

## Adsorption of bisphenol A and phenoxyacetic acid onto new polymeric adsorbents

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New quaternary amine-containing resins were prepared and used for adsorption of phenoxyacetic acid (PAC) and bisphenol A (BPA). For this purpose, crosslinked poly (glycidyl methacrylate (GMA)-co-ethylene glycol dimethacrylate (EGDMA)) beads (PGMA) were prepared and modified with N,N-diethylethylenediamine to obtain tertiary amine function carrying (BR) resin. Other quaternary amine function carrying resins were prepared starting from crosslinked poly (vinyl benzyl chloride (VBC)-co-EGDMA) (PVBC) resin. PVBC resin was reacted with imidazole and ethyl piperazine to obtain imidazole- and ethyl piperazine-modified resins, respectively. Then, these resins were reacted with chloroacetamide to prepare quaternary amine resins, PVBCIM (quaternized imidazole modified PVBC), PVBCPEP (quaternized ethylpiperazine PVBC). The adsorption isotherm experiments of adsorbed pesticides on the new polymeric resins were performed at 25°C by using Freundlich and Langmuir models. The maximum BPA sorption capacities of the new polymeric adsorbents were obtained as BR>PVBCPEP>PVBCIM, respectively. For PAC, the adsorption maximum capacities of the new polymeric adsorbents changed to PVBCPEP>PVBCIM>BR. Characterization of adsorbents was performed by SEM and FTIR method before and after adsorption experiments. The adsorption kinetics of pesticides was studied depending on temperature (25°C-40°C) and also kinetic models were applied such as pseudo-first order, corrected-second order and intraparticle diffusion model.

**Keywords:** Bisphenol A; Phenoxyacetic acid; Pesticide; Adsorption; Polymeric resin.

### INTRODUCTION

Environmental pollution increases day by day in a proportion of the population and the industrial development increases. This contamination is mainly caused by the mixing of organic and inorganic chemicals into the groundwater. The increased uses of pesticides in agriculture to control insects increasingly pollute water resources. Since the pesticide structures are rarely biodegradable, this effect is highly pollutant to the environment and some carcinogenic properties for living organisms are observed as well [1]. The use of phenolic materials in pesticides made them harmful to organisms even at low concentrations. They are considered as primary pollutants and classified as hazardous to people's health. Even though the amount of contamination with phenolic materials in drinking water is 0.005 ppm, it causes some significant problems of taste, odor and loss of suitability for use [2].

Bisphenol A (BPA) plays an important role because of its widespread usage in materials as a component of industrial polymers and fungicides [3]. The effect of toxicity of BPA is really serious for freshwater and salty algae, invertebrates and fish. Bisphenol A has been listed by China and the EPA as the main pollutant for the aquatic environment due to its stability, bioaccumulation and toxicity [4]. Wang *et al.* (2015) used modified

montmorillonite to control interfacial hydrophobicity with an improved matrix. The inner layer hydrophilic properties of the clay molecules, the inner layer chelating properties of the alkyltrimethylammonium ions and their adsorption balance with BPA were investigated in details and the BPA concentration level was observed as the inner layer chelate chain length predicted to increase [5]. Mao *et al.* (2014) synthesized a surface-active polymer on modified kaolin and selectively studied adsorption of BPA, 4,4-biphenyldiphenol and 2,6-dichlorophene. It was thought that the chemical process could be also involved in this study as a rate-limiting step for BPA adsorption. This synthesized polymer had proven to have high affinity and selectivity for BPA compared to other components [6]. Zainab *et al.* (2015) used coconut fiber, coconut shell and durian fruit husk from organic agricultural wastes for BPA removal. All three adsorbents showed similar low adsorption. The optimum adsorption time was found to be 24 h [7]. Soni and Padmaja (2014) used active carbon from the palm kernel as adsorbent and investigated the effect of variable pH, concentration, time and temperature parameters. It was found that the adsorption process was spontaneous and exothermic and there was a weak physical interaction between adsorbents. The disadvantage was the quite costly and difficult work and impossibility to recycle [8]. Other similar

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studies in the literature until today were done with polymeric adsorbent [9], nanotube [10], graphene [11], lignin [12], mesoporous silicon dioxide [13], activated sludge [14], modified zeolite [15], chitin [16].

Phenoxy acid belongs to a class of herbicides which exhibits auxin-like activities in excessive use for the control of broad-leaved weeds growing in products such as rice, winter wheat, soya bean, long grass. Phenoxy acetic acid (PAC) is highly toxic and it can be irritant to the skin and eyes. Prolonged exposure may cause serious damage to internal organs and biological systems. It can be transported in the agricultural ecosystem causing pollution in surface and ground waters, because of its water solubility. Young *et al.* (2006) studied the removal of CPA (chlorophenoxyacetic acid), MCPA (4-chloro-2-methylphenoxyacetic acid) with activated carbon [17]. Aksu *et al.* (2004) investigated the removal of 2,4-dichlorophenoxyacetic acid used by activated granular carbon depending on pH, temperature and initial concentration [18]. Moustapha *et al.* (2000) also worked on removal of 2,4-dichloro-phenoxyacetic acid with two different activated carbons in terms of contact time, adsorbent dose, effect of ionic strength, pH variables [19]. Cserhati *et al.* (1998) studied 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, 4-chloro-2-methylphenoxyacetic acid, 2,4-dichlorophenol, 2,4,5-trichlorophenol and p-chlorocresol pesticides [20].

In this study, quaternized amine- and tertiary amine-modified resins were used for removal of pesticides such as bisphenol A (BPA) and phenoxyacetic acid (PAC). Adsorption kinetics of pesticides on the resins was studied at constant concentration from 25°C to 40°C. The sorption experiments of the pesticide were studied with different concentrations at 25°C. The adsorption isotherms were fitted to Langmuir and Freundlich models. SEM and FTIR characterization methods were used to evaluate both sorbent resins and pesticide.

