

Evaluation of 2,4-D removal via activated carbon from pomegranate husk/polymer composite hydrogel: Optimization of process parameters through face centered composite design

Fulya Taktak*, Zeynep İlbay**,*†, and Selin Şahin**

*Department of Chemical Engineering, Engineering Faculty, Uşak University, Uşak 64200, Turkey

**Department of Chemical Engineering, Engineering Faculty, Istanbul University, Avclar, Istanbul 34320, Turkey

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Abstract—A new type of polymer composite hydrogel was prepared by introducing activated carbons from pomegranate husk into poly ((2-dimethylamino) ethyl methacrylate) network. The removal of 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution was studied with respect to pH of the media, initial 2,4-D concentration and activated carbon content into the polymeric network. Face centered composite design (FCCD) through response surface methodology (RSM) was used for designing the experiments as well as for studying the effects of the process parameters. A quadratic model and a two factor interaction design model were developed for the removal of 2,4-D and adsorption capacity, respectively. The optimum pH of the pesticide solution, activated carbon content into the polymeric network and initial concentration of 2,4-D were found as 3, 2.5 wt% and 100 mg/L. 63.245% and 68.805 (mg/g) for the removal of 2,4-D and adsorption capacity were obtained by using Simplex optimization method. Furthermore, the surface characteristics of the adsorbent prepared under optimized conditions were examined by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR).

Keywords: 2,4-Dichlorophenoxyacetic Acid, Pomegranate Husk, Polymer Composite Hydrogel, Optimization

INTRODUCTION

A growing world population brings about scarcity of water resources, which is one of the most vital environmental problems confronting us all over the world. Besides, the massive global use of pesticides in agriculture for supporting in harvest quality and food protection by controlling pests leads to water pollution [1]. Most extensive factors such as drift, runoff, leaching from agricultural and disposal of industrial wastewater result in this water pollution [2]. Pesticide is a chemical weapon along with insecticides, fungicides, and herbicides and so on which have some drawbacks such as toxicity, carcinogenicity and mutagenity. Furthermore, it might be non-biodegradable, which is an unavoidable threat to human as well as animal and plant health [3]. Exposure to larger doses of pesticides has been shown to cause damage to sex hormones and do harm to the reproductive system [4]. Several researchers have looked for many ways to remove the aromatic pollutants which are used for pesticide extenders. Wang et al. used high-quality reduced graphene oxide as an effective adsorbent to investigate 4,4'-dichlorobiphenyl adsorption capacity [5]. Wang et al. examined the adsorption of polycyclic aromatic hydrocarbons such as naphthalene and 1-naphthol which are used as fumigant pesticide and insecticides on graphene oxides and reduced graphene oxides [6,7]. They had a significant solution when they used an attractive graphene oxide to remove aromatic pollutants. On the other hand, 2,4-dichlo-

rophenoxyacetic acid (2,4-D) is a widespread phenoxy acid herbicide found in surface and ground water, since it is mostly preferred due to its low cost and good selectivity. However, the World Health Organization (WHO) recommends its maximum allowable concentration as 100 ppb in drinking water [8,9]. Therefore, various methods such as ozonation [10], advanced electrochemical oxidation processes [11], aerobic and anaerobic degradation [12], nanofiltration membranes [13], and adsorption [14]; Salman and Al-Saada [15] have been applied for removal of pesticides. These techniques other than adsorption need higher capital investment and operating cost, and have complicated operation so they cannot be suitable for industrial application. Hence, adsorption is one of the most preferred separation methods because of its easy operation, higher adsorption capacity, economical process and simple design [16]. Activated carbon is extensively used for treatment of wastewater because of its large surface area and high adsorption capacity [17]. However, commercial activated carbons have high-cost, since they require additional agents to improve efficiency, causing more environmental pollution such as concentrated acid (H_3PO_4 and HCl) and base (KOH Na_2CO_3 and NaOH) [18]. Therefore, researchers have been looking for inexpensive raw materials to prepare adsorbent for economical wastewater treatment. Agricultural by-products containing lignin, cellulose and some proteins make them a powerful source for adsorbents [19]. In this study, pomegranate husk was used as the raw material of activated carbon. Pomegranate (*Punica granatum* L.) husk consists of several constituents containing ellagic acid and its derivatives, gallagic acid, polyphenols and tannins [20]. If this waste is carbonized without adding any functional groups, adsorption capacity and adsorption time

†To whom correspondence should be addressed.

