

Adsorption of Some Phenolic Compounds on a New Styrene-15% Divinylbenzene Copolymer Functionalized With Carboxylic Groups

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Abstract: A new styrene-divinylbenzene copolymer (PC15) grafted with carboxylic acid groups was prepared. The content of divinylbenzene in the copolymer was 15 %. The copolymer was characterized by Fourier transform infrared (FTIR) spectroscopy, thermal analysis (DSC-TG), scanning electron microscopy (SEM), specific surface area and particle size measurements. The PC15 copolymer was investigated as adsorbent for the removal of phenol, 3-aminophenol (3-AP) and p-nitrophenol (p-NP) from aqueous solution. From the three investigated pollutants, the PC15 copolymer has shown the highest removal efficiency for p-nitrophenol. The kinetic of p-NP adsorption onto PC15 copolymer was described by the pseudo-second-order model and the equilibrium adsorption data were well fitted to the Redlich-Peterson isotherm. The good adsorption capacity, recommend the PC15 copolymer as promising candidate for the removal of p-nitrophenol from wastewater.

Keywords: adsorption, functionalized copolymer, phenolic compounds

1. Introduction

Industrial progress and continuous evolution generated a variety of pollutants, among which phenolic compounds are the most common and dangerous water pollutants due to their high toxicity even at low concentration [1, 2]. Phenolic compounds are considered the most harmful organic pollutants that alter the taste and smell of water for consumption. The negative impact of phenolic compounds on human life [3, 4] and environment has been very intense studied [5].

Phenol and its derivatives appear into wastewater of various industrial processes such as: petrochemical [6, 7], refining [8, 9], pharmaceutical synthesis [10, 11], water chlorination [12], pesticides production [13], and textile manufacture [14]. In order to respect the environmental legislation concerning wastewater, the removal of these pollutants from industrial effluents has to be considered as a matter of urgency and high importance.

During the time different methods were developed for reduce or even eliminate if possible the content of pollutants; among these can be mentioned: solvent extraction [15], biodegradation [16], catalytic oxidation [17], photochemical treatment [18, 19], reverse osmosis [20] and adsorption [21]. Adsorption proved to be the most effective and attractive method, due to its simplicity in operation and the cost [22]. Various adsorbents [23] were used for wastewater treatment such as: activated carbon [24, 25], silica gel sludge [26], alumina [27], red mud [28], hydroxyapatite [29], bentonite [30], magnetic iron oxide [31, 32], polymers [33], resins [21] and copolymers [34, 35].

In this study we introduce a new styrene–15% divinylbenzene copolymer functionalized with carboxylic acid groups (PC15). The copolymer was characterized and tested as adsorbent for the removal of phenol, 3-aminophenol (3-AP) and p-nitrophenol (p-NP) from aqueous solutions. The kinetic and adsorption isotherm were also evaluated.

2. Experimental

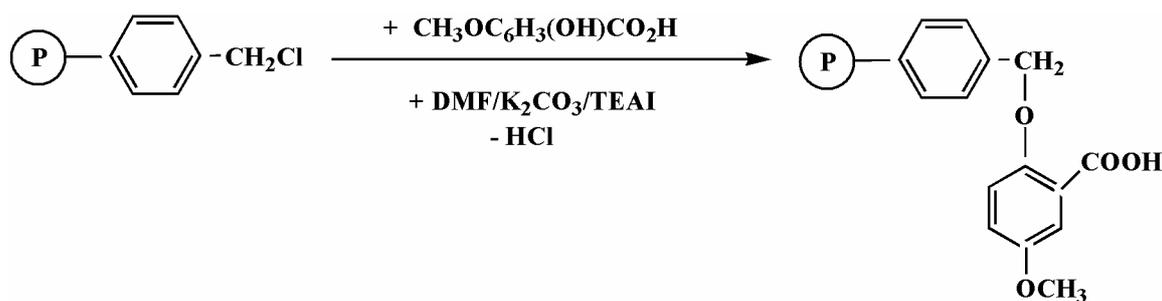
2.1. Materials

Chloromethylated styrene–15% divinylbenzene copolymer (Synthesized in our laboratory [36]), tetraethylammonium iodide (Merck, 98%), 2-hydroxy-5methoxybenzoic acid (Sigma–Aldrich, 98%), dimethylformamide (Sigma–Aldrich, 99%), potassium carbonate (Sigma–Aldrich, 99%), methanol, acetone and diethyl ether (Chimopar, 99%) were used as starting materials for the polymeric adsorbent preparation.