## EXPERIMENTAL

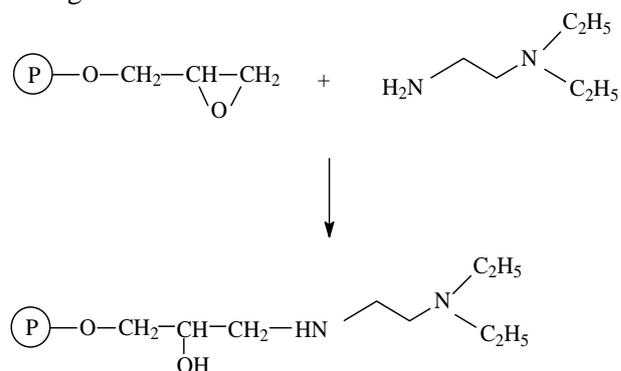
### Materials

BPA and PAC were purchased from Sigma-Aldrich and Merck companies. The stock solutions were prepared in aqueous media as 114.12 ppm for BPA and 760 ppm for PAC. The maximum wavelengths of BPA and PAC were determined in aqueous solution, respectively 227 and 276 nm. Glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EGDMA), ethyl piperazine, imidazole, vinyl benzyl chloride and 2-

chloroacetamide were purchased from Sigma-Aldrich.

### Synthesis of the resins

**Preparation of BR resin (N,N-diethylethylenediamine modified GMA-EGDMA).** Tertiary amine modified methacrylate based resin was synthesized by modification of crosslinked PGMA resin. This resin was prepared starting from copolymerization of GMA (glycidyl methacrylate) (90% mol) and EGDMA (ethylene glycol dimethacrylate) (10% mol) as monomers in the presence of AIBN (azobisisobutyronitrile) as initiator, polyvinylpyrrolidone as stabilizer and toluene as porogen by using suspension polymerization method [21]. In the second step, 5 g of PGMA resin were added in portions to the excess of N,N-diethylethylenediamine in 50 mL of N-methyl-1-pyrrolidone (NMP). The mixture was continuously shaken on a shaker for 24 h at room temperature and heated at 80°C for 2 h. Then, the reaction mixture was cooled and poured into 250 mL of distilled water. Tertiary amine modified resin was filtered and washed with excess of water and 150 ml of methanol, respectively. The obtained resin (BR) was dried under vacuum at room temperature for 24 h (Scheme 1). The yield was 7.59 g.



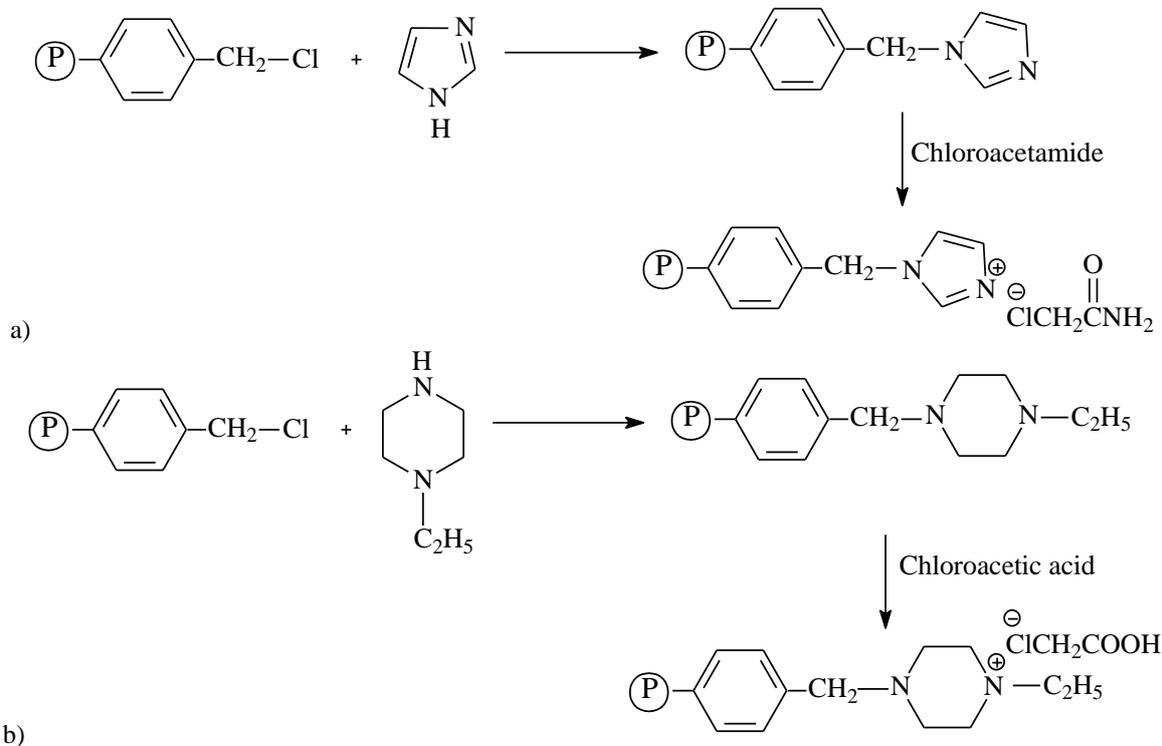
**Scheme 1.** Structure of BR resin molecule

**Preparation of PVBCIM and PVBCEP resins.** These resins were prepared starting from modification of crosslinked poly (vinyl benzyl chloride) (PVBC) described in the literature [22]. 5.0 g of PVBC resin was added to 2.50 g of imidazole in 50 ml of NMP and 15 ml of ethyl piperazine solution in 30 ml of NMP at 0°C to obtain imidazole- and ethyl piperazine-modified PVBC, respectively. The reaction mixtures were continuously shaken with a shaker at room temperature for 24 h. Then, the reaction contents were poured into 1 L of water, filtered and washed with excess of water and methanol, respectively. The resins were dried under vacuum at room

temperature for 24 h and the yields were found as 5.8 g for PVBCIM and 8.4 g for PVBCEP.

**Quaternization of PVBCIM and PVBCEP.** PVBCIM was quaternized with chloroacetamide. For this purpose, 5.0 g of PVBCIM was reacted with 3.5 g of chloroacetamide in 25 ml of DMF solution. The reaction mixture was stirred at room

temperature for 24 h. The reaction mixture was heated at 70°C for 8 h. Then, the reaction mixture was filtered and washed sequentially with DMF, water and ethanol. The quaternized (PVBCIM) resin was filtered and dried under vacuum at room temperature for 24 h to give 7.20 g of the final product (Scheme 2a).



