}	average molecular weight of the repetitive unit of the initial copolymer
M_{mf}	average molecular weight of the repetitive unit of the final copolymer
M_S	molecular weight of the repetitive unit of the styrene
M_{DVB}	molecular weight of the repetitive unit of the divinylbenzene
M_{SFi}	molecular weight of the repetitive unit of the styrene functionalized unit Fi groups
M_{SFf}	molecular weight of the repetitive unit of the styrene functionalized with Ff groups
$M_{SFCH2Cl}$	molecular weight of the repetitive unit of the styrene functionalized unit $-CH_2Cl$ groups
G_F	functionalization degree
η_F	functionalization yield

Introduction

Since the early 1990s α-hydroxyphosphonates have attracted much attention due to their wide ranging biological activity [1–5] and their usefulness as synthetic intermediates for other biologically important α-substituted phosphoryl compounds.

The first use of polymers in organic synthesis was made by Merrifield [6] when he introduced his “solid phase technique” for the synthesis of peptides. Polymeric resins have since been increasingly viewed as an alternative to activated carbon for the removal of specific organics from contaminated water.

Synthetic dyes are widely used in such industries as textile, leather, paper, and plastics, to color their final products [7]. Colored dye effluents are highly toxic to aquatic life. Synthetic polymeric sorbents of diverse types are quite extensively used in the sorption of organic compounds from aqueous solutions. Ion exchangers and chelating resins are very often used in the removal, preconcentration and determination of various metal ions [8] and dye [9] in aqueous solutions. There are literature reports of resins, functionalized with phosphonate [10], phosphinic [11–13], and phosphonic [14, 15] groups, and determination of their catalytic and ion-exchange properties.

Phase-transfer catalysis (PTC) is a well-known, very convenient and useful method for organic synthesis. This method can also be used for the chemical modification of polymers to synthesize diverse functional polymers [16, 17]. These polymers with specific properties belong to a new class of polymers namely functional synthetic polymers. The functionality may be introduced as side groups, chain-end, in-chain, block, or graft structures [18].

The obtaining of styrene–divinylbenzene copolymers, with a degree of cross-linkage 6.7 and 1%, grafted with aldehyde side groups by the PTC method [19] is done and their use for the preparation of the new α-hydroxyphosphonic acid grafted on styrene–divinylbenzene is presented. The adsorptive properties of the resins containing new α-hydroxyphosphonic acid groups were investigated. Chelating polymers are characterized by the presence of reactive functional groups containing

O and P donor atoms. The kinetics of adsorption of three test dyes on St–6.7%DVB$_{\mathrm{HOPHOS}}$ polymer was also studied.

Experimental

Reagents

Dimethyl-sulfoxide (Fluka, p.a.), tetrahydrofuran (Fluka, p.a., 99.5%), 1,2-dichloromethane (Chimopar, purum, 98.0%), ethyl ether (Chimopar, purum, 97.0%), acetone (Chimopar, p.a., 99.9%), sodium hydrogen carbonate (Chimopar, p.a.), methanol (Chimopar, p.a.), phosphorous acid (Aldrich, 99%), tripotassium phosphate (K_3PO_4), (Chimopar, p.a.), chloromethylated styrene–divinylbenzene copolymer used as starting materials was supplied by Purolite Victoria Romania (St–6.7%DVB, %Cl = 14.22, $G_F = 4.01$ mmoles Cl/grams copolymer) and Merrifield (St–1%DVB, $G_F = 1.7$ mmoles Cl/grams copolymer, Fluka). All reagents were used as received from suppliers.

For adsorption studies three dyes as test compounds were used as adsorbates: monoazoic dye *AI* (anthranilic acid → 2-amino-5-naphtol-7-sulfonic acid), monoazoic dye *ABS* (*p*-aminobenzoic acid → salicylic acid), and anthraquinone dye *ABA* (bromaminic acid). The investigated dyes were synthesized using known method [20], and were used after purification by several recrystallizations from distilled water.

Synthesis of chloromethylated styrene–divinylbenzene copolymer with aldehyde groups

The synthesis of the aldehyde functionalized on polymer was obtained following our previously published method [19, 21]. 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 (3 × 20 mL), hot distilled water (3 × 20 mL), methanol (3 × 20 mL), acetone (3 × 20 mL), and finally with diethyl ether (3 × 20 mL) and dried at 50 °C for 24 h.