E-mail: zilbay@gmail.com

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might be affected adversely. Therefore, many studies have been conducted as an alternative material to activated carbons. Kyriakopoulos et al. [21] reported the adsorption of pesticides on porous polymeric adsorbents such as Amberlite XAD-4 (polystyrene-divinylbenzene copolymer) and XAD-7 (nonionic aliphatic acrylic polymer), while Chang et al. [22] investigated the hypercrosslinked polymers Macronet MN-150 and MN-500 to remove the pesticide methomyl from aqueous solutions via adsorption. Alternatively, Bojemueller et al. [23] used clay mineral to enhance pesticide adsorption by trying thermally modified bentonites. However, the adsorption capacities of these adsorbents are not successful enough to recover the target materials. Therefore, more effective adsorbents have to be searched for a better separation. Recently, polymer composite hydrogels have attracted increasing interest because of relatively low production cost and high adsorption capacity [24]. In the present study, pomegranate activated carbon was added to the poly(dimethylaminoethyl methacrylate (PDMAEMA) hydrogel matrix in order to increase mechanical and physical properties such as thermal electrical [25]. Tertiary amine pendant groups on the PDMAEMA backbone are capable of providing polyelectrolyte behaviors. It swells in water or acidic media at lower critical solution temperature (LCST), while shrinks in alkaline at above LCST. PDMAEMA has drawn attention in medical and pharmaceutical applications, and water treatment because of its thermo and pH-sensitive nature [26]. To the best of our knowledge, no information exists with respect to the adsorption of 2,4-D by activated carbon from pomegranate husk/polymer composite hydrogel. First, activated carbon was prepared from pomegranate husk by microwave-assisted thermal treatment, providing reduced processing time with consequent reduction in energy consumption without using any chemical material. By introducing the activated carbon into the poly((2-dimethylamino) ethyl methacrylate) polymeric network, a series of activated carbon/poly((2-dimethylamino) ethyl methacrylate) composite hydrogels were synthesized. Then, the application of face centered composite design (FCCD) has been reported for the optimization of the process parameters (activated carbon content, pH of the media, and initial concentration of the 2,4-D solution) on the removal of 2,4-D from its aqueous solutions through response surface methodology (RSM).

EXPERIMENTAL

1. Material

1-1. Chemicals

2,4-Dichlorophenoxyacetic acid (2,4-D) whose purity was 98% was obtained from Sigma Aldrich without further purification. 2-(Dimethylamino) ethyl methacrylate (DMAEMA) was purchased from Aldrich, and passed through a basic alumina column in order to remove the hydroquinone methyl ether inhibitor, and distilled under vacuum before use. N, N'-methylenebisacrylamide (MBAM, Aldrich) as crosslinker and ammonium persulfate (APS, Merck) as initiator were used as received. 0.1 N NaOH and 0.1 N HCl were used for adjusting pH levels of stock solutions. All chemicals were analytical reagent-grade. Bidistilled water was used for all experiments.

1-2. Preparation of Activated Carbon

Pomegranates were purchased from a local market. They are widely

cultivated in Adana whose location is the Mediterranean coast southeast of Turkey. Pomegranate husk was washed with tap water, then bidistilled water, and stored at ambient temperature in dark. Before microwave-assisted thermal treatment, the dried material was mechanically milled. The dried and ground material (10 g) was immersed in quartz container (100 mL), which was placed inside a household microwave oven (Ideline 753-110). Carbonization process was slightly modified according to the procedure of Franca et al. [27]. Briefly, microwave irradiation time was 5 min at 500 W followed by 30 s cooling per 1 minute with four cycle, so total processing time took 7 min.

1-3. Preparation of AC/PDMAEMA Composite Hydrogels

In situ polymerization route was used for preparation of AC/PDMAEMA composite hydrogels. Dry AC powder (2.5-20% based on monomer weight) was transferred in 5 mL of distilled water and stirred (500 rpm) to obtain a homogeneous suspension for 2 h. DMA monomer (20%) and MBAM (20 mg/mL) were added into this suspension, and stirred vigorously for 1 h. Then, ammonium persulfate (APS) (5 mg/mL) was added. Well-dispersed reaction mixture was loaded in polyvinylchlorua (PVC) straw to keep at 25 °C for about 24 h until the gelation was completed. The AC/PDMAEMA composite hydrogel samples were cut into small sizes, and washed with bidistilled water. After being dried in a vacuum oven at 50 °C for 24 h, the gel samples were ground into 28-mesh.

2. Methods

2-1. Characterization of AC and AC/PDMAEMA Composite Hydrogels

Activated carbon and dried polymer composite hydrogels were analyzed through a Perkin Elmer Two UATR IR spectrophotometer in the range of 4,000-450 cm^{-1} . The morphology of AC and AC/PDMAEMA was examined by scanning electron microscopy (SEM) at an operating voltage of 20 kV under high vacuum (SEM-EDX, FEI Quanta FEG-450) after coating the sample with gold film in order to avoid electrostatic charge on the surface. On the other hand, the structural changes of AC and AC/PDMAEMA were determined from X-ray powder diffraction (XRD) patterns taken on a Rigaku SmartLab diffractometer operated at 40 kV and 35 mA using $\text{Cu K}\alpha$ radiation.