**Scheme 2.** a) Preparation of quaternized PVBCIM resin; b) Preparation of quaternized PVBCEP resin

Quaternization of PVBCEP was performed by chloroacetic acid. According to the procedure, 18.9 g of chloroacetic acid (0.20 mol) was dissolved in 20 ml of water and this solution was dropped by a dropping funnel into 13.8 g of  $K_2CO_3$  (0.1 mol) in 25 ml of distilled water at 0 °C. Then, 5 g of PVBCEP was added to the solution. The reaction mixture was continuously shaken on the shaker for 48 h at room temperature and was stirred at 70°C for 3 h. At the end of the reaction, quaternized resin (PVBCEP) was filtered and washed with excess of water. PVBCEP was dried under vacuum at room temperature for 24 h. The yield was found as 7.0 g (Scheme 2b).

#### Adsorption experiments

Preparation of working solutions from the BPA and PAC stock solutions: working BPA solutions were prepared in five different concentrations between 8.67 ppm and 22.5 ppm for the isotherm studies. In the kinetic studies, optimum BPA concentration was chosen as 17.11 ppm. The concentrations of PAC varied from 38 ppm to 380 ppm for the isotherm studies. The best

concentration of PAC for the kinetic studies was chosen to be 121.7 ppm. In adsorption experiments, 0.01 g of resin sample was reacted with 10 mL of pesticide solution for 90 min at 25°C and aliquots were taken every 15 min for spectrophotometric analysis.

#### Adsorption studies

Adsorption capacity of the sorbents ( $mg\ g^{-1}$ ) was calculated using the following equation (1):

$$q_d = \frac{c_o - c_d}{W} \times V \quad (1)$$

where  $c_o$  and  $c_d$  are the initial and equilibrium concentration of pesticide, respectively ( $mg\ L^{-1}$ ),  $W$  is the weight of sorbent (g),  $V$  is the volume of pesticide solution (L).  $V/W$  ratio was held as  $1\ L\ g^{-1}$  during adsorption isotherm experiments [23].

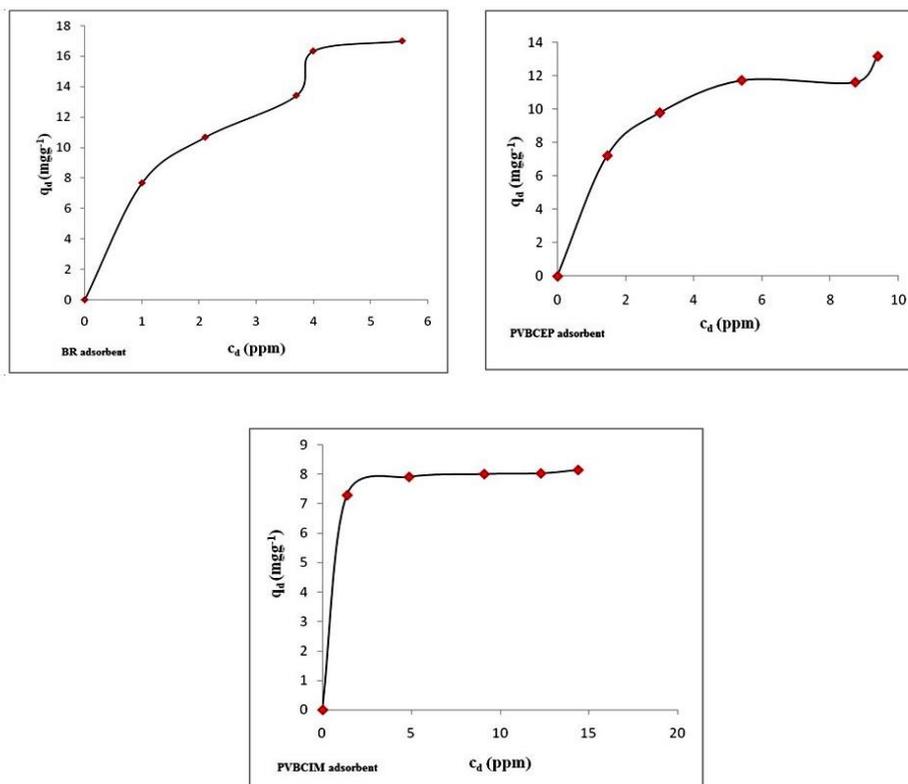


Figure 1. Giles isotherms of BPA (L type)

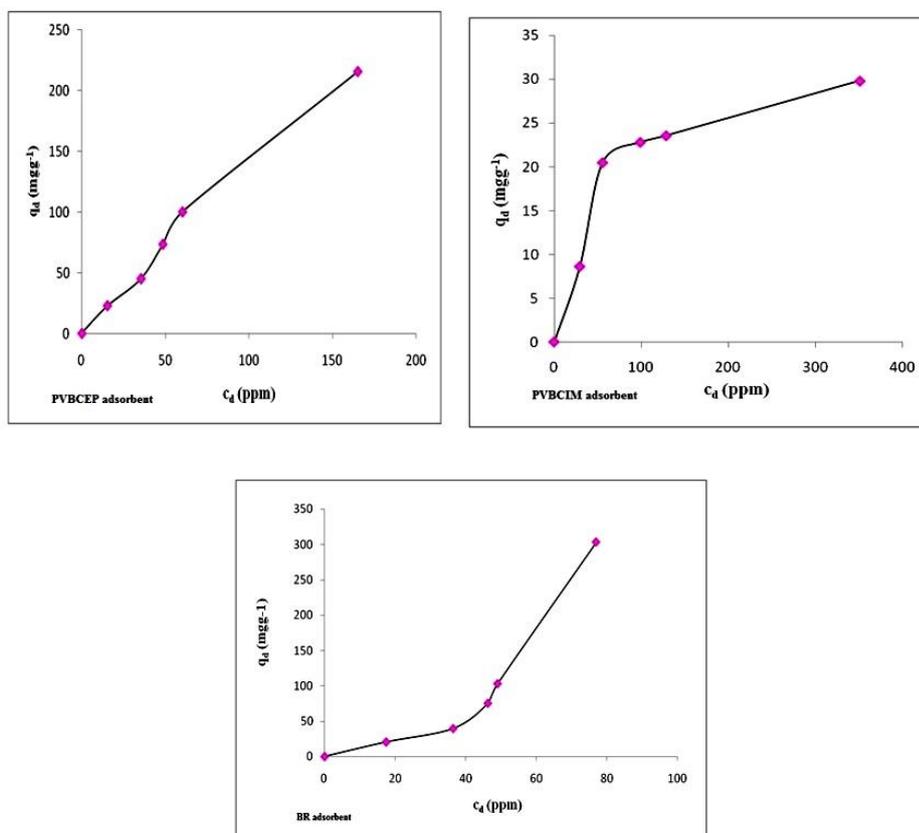


Figure 2. Giles isotherms of PAC (S type)

