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Removal of Aromatic Amino-derivatives from Aqueous Solutions Using Polymeric Supports Functionalized with Aminophosphonated/aminoacid-phosphonated Groups

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Abstract: *Aromatic amines are the significant compounds used as intermediates in the organic synthesis, for obtaining such as azo dyes, antioxidants, fuel additives, corrosion inhibitors, pesticides, antiseptic agents, poultry medicine, and pharmaceutical synthesis. However, the presence of aromatic amines in water, even at very low concentrations, is extremely harmful to aquatic life and human health. Pollution of natural waters by aromatic amines is a serious environmental concern. The aim of this work was to obtain new adsorbents for use in the removal of aromatic amines from aqueous solutions. Styrene-15%divinylbenzene copolymers grafted with aminophosphonate groups (code: AP-S15%DVB) and amino acid-phosphonate groups (code: AM-S15%DVB) were used for the removal of pollutants such as: aniline, 2-methyl-aniline and 4-methyl-aniline. The adsorption capacity and the adsorption kinetic using the pseudo-first order and pseudo-second order equations were examined. From a kinetic point of view, it was established that the adsorption of the studied amino derivatives on the used adsorbents took place according to the pseudo-second order model. It was found that the adsorption rate constant increased with the increase of temperature, so the speed of the adsorption process increased. The obtained results confirm that the polymer adsorbents studied can be successfully used for the removal of aromatic amino derivatives from aqueous solutions for the purpose of wastewater treatment.*

***Keywords**: styrene-15%divinylbenzene copolymer, aromatic amines, removal, aminophosphonate groups, amino acid-phosphonate groups*

1. Introduction

Aromatic amines are the synthetic organic compounds used as intermediate or precursor in the manufacture of organic compounds such as azo dyes, antioxidants, fuel additives, corrosion inhibitors, pesticides, antiseptic agents, medicines for poultry and the synthesis of pharmaceuticals [1]. The presence of these aromatic amines represents a potential hazard for the health [2]. Aniline is toxic and hard to be degraded, and thereby causes the environmental pollution seriously [3]. Toluidine is an organic chemical raw material, which is widely used in the production of dyes, medicines, pesticides and other industries. It is an organic compound with three isomers (o-toluidine, m-toluidine and p-toluidine) [4]. O-toluidine has attracted great interest due to its carcinogenicity, while in meta and para isomers this effect is not significant [5]. The oral LD_{50} values in the rat are as follows: 670 mg/kg for o-toluidine, 450 mg/kg for m-toluidine and 656 mg/kg for p-toluidine [5].

The environmental problems increased because of increasing population, consumption of natural habitat, and development of industrialization. However, the presence of aromatic amines in water, even at very low concentrations, is extremely harmful to aquatic life and human health [4, 5].

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The pharmaceutical manufacturing industry produces a wide range of products to be used as human and animal medications [6]. The pollution of natural waters with aromatic amines is of serious environmental concern. Several physical and chemical methods, including oxidation, adsorption, bio-degradation, photodegradation have been used to treat aniline-containing wastewaters [7-9]. Traditionally, adsorption is the most widely used technique to remove the high levels of organic pollutants from the polluted wastewater because of its simple operation, and non-generation of harmful byproducts [10, 11].

Many types of adsorbent materials are used to remove pollutants from wastewater, such as activated carbon [12], chitosan [13], various low-cost [14] and polymeric adsorbents [15].

The polymeric materials have become more attractive than other adsorbents because they have demonstrated good adsorption capacity for pollutants due to their functionalization with pendant groups that involve specific interactions in the adsorption process. In 1952, Fields has published, for the first time, the synthesis of α-aminophosphonate [16]. In 1998, Qian and Huang have presented the one-pot synthesis of α-aminophosphonates [17]. This method has been adapted by our research group [18-20] and was used for the "one-pot" Kabachnik-Fields synthesis of styrene–divinylbenzene (S-DVB) co-polymers with aminophosphonate groups.