Phenol, 3-aminophenol and p-nitrophenol used as adsorbates were of analytical grade and were purchased from Reactivul (Romania).

2.2. Copolymer synthesis

Chloromethylated styrene–15% divinylbenzene copolymer (S-15%DVB) was used for the synthesis of the new functionalized copolymer (PC15) according to the method presented in our previous paper [34] (Scheme 1).



Scheme 1. Preparation of the functionalized PC15 copolymer

2.3. Polymeric adsorbent characterisation

The PC15 copolymer was characterized by means of FTIR spectroscopy. The FTIR spectrum was carried out using a Shimadzu Prestige-21 spectrometer in the range 400–4000 cm^{-1} , using KBr pellets and resolution of 4 cm^{-1} . Thermal analysis (TG/DSC) was performed using a NETZSCH-STA 449C instrument, in the range of 25–1000 $^{\circ}\text{C}$ with a heating rate of 10 K min^{-1} , using platinum crucibles. The experiments were carried out in artificial air at a flow rate of 20 mL min^{-1} . N_2 adsorption–desorption isotherms of copolymer were performed on Micromeritics ASAP 2020 instrument. The specific surface area was calculated using the Brunauer–Emmett–Teller (S_{BET}) method. The surface area of pores, volume and pore diameter were calculated using the Barret-Joyner-Hallenda (BJH) method from the desorption curves. The morphology of the PC15 copolymer was investigated by scanning electron microscopy (SEM), using a FEI Quanta FEG 250 microscope.

2.4. Adsorption experiments

The adsorption experiments were performed at 25 $^{\circ}\text{C}$, using 2 g L^{-1} adsorbent mass and 100 mg L^{-1} initial concentration of phenol, 3-aminophenol (3-AP) and p-nitrophenol (p-NP), respectively. All experiments were performed at a 200 rpm shaking speed for 8 h to ensure reaching the equilibrium of adsorption process.

The concentration of phenol, 3-aminophenol and p-nitrophenol was monitored by spectrophotometric analysis using a Shimadzu UV–VIS Spectrophotometer. The absorbance values were measured at the wavelength of: 270 nm for phenol, 280 nm for 3-aminophenol and 316 nm for p-nitrophenol.

The amount of adsorbed pollutant, q_t [mg g^{-1}], was calculated according to Eq. (1):

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (1)$$

where C_0 and C_t are the concentration of pollutant, initially and at any time, t , [mg L^{-1}], respectively; V is the volume of solution [L] and m is the mass of adsorbent [g].

The removal efficiency R (%) was calculated by Eq. (2):

$$R = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (2)$$

where C_0 and C_e are the initial and the equilibrium concentration of pollutant [mg L^{-1}].

3. Results and Discussion

3.1. Copolymer characterisation

The FTIR spectrum of PC15 copolymer (Fig. 1) confirms its polystyrene-type structure. The presence of grafted COOH groups is confirmed by the broad band situated at 3410.15 cm^{-1} attributed to the OH stretching vibration and by the band at 1678.07 cm^{-1} assigned to the C=O stretching vibration in aryl-COOH group [37].

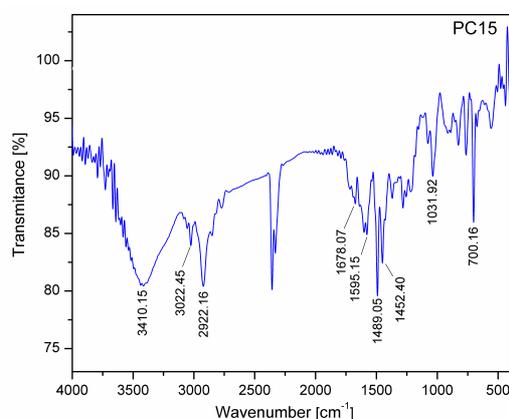


Figure 1. FTIR spectrum of the PC15 copolymer

The thermal behavior of the copolymer was investigated by thermal analysis. The TG and DSC curves of the copolymer are shown in Fig.2.