**Table 1.** Adsorption isotherm parameters of resins for BPA

Isotherms	PVBCEP	BR	PVBCIM
Freundlich			
$K_F$	6.77	7.61	7.25
$n$	0.29	0.48	0.05
$R^2$	93	97	95
Langmuir			
$b \text{ L mg}^{-1}$	0.676	0.53	593
$q_{\max} \text{ mg g}^{-1}$	14.55	21.7	8.13
$R^2$	98	99	97

**Table 2.** Adsorption isotherm parameters of resins for PAC

Isotherms	PVBCEP	BR	PVBCIM
Freundlich			
$K_F$	1.55	0.097	1.97
$n$	0.95	1.78	0.5
$R^2$	98	92	88
Langmuir			
$b \text{ L mg}^{-1}$	0.00195	-0.0083	0.00759
$q_{\max} \text{ mg g}^{-1}$	769	-118	48.31
$R^2$	98	95	98

*Adsorption isotherms*

The results of the adsorption studies of BPA and PAC were expressed by Freundlich and Langmuir isotherm models. Adsorption isotherm type graphics of BPA were drawn as  $q_e$  vs  $c_e$  as seen in Figure 1. The Giles isotherm lines of BR, PVBCEP and PVBC IM appear to be the same as L3, L4 and L2 types, respectively. For PAC, Giles isotherm types of PVBCEP, PVBC and BR were found L4, L3 and S3, respectively in Figure 2 [24]. These L types suggest that first monolayer line and then multilayer line occurs during adsorption process. This S type indicates that the adsorption of pesticide was reluctant onto the adsorbates.

*Langmuir isotherm:* The Langmuir equation is represented as follows:

$$\frac{1}{q_d} = \frac{1}{q_{\max} b C_d} + \frac{1}{q_{\max}} \quad (2)$$

where  $C_d$  gives a straight line,  $q_{\max}$ , is the maximum adsorption at monolayer coverage ( $\text{mol g}^{-1}$ ) and  $b$  the adsorption equilibrium constant ( $\text{L}$

$\text{mol}^{-1}$ ).  $1/q_d$  vs  $1/c_d$  with slope  $b$  and intercept  $1/q_{\max}$  is obtained (Tables 1, 2).

*Freundlich isotherm:* The Freundlich isotherm model can be applied by the following:

$$q_d = K_F c_d^n \quad (3)$$

The linear equation of the Freundlich isotherm is fitted in the logarithmic form as given below:

$$\log q_d = \log K_F + n \log c_d \quad (4)$$

where:  $q_d$  is the amount adsorbed ( $\text{mol g}^{-1}$ ),  $C_d$  the equilibrium concentration in aqueous phase ( $\text{mol L}^{-1}$ )  $K_F$  and  $n$  are Freundlich constants related to adsorption capacity and adsorption intensity.

*Kinetic studies*

The kinetics of BPA and PAC were studied at four different temperatures. The concentrations of BPA and PAC used in the kinetic experiments were 17.11 and 121.7 ppm, respectively. In order to investigate the kinetics of pesticides adsorption, pseudo-first-order and pseudo-second-order models were examined (Tables 3-8).

**Table 3.** Kinetic parameters of the aqueous solution of BPA on PVBCEP resin.

t <sup>0</sup> C	q <sub>d</sub> exp.	q <sub>d1</sub> calc.	k <sub>1</sub> / dk <sup>-1</sup>	R <sup>2</sup>	q <sub>d2</sub> calc.	k <sub>2</sub> / g mg <sup>-1</sup> dk <sup>-1</sup>	R <sup>2</sup>	k <sub>i</sub> / mg g <sup>-1</sup> dk <sup>-1/2</sup>	R <sup>2</sup>
25	0.0105	0.0087	0.0197	83	0.009	3.2	99.2	0.0003	98.7
								0.0014	97
								0.0007	95
35	0.0088	0.0072	0.0175	81	0.008	8.56	99.8	0.0004	99
								0.0019	100
40	0.0038	0.0036	0.0233	92	0.004	9.34	99.9	0.0004	96
								0.0007	100

**Table 4.** Kinetic parameters of the aqueous solution of BPA on BR resin.

t <sup>0</sup> C	q <sub>d</sub> exp.	q <sub>d1</sub> calc.	k <sub>1</sub> / dk <sup>-1</sup>	R <sup>2</sup>	q <sub>d2</sub> calc.	k <sub>2</sub> / g mg <sup>-1</sup> dk <sup>-1</sup>	R <sup>2</sup>	k <sub>i</sub> / mg g <sup>-1</sup> dk <sup>-1/2</sup>	R <sup>2</sup>
25	0.014	0.0019	0.0357	95	0.0137	4.81	99.9	0.0001	98.7
								0.0002	97
30	0.0116	0.0032	0.0255	88	0.012	13	99.8	0.0003	94
35	0.0084	0.0042	0.0245	85	0.0081	15.4	99.7	0.0001	97
								0.0007	99.8
40	0.0098	0.0054	0.068	90	0.01	28.4	99.9	0.0003	98

**Table 5.** Kinetic parameters of the aqueous solution of BPA on PVBCIM resin.

t <sup>0</sup> C	q <sub>d</sub> exp.	q <sub>d1</sub> calc.	k <sub>1</sub> / dk <sup>-1</sup>	R <sup>2</sup>	q <sub>d2</sub> calc.	k <sub>2</sub> / g mg <sup>-1</sup> dk <sup>-1</sup>	R <sup>2</sup>	k <sub>i</sub> / mg g <sup>-1</sup> dk <sup>-1/2</sup>	R <sup>2</sup>
25	0.007	0.0083	0.0315	94	0.0081	31.87	98.9	0.0008	98
30	0.0045	0.002	0.0167	80	0.0041	41.85	97.9	0.0001	99.5
								0.0006	100
35	0.0037	0.0016	0.0342	96	0.0037	54.16	98.5	0.0002	99.7
40	0.0021	0.0072	0.0231	91	0.002	113	98.7	0.00007	98

A linear form of pseudo-first-order equation of Lagergren is generally expressed as:

$$\ln (q_d - q_t) = \ln q_d - kt \quad (5)$$

where: k<sub>1</sub> is first order adsorption rate constant (min<sup>-1</sup>), q<sub>t</sub> is amount of adsorbed material at time t (mg g<sup>-1</sup>), q<sub>d</sub> is amount of adsorbed material in equilibrium (mg g<sup>-1</sup>).