One-pot synthesis of α-hydroxyphosphonic acid grafted on styrene–divinylbenzene copolymer

A mixture of 5 g of aldehyde grafted on styrene–divinylbenzene copolymer, phosphorous acid, K_3PO_4 as catalyst and 50 mL tetrahydrofurane was maintained under stirring for 35 h at 55 °C. The molar ratio of aldehyde groups:phosphorous acid:K_3PO_4 was 1:1.5:0.016.

After cooling, the polymer beads were separated by filtration, washed with distilled water (3 × 20 mL), methanol (3 × 20 mL), acetone (3 × 20 mL), and diethyl ether (3 × 20 mL) and dried at 50 °C for 24 h.

Adsorption procedure

For the dye immobilization on the copolymer microbeads (St–6.7%$\mathrm{DVB_{HOPHOS}}$), 100 mL dye solution and 0.1 g copolymer were stirred magnetically at 250 rpm. The mixture was maintained under continuous stirring for a specific time *t* (equilibrium time), at 45 °C. After reaction, the colored microspheres were separated through filtration, washed with distilled water (2 × 20 mL), and dried at 40 °C for 24 h.

The amount of the dye attached to St–6.7%$\mathrm{DVB_{HOPHOS}}$ was spectrophotometrically evaluated, by reading adsorption values of the dye at the beginning and at the end of the process.

The effect of initial concentration of the ABS dye was studied between 1×10^{-5} M and 5×10^{-5} M. The influence of pH was studied in the domain of 4.0–10.4, which was adjusted with CH_3COOH (0.02 M) or NaOH (0.02 M).

The amount of adsorbed dye per unit copolymer (mg dye/g dry copolymer) was calculated using the following relation [22]:

$$q_{\mathrm{t}} = \frac{(C_0 - C_{\mathrm{t}}) \cdot V}{W} \tag{1}$$

where q_{t} is the amount of dye adsorbed onto the copolymer unit (mg/g), C_0 is the initial concentration (mg/L), C_{t} is the dye concentration function of time (mg/L), V is the solution volume (L), and W is the amount of copolymer (g).

The percentage of dye removal was evaluated using relation (2):

$$\text{Percentage of removal} = \frac{C_0 - C_{\mathrm{t}}}{C_0} \times 100 \tag{2}$$

where C_0 is the initial concentration of dye (mg/L), C_{t} is the dye concentration after adsorption at equilibrium time (mg/L).

Characterization

The obtained materials were characterized by Fourier transform infrared spectroscopy with a Jasco FTIR spectrophotometer. The thermal properties of the α-hydroxyphosphonic acids were characterized through thermogravimetric analysis (TGA) and differential thermal analysis (DTA), which were performed on a TGA/SDTA 851-LF1100—Mettler apparatus at a heating rate of 10 °C/min under a nitrogen atmosphere and temperature range from 25 to 900 °C. The phosphorus content was determined according to modified Schoninger method [23, 24].

A sample of the polymer-supported phosphonates was burnt out in an oxygen atmosphere and P_2O_5 obtained was adsorbed in water. The solution obtained was titrated with an aqueous solution of cerium(III) 0.005 M in the presence of Eryochrome Black T as indicator.

The amount of the dye attached to St–6.7%DVB$_{\mathrm{HOPHOS}}$ was spectrophotometrically evaluated, by reading adsorption values of the dye at the beginning and at the end of the reaction. UV–visible absorption spectra were recorded on a CECIL CE 7200 spectrometer in the wavelength range 250–650 nm, in distilled water. Quartz cuvettes of pathlength 5, 1, and 0.5 cm were used in such a manner that the absorbance values did not exceed 2.0.

Results and discussions

Calculation of the fraction of units bearing pendant α-hydroxyphosphonic acid groups and functionalization degree

The fraction of repetitive units functionalized with α-hydroxyphosphonic acid groups was determined by accepting the statistical structure of the repetitive unit of final copolymer presented in Scheme 1.