The functionalization of the polymeric material with active groups allows obtaining new structures with desired properties for removal of pollutants from wastewater. Our previous studies have reported on the using of styrene-divinylbenzene copolymers functionalized with pendant groups at removal for phenol derivatives [19, 21], dyes [22], and antibiotics [23] from aqueous solutions.

In this article, we present the results obtained when a three-component one-pot reaction was used for obtaining functionalized styrene-15% divinylbenzene copolymers with aminophosphonate groups (code: AP-S15%DVB) and respectively aminoacid-phosphonated groups (code: AM-S15%DVB) and their use for the removal of pollutants such as: aniline, 2-methyl-aniline and 4-methyl-aniline from aqueous solutions. The adsorption capacity and the adsorption kinetic using the pseudo-first order and pseudo-second order equations were examined. The purpose of this work and its novelty consists in obtaining new adsorbents and their use in new applications for the removal of polluting aromatic amines from wastewater.

2. Experimental part

2.1. Materials and methods

Styrene-15% divinylbenzene copolymer grafted with aldehyde groups (the content of DVB in copolymer is 15 wt.%; G_F = 2.70 mmoles aldehyde groups/g copolymer, was synthesized in our laboratory by the method previously described [24]). An aminoacetic acid (glycine), diethylphosphite (Fluka, 99%), propylamine (Fluka, 99%), ethanol and acetone (Chimopar, p.a.) were used as starting materials. All other chemicals were used without further purification.

The residual concentrations of amino compounds were determined using a Shimadzu UV mini 1240 UV-VIS spectrophotometer, measuring the absorption of amino solution at wavelengths between 200 and 380 nm. The content of the flasks was maintained under mixing using a Julabo SW22 shaker. The concentration of pollutants was analyzed by using an UV-VIS spectrophotometer at the wavelength of 230 nm for aniline, 280 nm for 2-methyl-aniline, and 295 nm for 4-methyl-aniline.

Energy-dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM) were carried out using Quanta FEG Microscope equipped with EDX-ZAF quantifier (FEI Company, Nederland), at an accelerating voltage of 20 kV, under low vacuum. The powdered samples were placed on self-adhesive carbon tape support.

2.2. Obtaining of aminophosphonated groups/aminoacid-phosphonated groups grafted onto styrene-15%-divinylbenzene copolymer

The syntheses for obtaining AP-S15%DVB (Scheme 1) and AM-S15%DVB (Scheme 1) were carried out according to methods that we have previously published [21, 22].

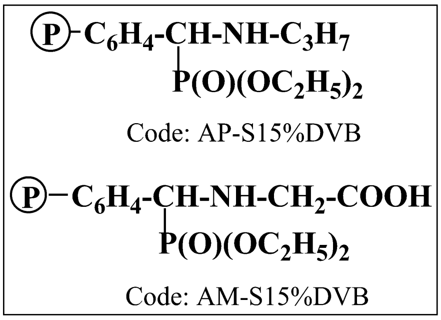
Obtaining of AP-S15%DVB sample

Five grams of styrene-15%divinylbenzene copolymer functionalized with 3-benzaldehyde groups (code: MP-S15DVB), propylamine and diethylphosphite were added to 50 mL of tetrahydrofuran to obtain a molar ratio of aldehyde groups:propylamine:diethylphosphite = 1:1:1. The mixture was stirred for 34 h at a reaction temperature of 65°C. After cooling, the polymer beads separated by filtration were washed with ethanol and finally dried at 50°C for 24 h.

Obtaining of AM-S15%DVB sample

Five grams of MP-S15DVB were reacted with glycine and diethylphosphite in a molar ratio of 1:1:1 and at reflux for 30 h in 50 mL of ethanol. Then, the functionalized copolymer with the phosphonate-aminoacid pendant groups was separated by filtration, washed with ethanol, acetone and dried at 50ºC for 24 h.