Until 160 $^{\circ}\text{C}$ a slightly mass loss (around 6%) can be observed on the TG curve, attributed to the water evaporation. Between 300 and 600 $^{\circ}\text{C}$, a succession of large and strong exothermic effects can be noticed on the DSC curve, attributed to the oxidative degradation of the copolymer. These effects are accompanied with significant mass loss on TG curve.

Over 600 $^{\circ}\text{C}$, the P15 copolymer degradation is practically complete.

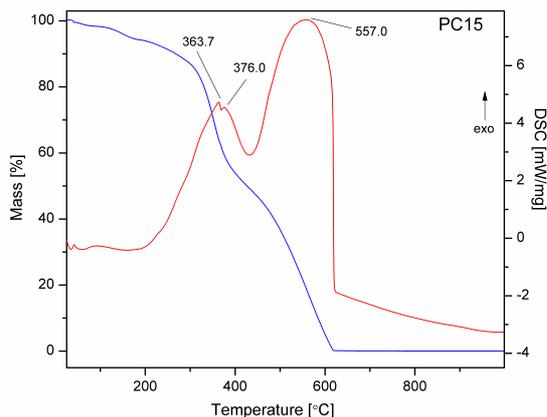
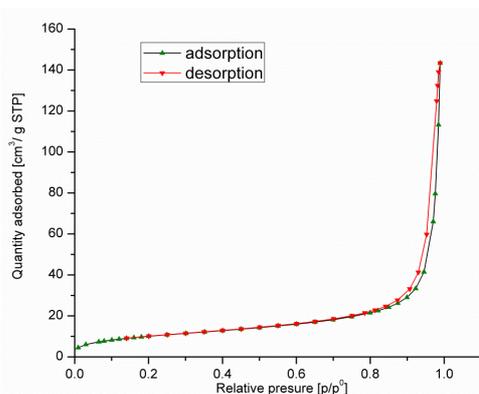


Figure 2. TG/DSC curves of the PC15 copolymer

The N_2 adsorption-desorption isotherms of PC15 copolymer are presented in figure 3. According to IUPAC classification, these isotherms are of type II with H3 hysteresis loop.

Figure 3. N_2 adsorption-desorption isotherms of the PC15 copolymer

Other characteristics of PC15 copolymer are: BET surface area: $37.45 \text{ m}^2 \text{ g}^{-1}$; BJH desorption cumulative surface area of pores: $38.04 \text{ m}^2 \text{ g}^{-1}$; BJH desorption cumulative volume: $0.223 \text{ cm}^3 \text{ g}^{-1}$; BJH desorption average pore diameter: 23.45 nm .

The SEM image shown in Figure 4 evidences the spherical shape of the copolymer particles with diameters between $280\text{--}450\mu\text{m}$.

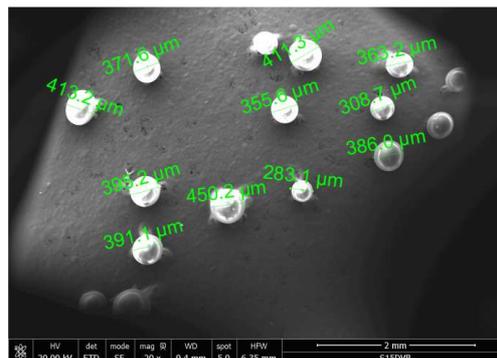


Figure 4. SEM image of the PC15 copolymer

3.2. Adsorption test

Effect of pollutant nature

The influence of pollutant nature on the adsorption capacity of PC15 adsorbent is presented in Table 1.

The results presented in Table 1 were correlated with the solubility and pK_a values of pollutants, factors that have a significant influence on the adsorption process. As can be observed, the removal efficiency of PC 15 copolymer increases with the decrease of the solubility and pK_a value of the pollutant. The PC 15 copolymer shows the highest removal efficiency for p-nitrophenol.

Due to the fact that the best removal efficiency of PC 15 copolymer was 75.3 %, the following adsorption studies were performed for p-nitrophenol removal from aqueous solutions.

Influence of adsorbent dose

The effect of PC15 copolymer dose, ranging from 2 to 5 g L^{-1} on p-NP adsorption is shown in Figure 5. It can be observed the continuously increase of the removal efficiency from 75.3 % to 91.9 % with the increase of adsorbent dose from 2 to 5 g L^{-1} . This behaviour can be explained by the increase of the available active sites on the copolymer surface as a result of the adsorbent dose increase.