From phosphorus percentage in the final copolymer, Eq. 3:

$$\mathrm{P}\% = \frac{z \cdot A_{\mathrm{P}} \cdot n_{\mathrm{P}}}{M_{\mathrm{mi}} + z(M_{\mathrm{SFf}} - M_{\mathrm{SFi}})} \cdot 100 \tag{3}$$

was obtaining the fraction of the styrene units bearing pendant α-hydroxyphosphonic acid (–P(O)(OH)$_2$) groups, it was calculated using Eq. 4:

$$z = \frac{\%\mathrm{P} \cdot M_{\mathrm{mi}}}{100 \cdot n_{\mathrm{P}} \cdot A_{\mathrm{P}} - \%\mathrm{P} \cdot (M_{\mathrm{SFf}} - M_{\mathrm{SFi}})} \tag{4}$$

On this basis, the functionalization degree with –P(O)(OH)$_2$ groups was calculated according to Eq. 5:

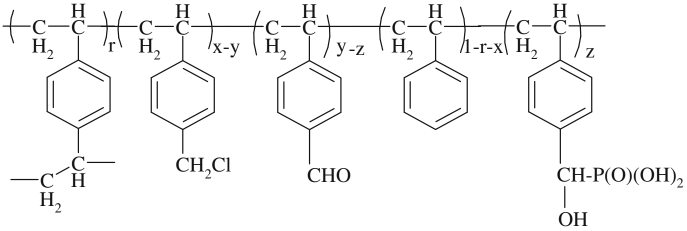
$$G_{\mathrm{F}} = \frac{z}{M_{\mathrm{mf}}}(\text{mmoles Ff groups/grams of copolymer}) \tag{5}$$

$$M_{\mathrm{mf}} = M_{\mathrm{mi}} + z \cdot (M_{\mathrm{SFf}} - M_{\mathrm{SFi}}) \tag{6}$$

where

$$M_{\mathrm{mi}} = r \cdot M_{\mathrm{DVB}} + (x - y) \cdot M_{\mathrm{SFCH2Cl}} + y \cdot M_{\mathrm{SFi}} + (1 - r - x) \cdot M_{\mathrm{S}} \tag{7}$$

The yields of the reaction were calculated with Eq. 8.



Scheme 1 Statistical structure of the repetitive unit of the functionalized copolymer

$$\eta_F = \frac{z}{y} \cdot 100(\%) \tag{8}$$

Characterization of α-hydroxyphosphonic acid groups grafted on styrene–divinylbenzene copolymer

The polymer-analogous reaction for the obtaining of aldehyde groups grafted on styrene–divinylbenzene copolymer is presented in Scheme 2:

Characterization of aldehyde grafted on St–DVB copolymer was obtained by the method previously described [17, 19].

The characteristics of aldehydes grafted on polymeric support by polymer-analogous reactions are given in Table 1.

The formation of the aldehyde groups was confirmed by the appearance of the peaks at 1698 and 1023 cm^{-1} corresponding to C=O and C–O stretching and 1600 cm^{-1} corresponding to the aromatic nucleus.

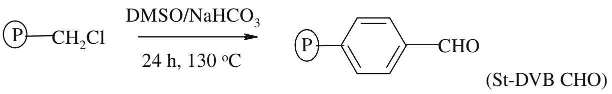
The polymer-analogous reaction for the obtaining of α-hydroxyphosphonic acid groups grafted on styrene–divinylbenzene copolymer is presented in Scheme 3:

The characteristics of α-hydroxyphosphonic acid groups grafted on polymeric support by polymer-analogous reactions are given in Table 2.

The decrease in the intensity of benzaldehyde group adsorption band at 1698 cm^{-1} confirms the formation of α-hydroxyphosphonic acid grafted on polymer. Also the band at 1160 cm^{-1}, from the spectrum (Fig. 1) was assigned to group P=O.

Thermograms of St–6.7%DVB CHO (a) and St–6.7%DVB$_{\mathrm{HOPHOS}}$ (b) are presented in Fig. 2.

The St–6.7%DVB$_{\mathrm{HOPHOS}}$ copolymer (b) has presented higher thermal stability than the St–6.7%DVB CHO copolymer (a), showing that the introduction of α-hydroxyphosphonic acid groups modifies their thermal decomposition pathways in relation to the CHO copolymer (a).