The structure of the copolymers is as follows:



$$\text{Ⓟ}-C_6H_4-\underset{\displaystyle P(O)(OC_2H_5)_2}{\underset{|}{CH}}-NH-C_3H_7$$

Code: AP-S15%DVB

$$\text{Ⓟ}-C_6H_4-\underset{\displaystyle P(O)(OC_2H_5)_2}{\underset{|}{CH}}-NH-CH_2-COOH$$

Code: AM-S15%DVB

Scheme 1. The structure of the tested copolymers

2.3. Adsorption experiments

Samples AP-S15%DVB and AM-S15%DVB were used to remove pollutants by type: aniline, 2-methyl-aniline and 4-methyl-aniline.

Determination of the adsorption capacity towards 2-methyl-aniline, 4-methyl-aniline and aniline on functionalized polymer supports

Batch adsorption tests were carried out in 200 mL Erlenmeyer flasks. To start the experiment, 0.200 g of polymeric adsorbents (AP-S15%DVB, AM-S15%DVB) were mixed with 25 mL of amino derivatives solution (3 mmol/L). The experiment was carried out at 3 different temperatures: 298 K, 308 K and 318 K. The content of the flask was mixed using a Julabo SW22 shaker. Samples were analyzed using an UV-VIS Shimadzu UV mini 1240 spectrophotometer. The absorbance of the amino-derivative was measured in the UV range, at wavelengths between 200 and 380 nm. Samples were taken every 5 min for 2h to determine the absorption of the solution. After measuring the absorbance, the samples were put back into the Erlenmeyer beaker. The final absorbance was read after 4h, time considered necessary to reach the adsorption equilibrium. The amount of adsorbed amino derivative was calculated as the difference between the concentration of the initial solution and that determined at time t. The adsorption capacity was calculated using the following equation:

$$q_e = \frac{V\left(C_i - C_e\right)}{m} \tag{1}$$

where: q_e is the equilibrium adsorption capacity (mmol/g), V is the volume of solution (L), m is the mass of dry adsorbent (g), C_i and C_e (mmoles/L) are the initial and respectively equilibrium concentration.

The recoveries (R, %) was calculated by the following equation [10]:

$$R = \frac{\left(C_i - C_e\right)}{C_i} \times 100 \qquad (2)$$

where: C_i and C_e (mmoles/L) are the initial and respectively equilibrium concentration.

Kinetic study

In order to study the adsorption process of all amino derivatives on AP-S15%DVB functionalized adsorbent from a kinetic point of view, the time variation of the absorbance of the amino derivative solution during the adsorption process was spectrophotometrically monitored, starting from an initial concentration of 3 mmol/L, at different temperatures (298 K, 308 K and 318 K).

The kinetic equations corresponding to pseudo-first order [21] and pseudo-second order [21] kinetic models, known from the literature, are used for the kinetic study of adsorption:

$$\ln\left(q_e - q\right) = \ln q_e - k_1 t \quad \text{- for pseudo-first order,} \qquad (3)$$

where: t - the time, min; q - the amount adsorbed at time t, mmoles/g; q_e - the amount adsorbed when the equilibrium is established, mmoles/g; k_1 - speed constant of the adsorption process, min^{-1}.

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{- for pseudo-second order,} \qquad (4)$$

where: t - the time, min; q - the amount adsorbed at time t, mmoles/g; q_e - the amount adsorbed when the equilibrium is established, mmoles/g; k_2 - speed constant of the adsorption process, (min^{-1}) $(mmoles/g)^{-1}$.

3. Results and discussions

3.1. Characterization of functionalized polymers

The peaks of both nitrogen and phosphorus, proving the functionalization of the AP-S15%DVB copolymer, are presented in Figure 1. SEM image (Figure 1) shows that the copolymer beads exhibit a perfect round shape, with the diameter varying from 247.7 µm to 410.6 µm.