TABLE 1. Effect of pollutant nature on the adsorption capacity of PC15 adsorbent

Adsorbent	Adsorbed	Solubility at $25 \text{ }^\circ\text{C}$ [g L^{-1}]	pK_a	R%
PC15	Phenol	83	9.95	32.5
	3-aminophenol	35	4.30	40.4
	p-nitrophenol	16	7.15	75.3

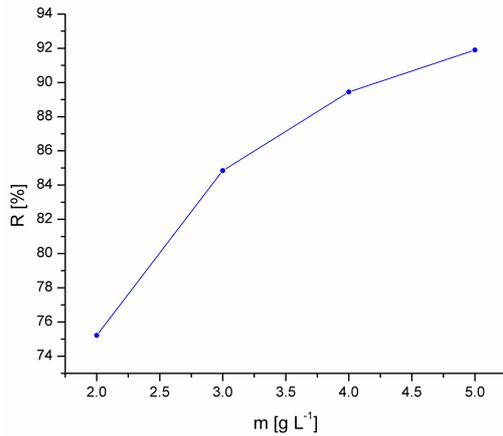


Figure 5. Influence of adsorbent dose on p-NP adsorption onto the PC15 copolymer

Kinetic study

The adsorption kinetic of p-nitrophenol on the PC15 copolymer was investigated by fitting the experimental data with the pseudo-second-order model. The linear form of the Ho and McKay pseudo-second-order equation is [38]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

q_e is the amount of solute adsorbed at equilibrium [mg g^{-1}],
 q_t is the amount of solute adsorbed at time t [mg g^{-1}],
 k is the adsorption rate constant [$\text{g mg}^{-1} \text{min}^{-1}$].

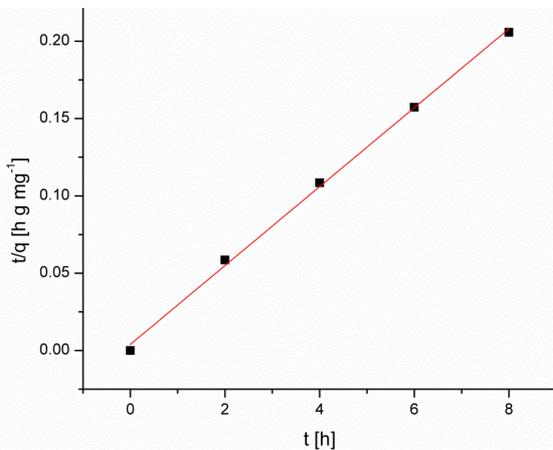


Figure 6. Plot of $t/q=f(t)$ for p-NP adsorption on the PC15 copolymer

From the slope and intercept of the plot presented in figure 6, were calculated: $q_e = 39.20 \text{ mg g}^{-1}$ and $k = 0.1660 \text{ g mg}^{-1} \text{ h}^{-1}$. The correlation coefficient close to unity, $R^2 = 0.99801$, confirms that the adsorption kinetic of p-NP onto PC15 copolymer was described by the pseudo-second-order model.

Adsorption isotherms

In this study, the experimental equilibrium data were fitted with the Freundlich, Langmuir, Sips and Redlich-Peterson isotherms.

Freundlich isotherm is expressed as follows [39]:

$$q_e = K_F C_e^{1/n} \quad (4)$$

q_e is the amount of solute adsorbed per unit mass of adsorbent at equilibrium [mg g^{-1}],
 K_F is the Freundlich constant [$\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$],
 C_e is the equilibrium concentration of the solute in the bulk solution [mg L^{-1}],
 n is a constant related to the intensity of adsorption.

Langmuir isotherm is represented by the equation [39]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

q_e is the amount of solute adsorbed per unit mass of adsorbent at equilibrium [mg g^{-1}],
 q_m is the maximum monolayer adsorption capacity [mg g^{-1}],
 C_e is the equilibrium concentration of the solute in the bulk solution [mg L^{-1}],
 K_L is the Langmuir sorption constant [L mg^{-1}].

Sips isotherm is an empirical equation with three parameters expressed as [40]:

$$q_e = \frac{q_m K_S C_e^n}{1 + K_S C_e^n} \quad (6)$$

K_S is the Sips constant [$(\text{L mg}^{-1})^n$],
 n is the Sips model exponent.