The kinetic data were treated with the following Ho's pseudo-second-order rate equation [25]. The linear form of the equation describing the adsorption kinetics by the pseudo-second-order model is as follows:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_d} \quad h = k_2 q_d^2 \quad (6)$$

h (mg g<sup>-1</sup> min<sup>-1</sup>) gives the initial sorption rate. If a graph of t/q<sub>t</sub> vs t is drawn, q<sub>d</sub> and k<sub>2</sub> are calculated

from the slope and cut-off points [26], where q<sub>d</sub> is the amount of pesticide adsorbed at equilibrium (mg g<sup>-1</sup>); q<sub>t</sub> is the amount of pesticide adsorbed at time t (mg g<sup>-1</sup>); and k<sub>2</sub> is the equilibrium rate constant of pseudo-second-order sorption (g mg<sup>-1</sup> min<sup>-1</sup>). The q<sub>d</sub> and k<sub>2</sub> values could be calculated from the slopes (1/q<sub>d</sub>) and intercepts (1/k<sub>2</sub>q<sub>d</sub><sup>2</sup>) of the linear plots of t/q<sub>t</sub> vs t. The intraparticle diffusion constant is given by Weber and Morris as follows [27]:

$$q_t = k_i t^{1/2} + C \quad (7)$$

where: q<sub>t</sub>: amount of adsorbate at any time (mg/g), k<sub>i</sub>: intraparticle diffusion rate constant (mg g<sup>-1</sup>min<sup>-1/2</sup>), t: time (min). Therefore, k<sub>i</sub> value is determined with this equation by plotting a graph of q<sub>t</sub> vs t<sup>1/2</sup>.

**Table 6.** Kinetic parameters of the aqueous solution of PAC on PVBCEP resin.

t <sup>o</sup> C	q <sub>d</sub> exp.	q <sub>d1</sub> calc.	k <sub>1</sub> / dk <sup>-1</sup>	R <sup>2</sup>	q <sub>d2</sub> calc.	k <sub>2</sub> / g mg <sup>-1</sup> dk <sup>-1</sup>	R <sup>2</sup>	k <sub>i</sub> / mg g <sup>-1</sup> dk <sup>-1/2</sup>	R <sup>2</sup>
25	0.0326	0.024	0.024	93	0.033	5.1	99	0.0026	98.9
								0.0033	97
30	0.038	0.027	0.0187	80	0.034	4.04	98.9	0.0004	98.7
								0.0046	97
35	0.0233	0.016	0.0415	98.9	0.0255	2.32	99.9	0.0028	98.7
								0.0009	99.7
40	0.0253	0.024	0.0224	92	0.024	2.18	99.3	0.0015	97

**Table 7.** Kinetic parameters of the aqueous solution of PAC on BR resin.

t <sup>o</sup> C	q <sub>d</sub> exp.	q <sub>d1</sub> calc.	k <sub>1</sub> / dk <sup>-1</sup>	R <sup>2</sup>	q <sub>d2</sub> calc.	k <sub>2</sub> / g mg <sup>-1</sup> dk <sup>-1</sup>	R <sup>2</sup>	k <sub>i</sub> / mg g <sup>-1</sup> dk <sup>-1/2</sup>	R <sup>2</sup>
25	0.06	0.055	0.0493	95	0.067	3	99.7	0.0046	98
30	0.043	0.0135	0.0255	92	0.042	6.51	98.5	0.0013	98
35	0.0355	0.0089	0.0301	96	0.035	11.5	98.9	0.0011	96
									98
40	0.045	0.0028	0.0366	95	0.044	20	99	0.0003	.7

**Table 8.** Kinetic parameters of the aqueous solution of PAC on PVBCIM resin.

t <sup>o</sup> C	q <sub>d</sub> exp.	q <sub>d1</sub> calc.	k <sub>1</sub> / dk <sup>-1</sup>	R <sup>2</sup>	q <sub>d2</sub> calc.	k <sub>2</sub> / g mg <sup>-1</sup> dk <sup>-1</sup>	R <sup>2</sup>	k <sub>i</sub> / mg g <sup>-1</sup> dk <sup>-1/2</sup>	R <sup>2</sup>
25	0.0174	0.011	0.0315	93	0.018	5.56	99.9	0.0011	96.3
30	0.026	0.0078	0.0288	85	0.0264	7.76	99.7	0.0001	98.7
								0.0013	99.8
35	0.0055	0.0048	0.0233	88	0.0056	8.2	98.4	0.0004	95
40	0.0156	0.0053	0.0327	97	0.0158	17.5	99.2	0.0009	98.7
								0.0004	98.3

## RESULTS AND DISCUSSION

In this study, three polymeric sorbents were prepared to remove BPA and PAC pesticides from water. BR (N,N-diethylethylenediamine modified GMA-EGDMA) was prepared starting from crosslinked PGMA. The latter was prepared by suspension polymerization of GMA monomer using EGDMA as crosslinking agent, AIBN as initiator and PVP as stabilizer at 65 °C for 5 h. PGMA resin was reacted with excess of N,N-diethylethylenediamine to obtain tertiary amine-modified resin (BR) PVBC resin was added to NMP in imidazole and ethyl piperazine solution in NMP at 0°C to obtain imidazole- and ethyl piperazine-modified PVBC, respectively. The resins were dried under vacuum at room temperature for 24 h giving PVBCIM and PVBCEP. Then, quaternization of PVBCIM with chloroacetamide and quaternization of PVBCEP with chloroacetic acid was performed.

### Characterization

Surface structure of samples before and after chemical modification process, as well as after adsorption with dye compounds was analyzed by scanning electron microscopy (SEM) on FEI Quanta FEG 450.

*SEM of BR polymer resin:* The SEM photographs were made for the adsorbents that best adsorbed pesticides. As shown in Figure 3a, the surface of the BR adsorbent has partially flat floor. But, budding-like structures were observed in certain of its regions. As shown in Figure 3b, after the adsorption of BPA on BR adsorbent, the flat base changed into cracker layers. The budding was seen to increase and spread in the medium.