Scheme 2 Formation of aldehyde side groups on styrene–divinylbenzene copolymer

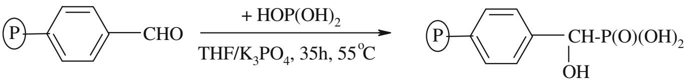
Table 1 Characteristics of aldehydes grafted on polymeric support

Code	Cl_f (wt%)	x	y^a	G_F^b (mmoles of CHO/ grams of copolymer)	M_{mf}^c
St–1%DVB CHO	3.09	0.19	0.09	0.79	113.71
St–6.7%DVB CHO	0.18	0.53	0.52	4.31	120.76

[a] $y = \frac{100 \cdot x \cdot A_{Cl} - \%Cl_f \cdot M_{mi}}{100 \cdot A_{Cl} + \%Cl_f \cdot (M_{SFf} - M_{SFi})}$

[b] $G_F = \frac{y}{M_{mf}}$

[c] $M_{mf} = M_{mi} + y(M_{SFf} - M_{SFi}),\ M_{mi} = r \cdot M_{DVB} + x \cdot M_{SF}CH_2Cl + (1 - r - x) \cdot M_S$



Scheme 3 Obtaining of α-hydroxyphosphonic acid on polymeric support

Table 2 Characteristics of α-hydroxyphosphonic acid groups grafted on styrene–divinylbenzene copolymer

Code	P (wt%)	*y*–*z*	*z*	G_F (mmoles of α-hydroxyphosphonic acid/grams of copolymer)	η_F (%)	M_{mf}
St–1%DVB$_{HOPHOS}$	2.06	0.01	0.08	0.66	88.88	120.27
St–6.7%DVB$_{HOPHOS}$	9.72	0.01	0.51	3.14	98.07	162.48

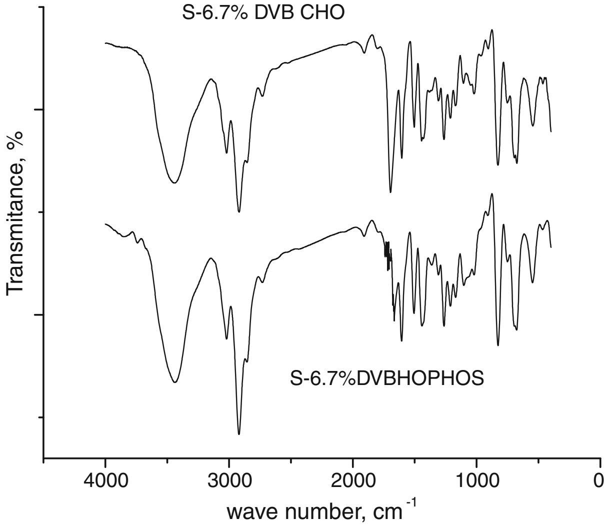


Fig. 1 The IR spectra of St–6.7%DVB CHO and St–6.7%DVB$_{HOPHOS}$

The thermal behavior of the St–6.7%DVB$_{HOPHOS}$ (b) sample shows characteristic "step weight" losses:

- in the first step 25–250 °C, the constant weight loss (~5%), was attributed to evaporation of physically absorbed water in polymer;
- in the second step 250–400 °C, the weight loss (~35%), was attributed to the depolymerization of polystyrene chains and the degradation of styrene oligomers and impurities such as phosphates and degradation of P–C bonds of the pendant groups, around 300 °C the phosphonic acid groups could undergo loss of water by dehydration involving two neighbor groups;
- the third step 400–750 °C, the weight loss (~30%), is mostly attributable to divinylbenzene degradation.