Redlich-Peterson isotherm is also an empirical with three parameters equation. This isotherm is a combination of Langmuir and Freundlich isotherms and is expressed as [40]:

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^\beta} \quad (7)$$

K_{RP} is the Redlich-Peterson constant [L g^{-1}],
 α_{RP} is a constant [$(\text{L mg}^{-1})^\beta$],
 β is an exponent varying between 0 and 1.

The optimum isotherm was determined by non-linear regression analysis, using ORIGIN 8 software. The correlation coefficient (R^2) and the Chi-square (χ^2) test were employed to find the best fitted isotherm model for the experimental equilibrium data.

The experimental equilibrium data for the adsorption of p-NP onto PC15 copolymer were fitted with the four above mentioned isotherms by plotting q_e versus C_e (Fig.7). The parameters of the four investigated isotherms with the corresponding correlation coefficient (R^2) and Chi-square value (χ^2) are listed in Table 2.

TABLE 2. Isotherms parameters for the adsorption of p-NP onto PC15 copolymer

Isotherm model	Parameter	Pollutant
		p-NP
Langmuir	q_m [mg g^{-1}]	86.95
	K_L [L mg^{-1}]	0.03227
	R^2	0.99408
	χ^2	4.04009
Freundlich	K_F [$\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$]	8.81486
	n	2.30852
	R^2	0.97075
	χ^2	19.96659
Redlich-Peterson	K_{RP} [L mg^{-1}]	3.31182
	α_R [$(\text{L mg}^{-1})^\beta$]	0.06308
	β	0.90203
	R^2	0.9944
Sips	K_S [L mg^{-1}]	0.0381
	q_m [mg g^{-1}]	93.68
	n	0.9015
	R^2	0.99387
	χ^2	4.18205

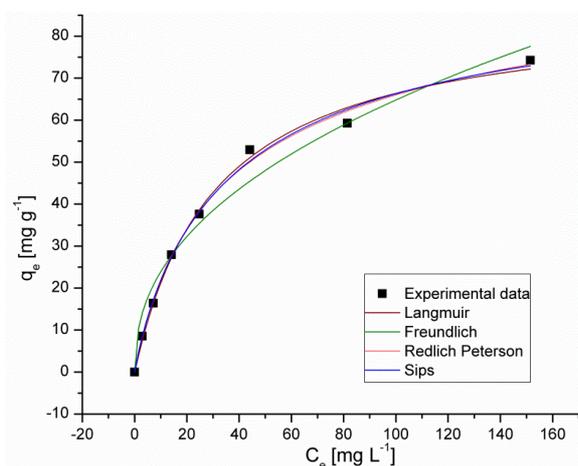


Figure 7. Isotherm plots for p-NP adsorption on the PC15 copolymer

Comparing the R^2 and χ^2 values shown in Table 2 for each model, it can be noticed that the equilibrium data of p-NP adsorption onto PC15 copolymer were best fitted by the Redlich-Peterson isotherm.

The maximum adsorption capacity calculated from the Langmuir isotherm is 86.95 mg g^{-1} . Compared with other q_m values reported in the literature, the adsorption capacity of p-NP onto the PC15 copolymer is higher than those reported by J. M. Li [41] using functional chitosan chemically modified by: salicylaldehyde (44.92 mg g^{-1}), β -cyclodextrin (20.56 mg g^{-1}), and a crosslinked β -cyclodextrin polymer (41.11 mg g^{-1}).

4. Conclusions

A new styrene-divinylbenzene copolymer, with 15% divinylbenzene content, functionalized with carboxylic acid groups (PC15) was synthesized, characterized and investigated as adsorbent for the removal of phenol, 3-aminophenol (3-AP), and p-nitrophenol (p-NP) from

aqueous solutions. The PC15 copolymer has shown the highest removal efficiency for p-nitrophenol which is the less soluble and the most acidic from the three studied pollutants. The kinetic studies indicated that the adsorption of p-NP onto PC15 copolymer followed the pseudo-second-order model and the equilibrium adsorption data were correlated with the Redlich-Peterson isotherm. The good adsorption capacity of PC15 copolymer suggests its potential application for the removal of p-NP from wastewater.

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