*SEM of PVBCEP polymer resin:* As shown in Figure 4a, the characterization images of the pure PVBCEP define that the adsorbent has a large porous smooth-bottomed structure such as the appearance of gravy cheese. After adsorption of PAC on PVBCEP the structure of the ground and large pores are deteriorated and PAC has retained

the dense and angular clusters on the surface (Figure 4b).

Identification of functional groups existing on the surface of samples (before and after sorption process) was stated by using Fourier transform

infrared spectroscopy (Thermo Scientific Nicolet ID5 ATR FTIR). FTIR interpretations of the new polymeric resins that provide the best adsorption for BPA and PAC are given below.

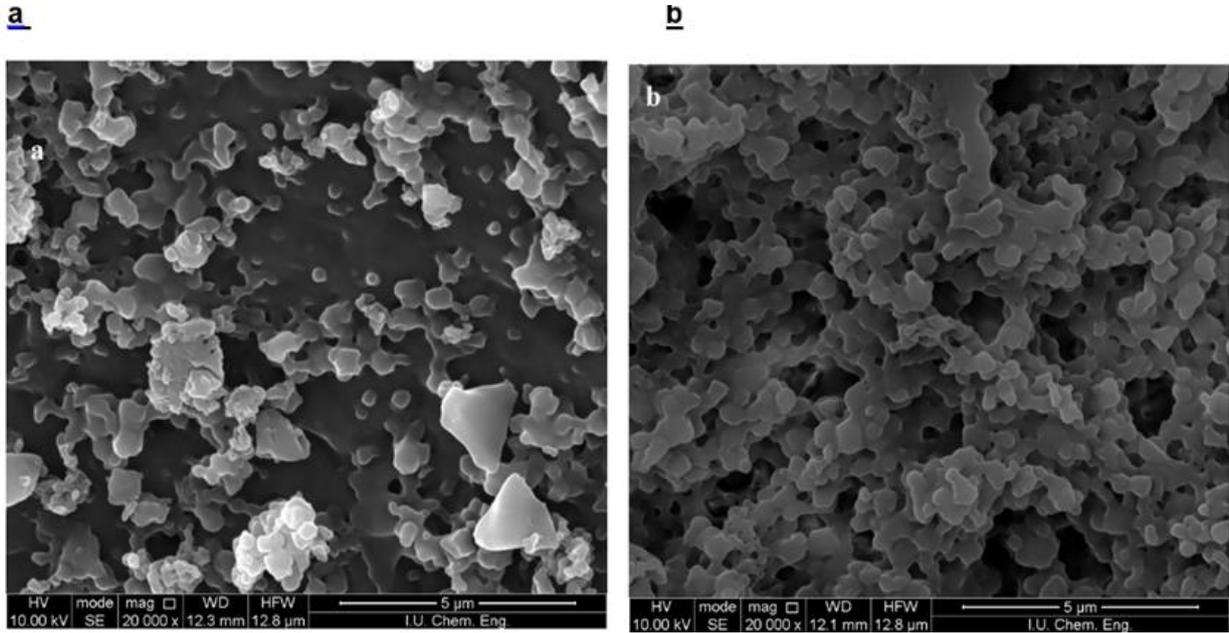


Figure 3. a) SEM image of the pure BR b) SEM image of BR-BPA

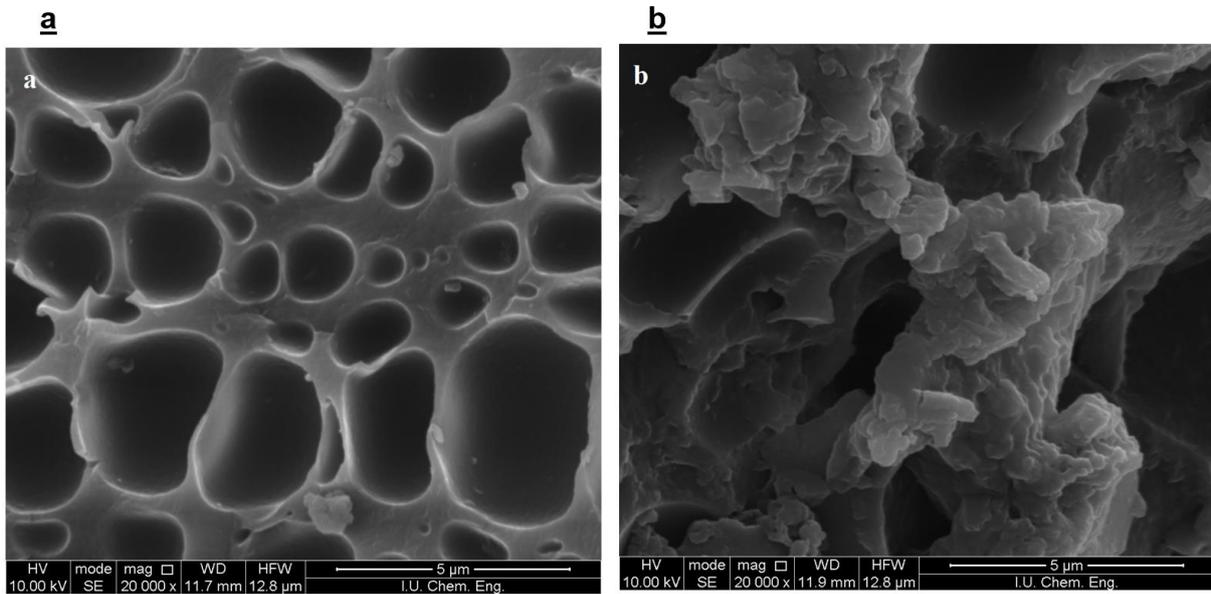


Figure 4. a) SEM image of the pure PVBCEP b) SEM image of PVBCEP-PAC

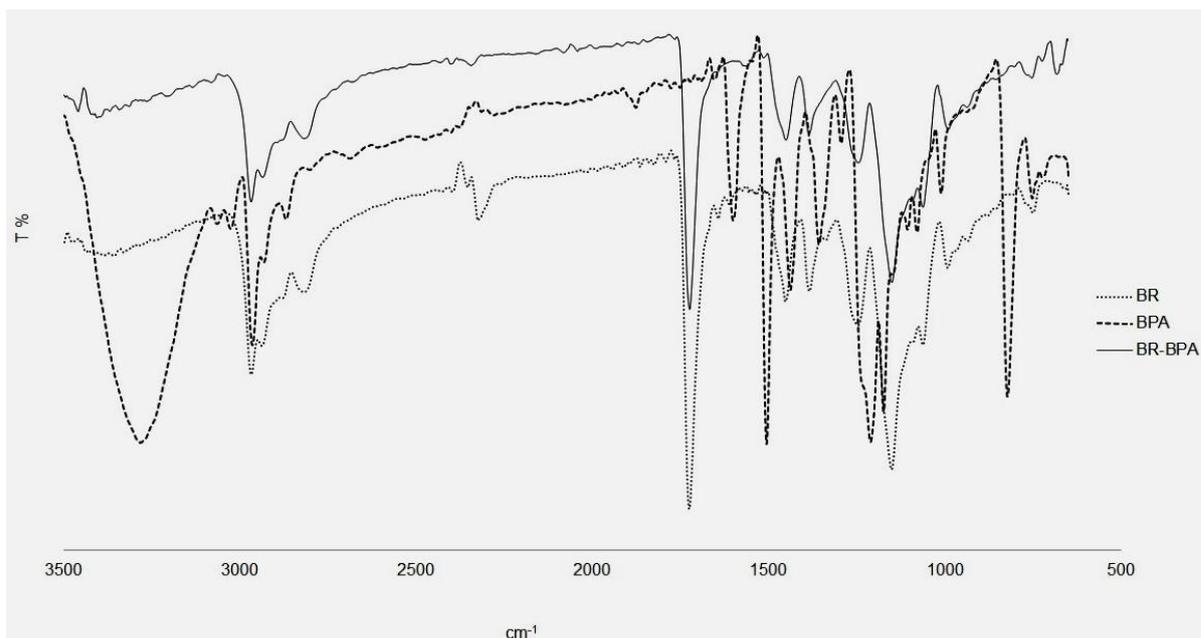


Figure 5. FTIR spectra of adsorption of BPA on BR

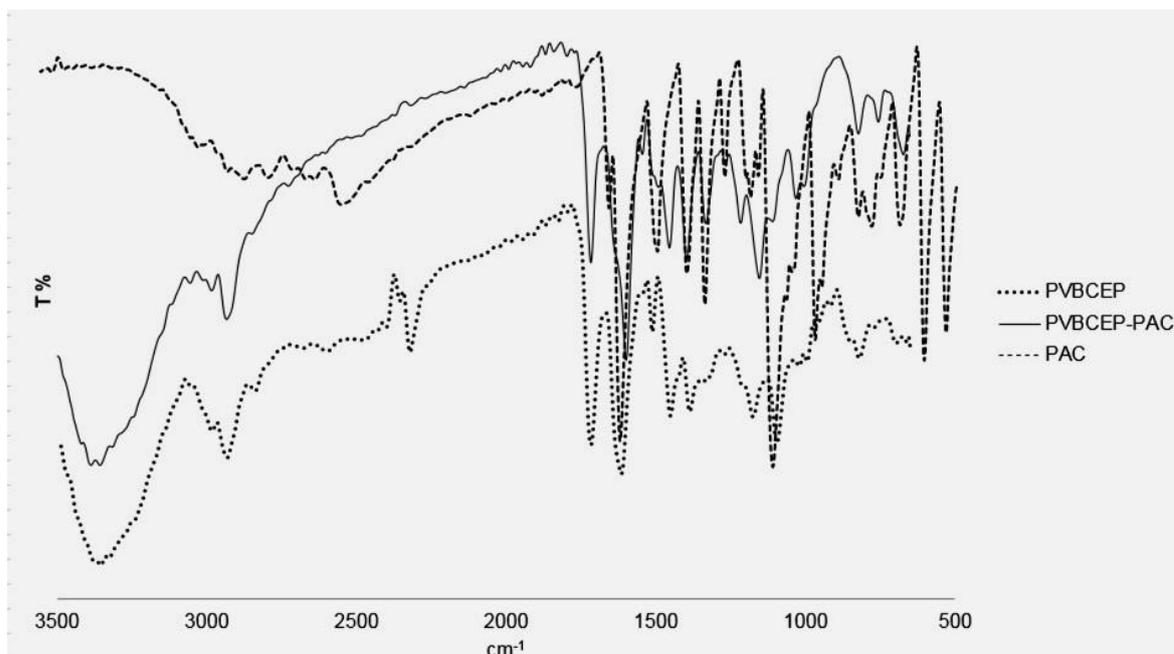


Figure 6. FTIR spectra of adsorption of PAC on PVBCEP

As shown in Figure 5, the IR spectrum of the pure state of the BR polymeric resin shows a strong -OH band peak at  $3380\text{ cm}^{-1}$ , and a strong C=O tension band peak at  $1663\text{ cm}^{-1}$  in the structure of polyvinylpyrrolidone. The characteristic C-N tension band of the group appears at  $1190\text{--}1130\text{ cm}^{-1}$ , and the C-H tension band of the methylene group appears at  $1485\text{--}1445\text{ cm}^{-1}$ . As shown in Figure 5, the BPA material shows the -OH stretching band at  $3300\text{ cm}^{-1}$ , the C-H stretch of the aromatic structure at  $2967\text{ cm}^{-1}$ . The C-C stretching band appears at  $1500\text{ cm}^{-1}$ , the deformation band of isopropyl and methyl groups appears at  $1361\text{ cm}^{-1}$  and the