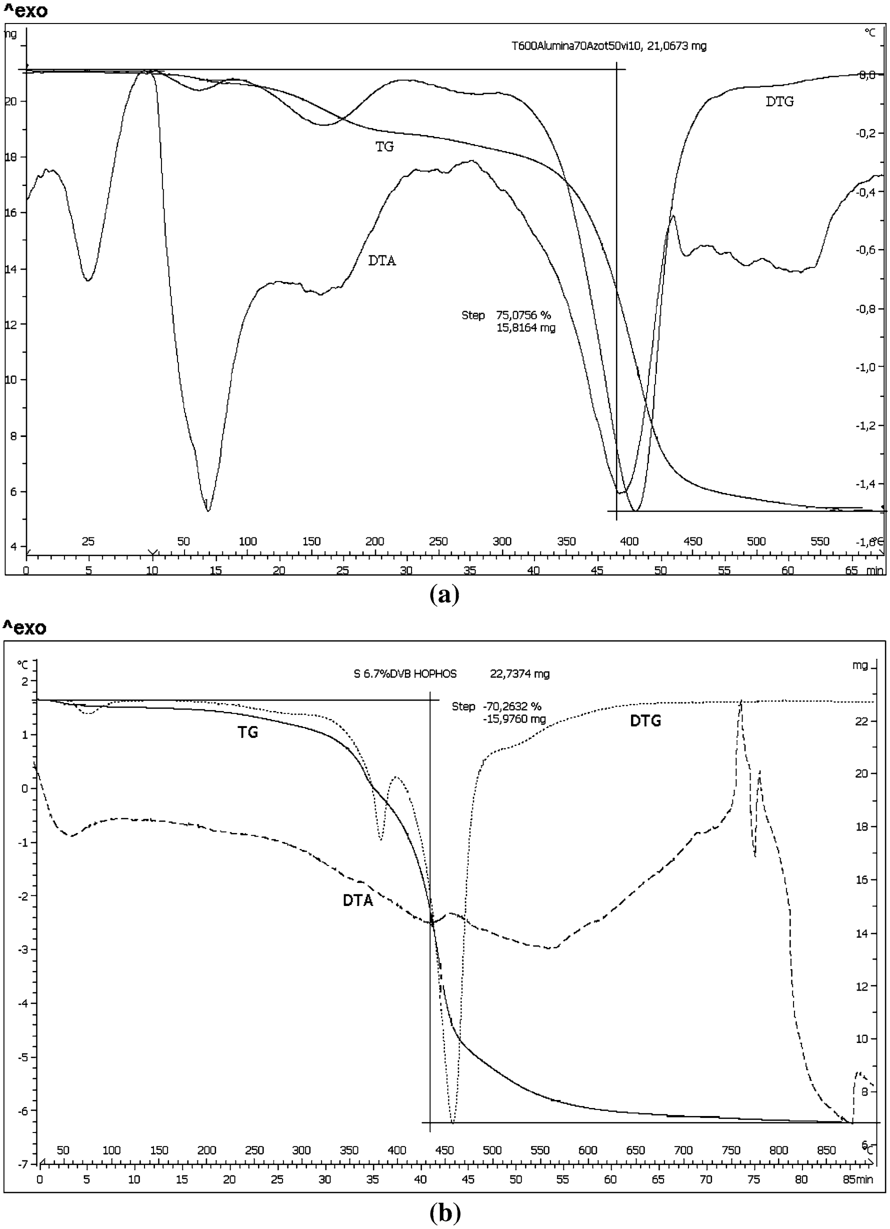


Fig. 2 Thermograms for St–6.7%DVB CHO (**a**) and St–6.7%DVB$_{\mathrm{HOPHOS}}$ (**b**)

The copolymer with hydroxyphosphonic acid (b) presented higher thermal stability than initial copolymer with aldehyde group (a), showing that the introduction of hydroxyphosphonic acid group modified it thermal decomposition pathways. Total weight loss for initial copolymer (a) was 75% and for copolymer with hydroxyphosphonic acid (b) was 70%.

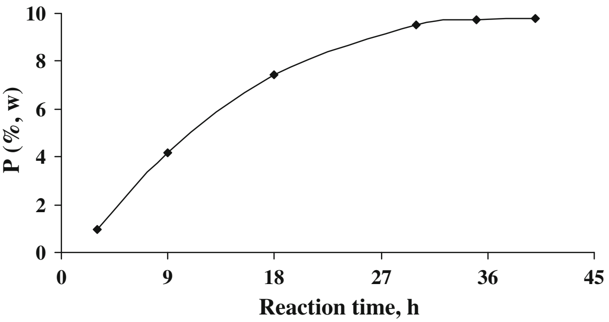


Fig. 3 Phosphorus percent versus the reaction time using aldehyde side groups on styrene–6.7%divinylbenzene copolymer

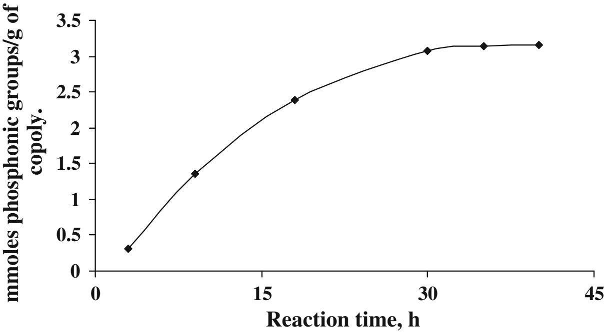


Fig. 4 The degree of functionalization with α-hydroxyphosphonic acid groups at the St–6.7%DVB copolymer versus the reaction time

The phosphorus percent increases with the increase of the reaction time until about 2.06 and 9.72 (%, w) and these were achieved after about 35 h (Fig. 3).