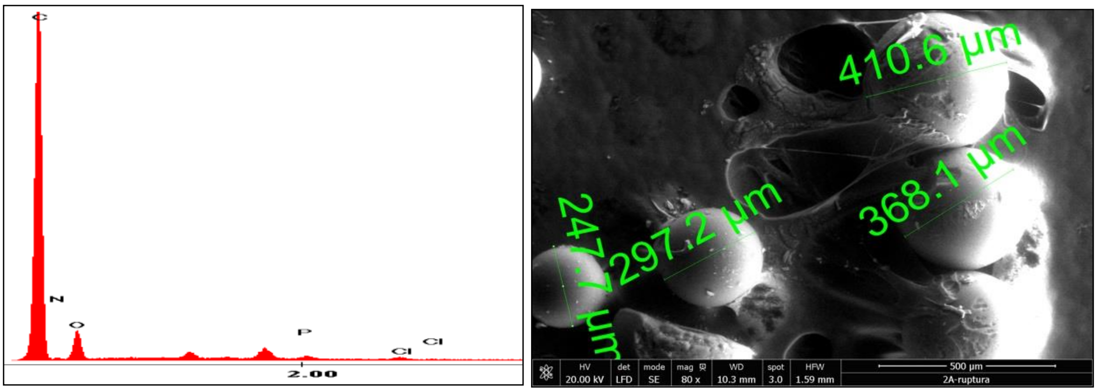


Figure 1. EDX and SEM images for characterization of AP-S15%DVB sample

The peaks of both nitrogen and phosphorus, proving the functionalization of the AM-S15%DVB copolymer, are presented in Figure 2. SEM image (Figure 2) shows that the sample has a homogeneous texture.

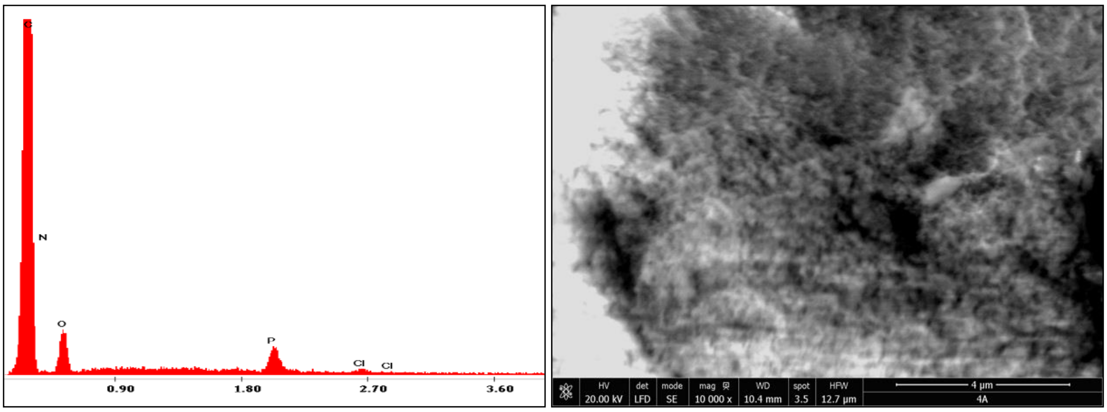


Figure 2. EDX and SEM images for characterization of AM-S15%DVB sample

Within the limits of inherent experimental errors, Table 1 presents the results obtained in the characterization of the functionalized copolymers.

Table 1. EDX analysis both AP-S15%DVB and AM-S15%DVB samples

Sample/ Element	AP-S15%DVB		AM-S15%DVB	
	Weight %	Atomic %	Weight %	Atomic %
C	78.87	83.03	85.89	88.99
N	3.02	2.73	1.76	1.56
O	17.95	14.18	11.95	9.29
P	0.10	0.04	0.37	0.15
Cl	0.06	0.02	0.04	0.01

According to the EDX analysis (Table 1), the nitrogen and phosphorus content for AP-S15%DVB and AM-S15%DVB samples were: 3.02 (%N, weight) and 0.10 (%P, weight), and 1.76 (%N, weight) and 0.37 (%P, weight), respectively.