characteristic C-O stretching band on phenol structure appears at  $1214\text{ cm}^{-1}$ . Figure 5 also shows that in the pair of BR-BPA after the adsorption the -OH and C-C stretching bands of BPA are not observed in the dual FTIR spectrum. The -OH peak of the BR disappeared in the dual FTIR spectra. We have thought that BPA is adsorbed forming a bond between the -OH group and the adsorbing BR. As shown in Figure 6, in the IR spectrum of the pure state of the PVBCEP polymeric resin, ethylene glycol dimethacrylate (EGDMA) shows the asymmetric stretching band of the methylene group band at  $2938\text{ cm}^{-1}$  and the symmetric methylene

group band at 2815 cm<sup>-1</sup>. Furthermore, the C-N asymmetric stretching bands on the piperazine ring structure exhibit moderate intensity peaks at 1323 cm<sup>-1</sup> and 1218 cm<sup>-1</sup>, and the C-N symmetric stretching band appears at 1160 cm<sup>-1</sup>. For the resin modified with carboxylic acid, O-H band and C=O vibrations bands are observed at 3365 cm<sup>-1</sup> and 1722 cm<sup>-1</sup>. As Figure 6 shows, in the pure state of the PAC substance, the OH stretching of COOH vibration is detected at 1750 cm<sup>-1</sup>, for the structure of PAC at 2550 cm<sup>-1</sup>. The OH bending band of the carboxylic acids appears at 1435 cm<sup>-1</sup> and the C-O stretching band - between 1226-1090 cm<sup>-1</sup>. Also in Figure 6, in the pair of PVBCEP-PAC after the adsorption, the -OH dimer and characteristic -COOH peaks of the PAC do not appear in the dual FTIR spectra. The PVBCEP adsorbent disappeared in the dual FTIR spectra of symmetric methylene and symmetric C-N band peaks. However, O-H and C=O peaks still appear in the adsorbent structure. Here, we have thought that the acid -OH bonds are adsorbed by symmetric C-H and C-N bonds of the piperazine ring.