This may be interpreted as showing that with a prolongation of the reaction time both the most accessible sites and, subsequently, the less accessible sites are involved in reaction.

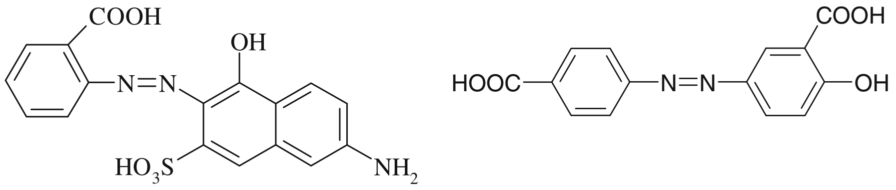
The degree of functionalization with α-hydroxyphosphonic acid groups is increased as the reaction time increases (Fig. 4).

Adsorption studies

The chemical structures of the investigated test dyes are presented in Fig. 5.

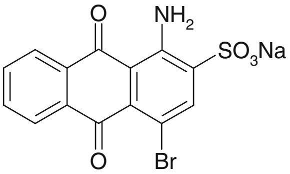
The effect of contact time on dye removal under similar physicochemical conditions was investigated.

As Fig. 6 shows, the removal of investigated dyes was rapid at the beginning of adsorption process during the first 60 min, and gradually decreased as equilibrium time was approached. This may due to the saturation of the active center, available for dye on the micromicrobeads. The amount of dye adsorbed at the equilibrium



AI (anthranilic acid→2-amino-5-naphtol-7-sulphonic acid)

ABS (*p*-aminobenzoic acid → salicylic acid)



ABA (bromaminic acid).

Fig. 5 Chemical structures of the dyes

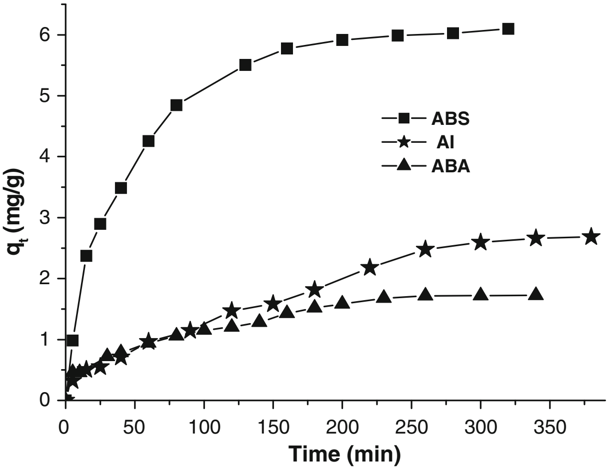


Fig. 6 Effect of contact time on the removal of dye: ABS, AI, ABA, dye concentration 5 × 10^{-5} M, 45 °C, pH 6.8

time reflects the maximum adsorption capacity of the adsorbents under those operating conditions. The obtained results of the adsorption study of dyes on St–6.7%DVB_{HOPHOS} microspheres are presented in Table 3.

The contact time period needed for effective adsorption depends on the nature of the test dyes. The results obtained in the present investigation reveal the capacity of St–6.7%DVB_{HOPHOS} microspheres in treating dye effluents. Although the yields of dye removal from wastewaters using St–6.7%DVB_{HOPHOS} are not significantly different, the ratio price/performance allows us to propose the St–6.7%DVB_{HOPHOS}

Table 3 Results of the adsorption study of investigated dyes on St–6.7%DVB$_{\text{HOPHOS}}$ microspheres

Dye	$\lambda_{\max}$ (nm)	Equilibrium time (min)	q_e (mg/g)	Percentage removal (%)
ABS	353.8	220	6.19	43.68
AI	478.6	260	2.68	32.46
ABA	464.2	230	1.72	24.71