2-2. Batch Studies

Defined pH (3-9) of solution was adjusted by Mettler Toledo SevenMulti pH meter using 0.1 N NaOH and 0.1 N HCl solutions. The used initial concentrations of 2,4-D solutions were in the range 20-100 mg/L in bidistilled water. In the batch adsorption experiments, 10 mg of adsorbent including 2.5-20% AC/PDMAEMA composite hydrogels were weighted and then 10 mL of desired solution put into an Erlenmeyer flask. In kinetic pre-experiments, optimal equilibrium adsorption time was found to be one-and-half hour. Solutions were placed into a temperature controlled Shaker (Nüve) at 20 °C and 100 rpm during equilibrium time. Samples (4 mL) were taken with a micropipette from the Erlenmeyer to determine concentrations of solutions at the end of optimal equilibrium adsorption time. Perkin Elmer Lambda 35 Uv-Vis spectrophotometer was used to determine the initial and final concentration of 2,4-D at 282 nm using a linear calibration curve [28]. All experiments were repeated three times for calculating standard deviations.

The percent pesticide removal (R %) was calculated with Eq. (1)

$$Y_1(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i and C_e were the initial and final concentration of 2,4-D in the solution in mg/L. The pesticide uptake loading capacity (mg/g) of polymer composite hydrogel for each concentration of pesticide at equilibrium was determined with Eq. (2)

$$Y_2(q_e) = \frac{C_i - C_e}{M} \times V \quad (2)$$

where C_i and C_e are defined above, V is the volume of the solution in mL, and M is the mass of the dry adsorbent (g).

2-3. Desorption and Reusability Tests

To assess feasibility of AC/PDMAEMA adsorbent, desorption and reusability experiments were also performed under optimal conditions. First, 10 mg of adsorbent and 10 mL of 100 mg/L solution at pH 3 were added in an Erlenmeyer flask. These tests were conducted at a shaker speed of 100 rpm during 90 min. The solution was filtered to separate the 2,4-D-coated AC/PDMAEMA. After 2,4-D-coated AC/PDMAEMA composite hydrogel dried in a vacuum oven, it dispersed into 10 mL of 0.5 M NaOH solution, and was shaken in a shaker at 100 rpm for 90 min. After the regenerated adsorbent was washed with bidistilled water of pH 3 at three times, it dried in a vacuum oven for reuse. Four cycles including adsorption and desorption steps were applied to evaluate the reusability performance of regenerated adsorbent.

2-4. Experimental Design

Central composite design (CCD) is the most famous of the many types of RSM designs by the virtue of its advantageous properties such as flexibility and efficiency [29]. Face-centered composite design (FCCD) is one of the varieties of CCD. It is used in many applications easily because its coded distance (α) is equal to 1 without requiring any other. The optimization of 2,4-D removal and adsorption capacity of the adsorbent were carried out by three selected independent variables (pH, adsorbate concentration and activated carbon ratio of polymer composite gel to monomer) as 2^3 full factorial design for the three variables, containing eight factorial points, six axial star points and six replicates at the center points. Twenty experiments were needed as calculated from Eq. (3).

$$N = 2^k + 2k + n_c \quad (3)$$

where k is the number of factors; used for predicting the residual error is the replicates in central points.

Therefore, Table 1 shows the coded level (-1, 0, +1) of twenty experiments.

The following equation represents the actual level of each factor (Eq. (4)) [30].

Table 1. Values of the independent variables and their coded forms with their symbols employed in RSM

Factors	Range and coded levels		
	(-1)	(0)	(+1)
pH (X_1)	3	6	9
2,4-D conc. (mg/L, X_2)	20	60	100
Activated carbon (% , X_3)	2.5	11.25	20

$$\text{Actual value} = \frac{(\text{Coded value} \times \text{high level} - \text{low level})}{2} + \frac{(\text{high level} + \text{low level})}{2} \quad (4)$$

In this design, the removal of 2,4-D (Y_1) and the 2,4-D adsorption capacity (Y_2) were taken as the responses. The quadratic equation model for estimating the optimal was expressed as Eq. (5):

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} x_i x_j + \varepsilon \quad (5)$$

where Y is the response; β_0 is the constant coefficient, β_i , β_{ii} , β_{ij} are coefficients for the linear, quadratic and interaction effect; x_i and x_j are factors; ε is error.

The root-mean-square deviations (*rmsd*) was calculated according to the following Eq. (6)

$$\text{rmsd} = \sqrt{\frac{\sum_{i=1}^n (q_{e,i,exp} - q_{e,i,cal})^2}{N}} \quad (6)$$

where n is the number of the experiments, $q_{e,i,exp}$ refers to the adsorption capacity of experiment i , $q_{e,i,cal}$ is the calculated adsorption capacity value of the i .