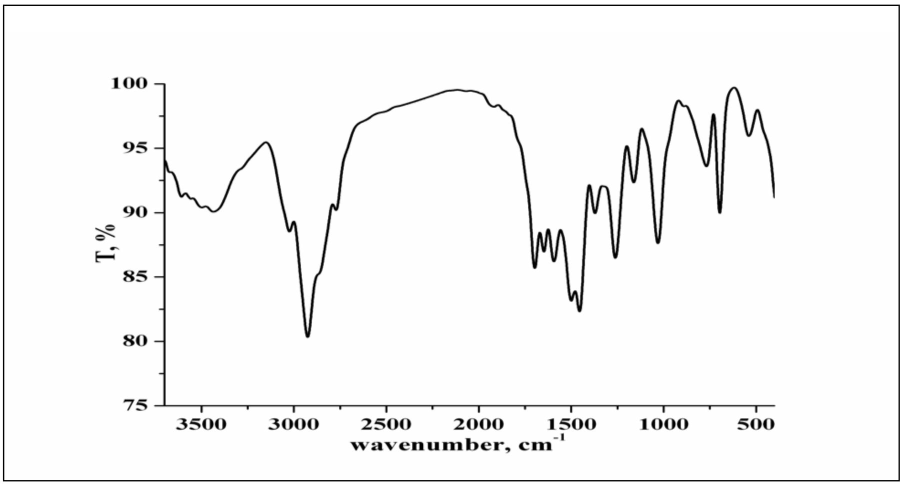


Figure 3. FTIR spectrum of AP-S15%DVB sample

FTIR spectrum (Figure 3) has presented [20, 21]:

- the wide band at 3550-3450 cm^{-1} indicates a secondary amine;

- the wide band at 3200-2700 cm^{-1} indicates the presence of -CH$_2$ and -CH$_3$ groups from aliphatic groups (ethyl and propyl);

- the increase in the intensity of adsorption band at around 1564 cm^{-1} is indicating N–H valence vibrations;

- the N–H band for substituted amino groups was observed at 756 cm^{-1};

- the adsorption bands from the interval 1140-1300 cm^{-1} were attributed to γCH_2 from $–CH_2–Cl$ group, $\gamma N\text{-}C_{aliphatic}$, and $\gamma P{=}O$ bond.

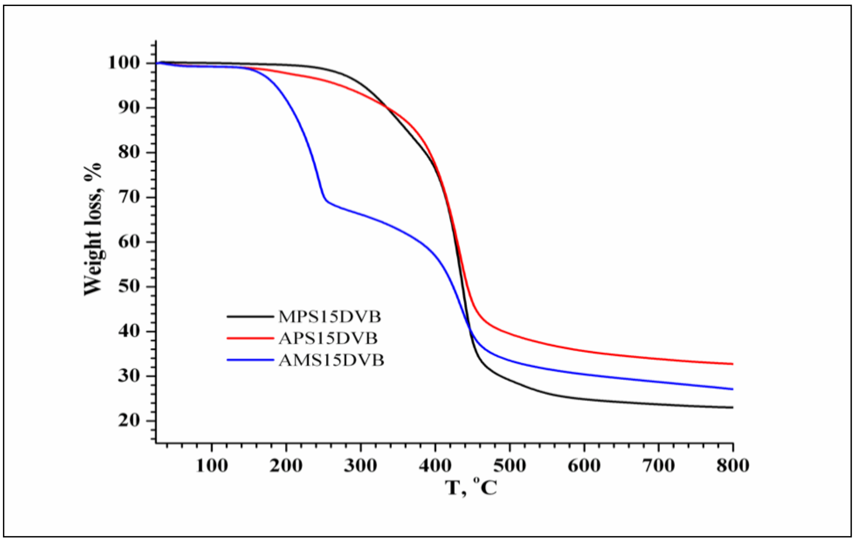


Figure 4. Termogravimetric analysis for MP-S15DVB, AP-S15DVB and AM-S15DVB

The thermogravimetric analysis of AP-S15DVB and AM-S15DVB samples were carried out from 25 to 800°C under a nitrogen flow, in 10°C/min heating step. The comparative interpretation of the TG spectra (Figures 4 and 5) for the synthesized samples (AP-S15DVB, AM-S15DVB) and aldehyde support (MP-S15DVB) shows:

- after 800°C, the decomposition of samples gives: MP-S15DVB ~22% residue; AM-S15DVB ~28% residue; AP-S15DVB ~33% residue.