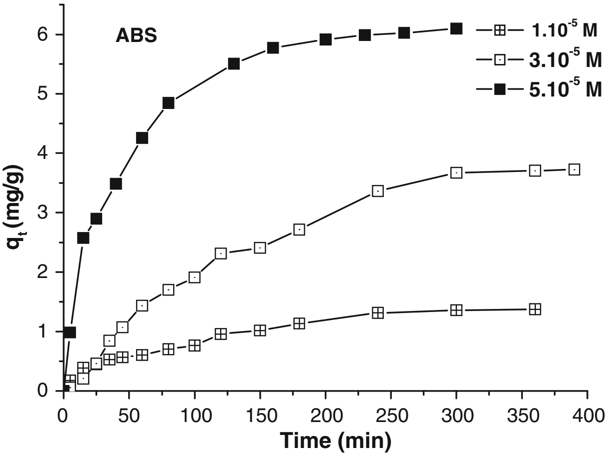


Fig. 7 Influence of initial dyes concentration on adsorption for ABS dye; 45 °C, pH 6.8

as a potential sorbent for the removal of dyes from wastewaters. Adsorption is highly dependent on the contact time and dye structure.

As the best result was obtained for ABS dye, the investigations were extended to the study of influence of dye concentration and pH on the adsorption. The amount of adsorbed ABS onto copolymer was studied as a function of dye concentration, varying the initial dye concentration between 1×10^{-5} M and 5×10^{-5} M (Fig. 7).

The adsorption capacity and the percentage of removal, increase with the increasing of the initial dye concentration. For an increase in the initial dye concentrations from 1×10^{-5} to 5×10^{-5} mol/L the adsorption capacity at equilibrium increased from 1.37 to 6.19 mg/g (Table 4). Also the percentage of removal increase with the increase of initial concentration.

The effect of pH on the adsorption of ABS dye on St–6.7%DVB$_{\text{HOPHOS}}$ microspheres was also investigated at an initial concentration 5×10^{-5} mol/L and 45 °C. Fig. 8 shows the effect of pH on the removal of ABS dye on St–6.7%DVB$_{\text{HOPHOS}}$, and results are presented in Table 4.

The adsorption capacity of ABS on St–6.7%DVB$_{\text{HOPHOS}}$ microspheres decreases with increasing pH. Maximum removal (54.74%) for ABS was found in the acidic medium (Table 4) at pH 4.0.

Table 4 Results of the influence of initial concentration and pH on the adsorption of ABS dye on St–6.7%DVB$_{HOPHOS}$ microspheres

Dye	Concentration (mol/L)	pH	q_e (mg/g)	Percentage removal (%)
ABS	1×10^{-5}	6.8	1.37	37.41
	3×10^{-5}	6.8	3.73	37.63
	5×10^{-5}	4.0	9.03	54.74
		6.8	6.19	43.68
		10.4	3.49	17.48

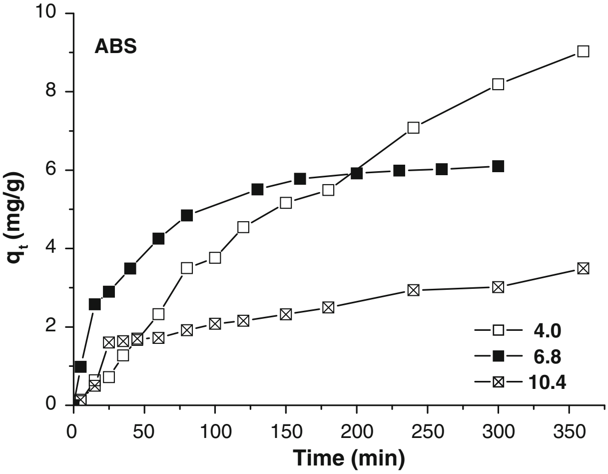


Fig. 8 Influence of pH on adsorption for ABS dye; dye concentration 5×10^{-5} M, 45 °C

Conclusions

The obtaining of the α-hydroxyphosphonic acids by reaction between phosphorous acid and aldehyde grafted on copolymers was confirmed by IR spectrum, the group P=O was identified. The thermal analysis of the α-hydroxyphosphonic acids was carried out (TG, DTA). The St–6.7%DVB$_{HOPHOS}$ copolymer presented higher thermal stability than the St–6.7%DVB CHO copolymer. The phosphorus content was determined in order to calculate the degree of functionalization with pendant α-hydroxyphosphonic group, whose values are 0.66 for St–1%DVB$_{HOPHOS}$ and 3.14 for St–6.7%DVB$_{HOPHOS}$.

Sorption is an effective process for the decoloration of textile wastewaters. In terms of environmental and economic problems, we can suggest the use of St–6.7%DVB$_{HOPHOS}$ for removal of dyes from wastewaters, with optimal conditions being a minimum temperature of 45 °C and at pH 4.0.

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