#### Adsorption isotherms

Adsorption intensity of BPA onto each of the polymeric resins  $n < 1$  was found, as seen in Table 1. The adsorption capacities ( $K_F$ ) are listed as BR > PVBCIM > PVBCEP. BR was observed to best adsorb the BPA, as seen in Table 1. The average correlation coefficient of adsorption of BPA on BR is 97% for Freundlich isotherm. Table 1 shows that the maximum amount of substance adsorbed in the single layer ( $q_{max}$ ) is BR > PVBCEP > PVBCIM for the Langmuir isotherm. The average correlation coefficient of adsorption of BPA on BR is 99% for Langmuir isotherm. According to these operating conditions, the highest value of  $q_{max}$  for adsorbed BPA on 0.01 g of BR was found to be 21.7 mg g<sup>-1</sup>. For PAC, the adsorption capacities ( $K_F$ ) are ranged as PVBCEP > PVBCIM > BR. For both Freundlich and Langmuir the average correlation coefficient of adsorption of PAC on PVBCEP was 98%. The

maximum adsorption at monolayer coverage ( $q_{max}$ ) was calculated for the adsorption of PAC on PVBCEP as 769 mg g<sup>-1</sup>, as shown in Table 2. But the value of  $q_{max}$  is negative for the adsorption of PAC on BR. This can be explained as follows: negative values for the Langmuir isotherm constants suggest that this model is not suitable to explain the adsorption process because the value of  $q_{max}$  is indicative of the surface binding energy and monolayer coverage. As a result, this implies that some heterogeneity in the surface or pores of the polymeric resins will play a weak role in the adsorption of dyes. The isotherm types were S-shaped for  $n > 1$ , and L-shaped for  $n < 1$ .

#### Kinetic and thermodynamic parameters

In this study, the adsorption of BPA and PAC on the polymer resins corresponded to pseudo-second order rate. For pseudo-second order rate, the values of the rate constant increased by increasing the temperature, as seen in Tables 3-8. Intraparticle rate constants were mostly found as  $k_{i1}$  and  $k_{i2}$ . The first step suggests that diffusion of soluble molecules is directed towards the boundary layer. The second step indicates that gradual adsorption showed diffusion rate of intraparticle at limited places. Thermodynamic parameters were calculated by Arrhenius and Eyring equation [28]. While the values of the free enthalpy change ( $\Delta H^\circ$ ) are positive, the values of the free entropy change ( $\Delta S^\circ$ ) are negative. The negative values of the free entropy change suggest that adsorbate solution in adsorbent is transferred from disorderly to orderly. As a result, adsorption occurred. For BPA, the values of activation energy found are between 52 and 86 kJ/mol (Table 9). For PAC, the values of activation energy are between 48 and 97 kJ/mol (Table 10). These values indicate that physical adsorption occurs. The positive value of free energy exchange indicates that the reaction does not take place spontaneously and this reaction can take place depending on the temperature.

**Table 9.** Thermodynamic parameter values of BPA adsorbed on polymeric resin.

Adsorbents	$E_a$ / kJ mol <sup>-1</sup> (25°C-40°C)	$\Delta H^\circ$ / kJ mol <sup>-1</sup> (25°C-40°C)	$\Delta S^\circ$ / J mol <sup>-1</sup> K <sup>-1</sup> (25°C-40°C)	$\Delta G^\circ$ / kJ mol <sup>-1</sup> (25°C)
PVBCEP	52.3	49.8	-66.4	49.8
BR	85.5	49	-65.1	48.5
PVBCIM	62.7	60.2	-15	60.2

**Table 10.** Thermodynamic parameter values of PAC adsorbed on polymeric resin.

Adsorbents	$E_a$ / kJ mol <sup>-1</sup> (25°C-40°C)	$\Delta H^\circ$ / kJ mol <sup>-1</sup> (25°C-40°C)	$\Delta S^\circ$ / J mol <sup>-1</sup> K <sup>-1</sup> (25°C-40°C)	$\Delta G^\circ$ / kJ mol <sup>-1</sup> (25°C)
PVBCEP	48.1	45.6	-86.3	45.6
BR	97	95	82.5	94.7
PVBCIM	54	51.5	-58.4	52

### CONCLUSIONS

Adsorption kinetics of pesticides complied with the pseudo second-order rate equation. Thermodynamic parameters were calculated with these rate constants. In this study, the heat of adsorption is found between 20 and 100 kJ/mol and these values indicate physical adsorption. The adsorption process is usually fast because of the values of  $E_a < 100$  kJ/mol. This is due to the presence of weak van der Waals bonds in the medium. When  $\Delta S^\circ$  is negative, it is considered that ions have an association mechanism, that activated complex formation occurs between the adsorbed material and the adsorbent, and there is a significant change during the adsorption process in the inner structure of the adsorbent.

In this study, it is assumed that the adsorption of pesticides on the new polymeric resin performs well. While the maximum value of adsorption ( $q_{max}$ ) is found as BR>PVBCEP>PVBCIM for BPA, these values ( $q_{max}$ ) are found as PVBCEP resin for PAC. The maximum value of adsorption ( $q_{max}$ ) of BPA on BR and the maximum value of adsorption ( $q_{max}$ ) of PAC on PVBCEP were calculated as 21.7 and 769 mg.g<sup>-1</sup>, respectively. As a result, it is considered that the new polymeric resins obtained will be effective in cleaning the pollution caused by pesticides and will contribute to cleaning of wastewater.

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