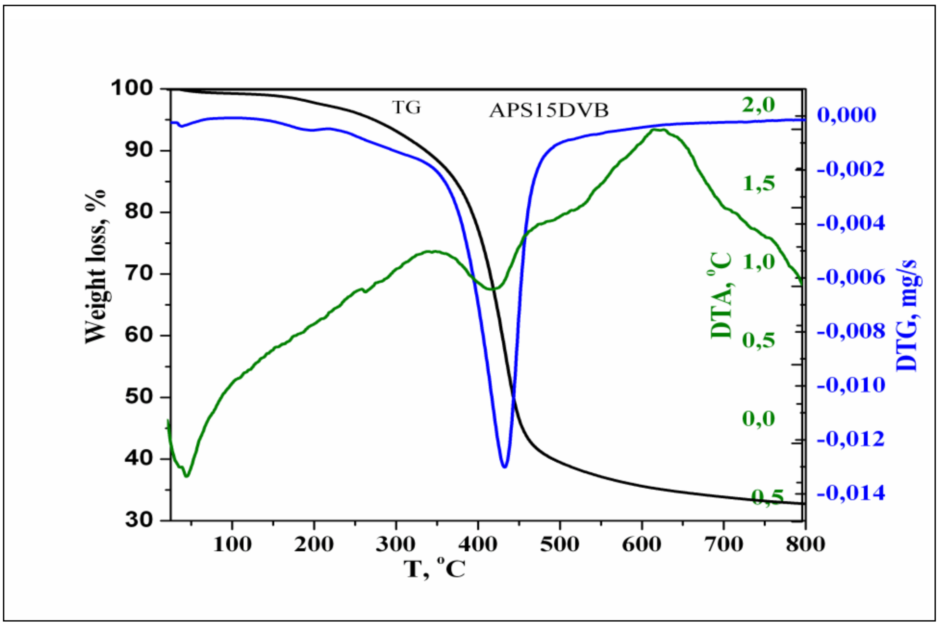


Figure 5. Termogravimetric analysis for AP-S15DVB sample

Thermogravimetric analysis for AP-S15DVB (Figure 5) shows weight losses in two temperature steps. In the first step (25-310°C), the weight loss (~2.69%) was attributed to evaporation physically adsorbed water in polymer and for the decomposition of organic groups. In the second step (310-570°C), the weight loss (~62.16%) is mostly attributable to DVB degradation and for the decomposition of organic groups. AP-S15DVB sample has stability up to a temperature of 420°C. Thus, AM-S15DVB sample becomes less stable compared with both AP-S15DVB sample and the raw material (Figures 4 and 5).

3.2. Adsorption characterization

The variation over time of the amount of 2-methyl-aniline, 4-methyl-aniline and respectively aniline adsorbed on the studied copolymers is presented below (Figure 6).

It was found that the speed of the adsorption process (Figure 6 a, b) was high at the beginning, in each case. After 30 min, more than 90% of the total adsorption capacity of the considered amino-derivative was achieved. The amount of adsorbed 4-methyl-aniline was in each case greater than the amount of 2-methyl-aniline and aniline. The adsorbent with the best adsorption capacity was AP-S15%DVB. In the graphical representations, we mostly present the data for the best-performing adsorbent, AP-S15DVB.

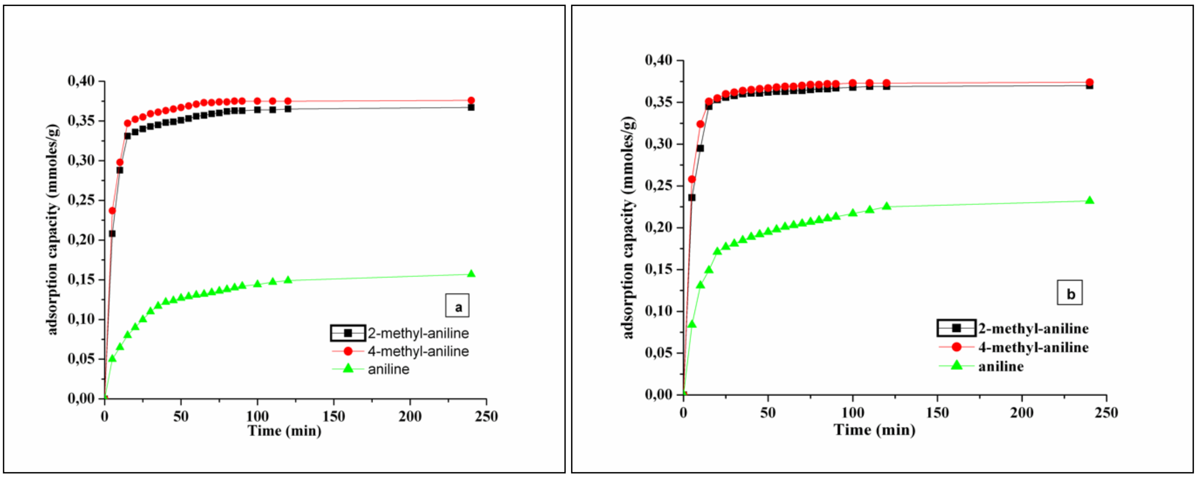


Figure 6. Comparative representation of the variation of the adsorption capacity for 2-methyl-aniline, 4-methyl-aniline and aniline as a function of time, at a temperature of 298 K, onto copolymers: (a) AM-S15DVB, (b) A-PS15DVB

Among the aromatic amino-derivatives used for the adsorption process (Table 2 and Table 3), the efficiency was higher for 4-methyl-aniline and for 2-methyl-aniline then aniline. We observed that the functionalized copolymers studied were effective in the removal of aromatic amines from aqueous solutions.

Table 2. Comparative representation of the adsorption capacity against 2-methyl-aniline, 4-methyl-aniline and aniline at 298 K and after 240 min

Aromatic amines	AM-S15%DVB	AP-S15%DVB
	Adsorption capacity, mmoles/g	
2-methyl-aniline	0.364	0.370
4-methyl-aniline	0.376	0.374
aniline	0.157	0.232

Table 3. Recoveries (R, %) of aromatic amines from aqueous solutions by aminophosphonated groups / aminoacid-phosphonated groups grafted onto styrene-15%-divinylbenzene copolymer

Aromatic amines	AM-S15%DVB			AP-S15%DVB		
	R[a], %	C_i, mmoles/L	C_e, mmoles/L	R[a], %	C_i, mmoles/L	C_e, mmoles/L
2-methyl-aniline	97.73	2.9988	0.0681	98.57	2.9989	0.0428
4-methyl-aniline	99.74	3.0098	0.0076	99.34	3.0098	0.0197
aniline	42.53	2.9505	1.6956	62.90	2.9505	1.0945

[a] The recoveries (R, %) were calculated by using equation equation 2.

C_i and C_e (mmoles/L) denote the initial and equilibrium concentration of aromatic amines (at 240 minutes; and 298K) in aqueous solution, respectively.

To check if the adsorption process proceeds according to the pseudo-first order kinetic model and to study the influence of temperature on the rate constant, Lagergren's equation [21] (3) was used, representing ln(q_e-q) as a function of time (Figure 7a). To check if the adsorption process follows a pseudo-second order kinetic model, the equation of Ho and McKay [21] (4) was used, and the t/q ratio was plotted as a function of time (Figure 7b).

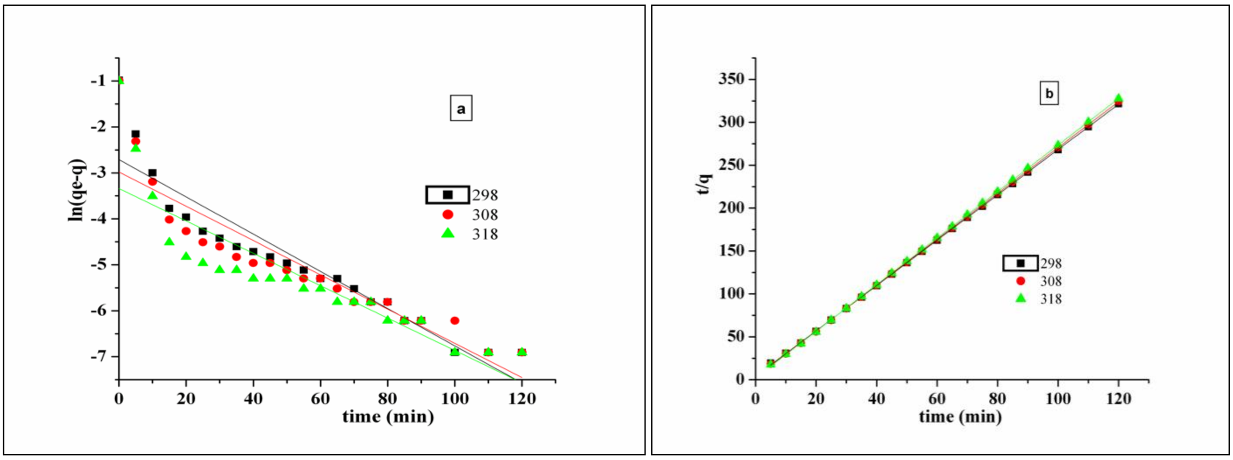


Figure 7. Kinetic models for 4-methyl-aniline adsorption onto AP-S15%DVB, at 298 K, 308 K, 318 K and initial concentration of 3 mmol/L: (a). Pseudo-first order; (b). Pseudo-second order

Comparing the kinetic parameters presented in Table 4 for the pseudo-first order and pseudo-second order (PSO) kinetic models, it can be concluded that the adsorption of 4-methyl-aniline onto AP-S15%DVB is best described by the PSO kinetic model because the highest correlation coefficient R^2 was obtained in this case (Table 4).

Therefore, it would seem that the removal of 4-methyl-aniline from aqueous solutions is due to chemisorption processes [21, 25].

Table 4. Kinetic models parameters for 4-methyl-aniline adsorption onto AP-S15%DVB

Model	Parameter/ Temperature	Values		
		298 K	308 K	318 K
	q_{eexp} (mmoles/g)	0.374	0.372	0.368
Pseudo-first order	k_1 (min^{-1})	0.0349	0.0365	0.0399
	R^2	0.8698	0.8457	0.7385
Pseudo-second order	k_2 (min^{-1}) $(mmoles/g)^{-1}$	1.657	2.135	3.104
	R^2	0.99991	0.99993	0.99998

4. Conclusions

It is observed that the tested functionalized adsorbents adsorb 2-methyl-aniline, 4-methyl-aniline and aniline, the efficiency being higher in the case of 4-methyl-aniline adsorption (percent recoveries, R%, in Table 3). The alkyl substituted anilines are better adsorbed most probably due to the inductive effects (-I) of the alkyl substituents affecting the substrate polarity. The speed of adsorption process is high in the first 30 min, when more than 90% of the total amount of amino derivative was adsorbed until the equilibrium was established. The time required to establish the adsorption equilibrium was 240 min. Since the adsorption process is fast, this type of functionalized polymers could be used in fixed bed adsorption processes on column. The adsorption capacity depends on the nature and structure of the functional groups grafted on the polymer support. The most effective of the adsorbents tested for the adsorption of aromatic amino derivatives was AP-S15%DVB. Among the aromatic amino derivatives used for the adsorption process, 4-methyl-aniline was the best adsorbed and aniline the least adsorbed.

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