3. Statistical Analysis

Three replicate experiments were carried out for each of the samples followed by a minimum of three spectrophotometric measurements from each sample. The analysis of variance (ANOVA)

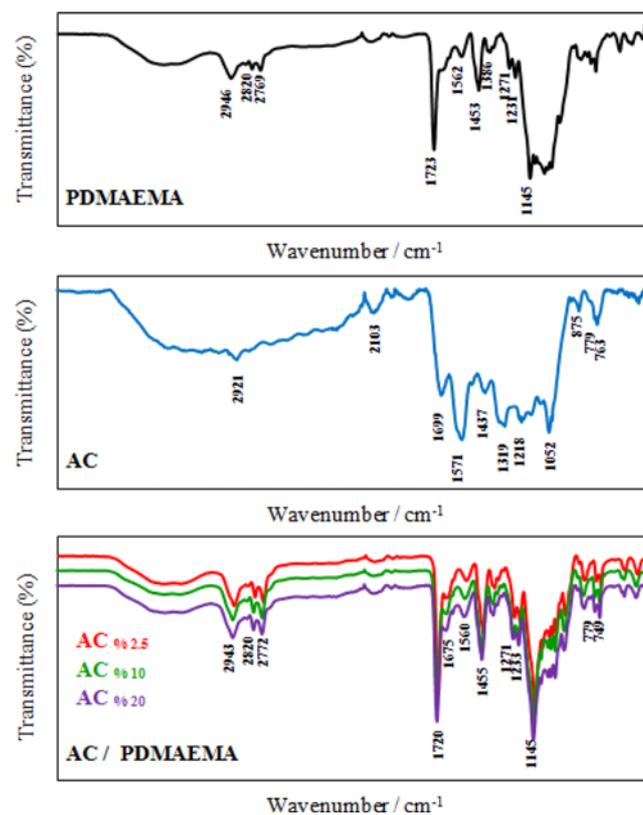


Fig. 1. ATR-FTIR spectra of AC from pomegranate husk (a), PDMAEMA (b) and AC/PDMAEMA (c) samples.

test was applied to identify the interaction between the variables and the response using Design Expert Version 8.1.0.7 (Stat Ease, USA). The multiple correlation coefficients (*adjusted correlation coefficient* (R_{adj}^2) and *predictive correlation coefficient* (R_{pred}^2)) were considered as statistical indicators to obtain the best model with highest R_{adj}^2 and R_{pred}^2 values. The optimal conditions of adsorption process were calculated by simplex method using optimization toolbox of this program.

RESULTS AND DISCUSSION

1. Fourier Transform Infrared Analysis of Adsorbent

FTIR analysis of AC from pomegranate husk (a), PDMAEMA (b) and AC/PDMAEMA samples (c) at wavelengths in the range of 450-4,000 cm^{-1} are presented in Figs. 1(a), (b) and (c).

The FTIR spectrum for AC is as shown in Fig. 1(a). The characteristic functional groups derived from the pomegranate activated carbon are the band between 3,500-3,000 cm^{-1} due to the O-H stretching of hydroxyl groups and adsorbed water; a band at

2,921 cm^{-1} is attributed to aliphatic C-H stretching; the band at 1,699 cm^{-1} is due to the presence of carbonyl groups in α, β unsaturated ketones or aldehydes; the peak around 1,437-1,319 cm^{-1} corresponded to phenolic OH and C-N groups; the peaks at 1,571 and 1,052 cm^{-1} corresponding to the C-O stretching; the peaks around 1,218-875 cm^{-1} assigned to C-C stretching and C-OH bending and a peak from 763 cm^{-1} attributed to amide N-H wagging. In FTIR spectra for PDMAEMA (Fig. 1(b)), the broad band around 3,000-3,400 cm^{-1} corresponds to the H_2O stretching vibrations; the peak at 1,640 cm^{-1} is assigned to the bending vibration of H-OH bond; the broad band around 3,200-3,500 cm^{-1} could be attributed to the -OH stretching vibration; the strong band at 1,720 cm^{-1} is assigned to the carbonyl groups from ester groups; the aliphatic -CH stretching and of PDMAEMA are also observed at 2,768 cm^{-1} ; The C-N stretching bands are observed at 1,268 and 1,235 cm^{-1} that belong to the tertiary amine groups of DMAEMA residue. The FTIR spectra of AC/PDMAEMA composites are shown in Fig. 1(c). As seen in Fig. 1(c), AC/PDMAEMA composite hydrogel samples include all of the AC and PDMAEMA peaks.

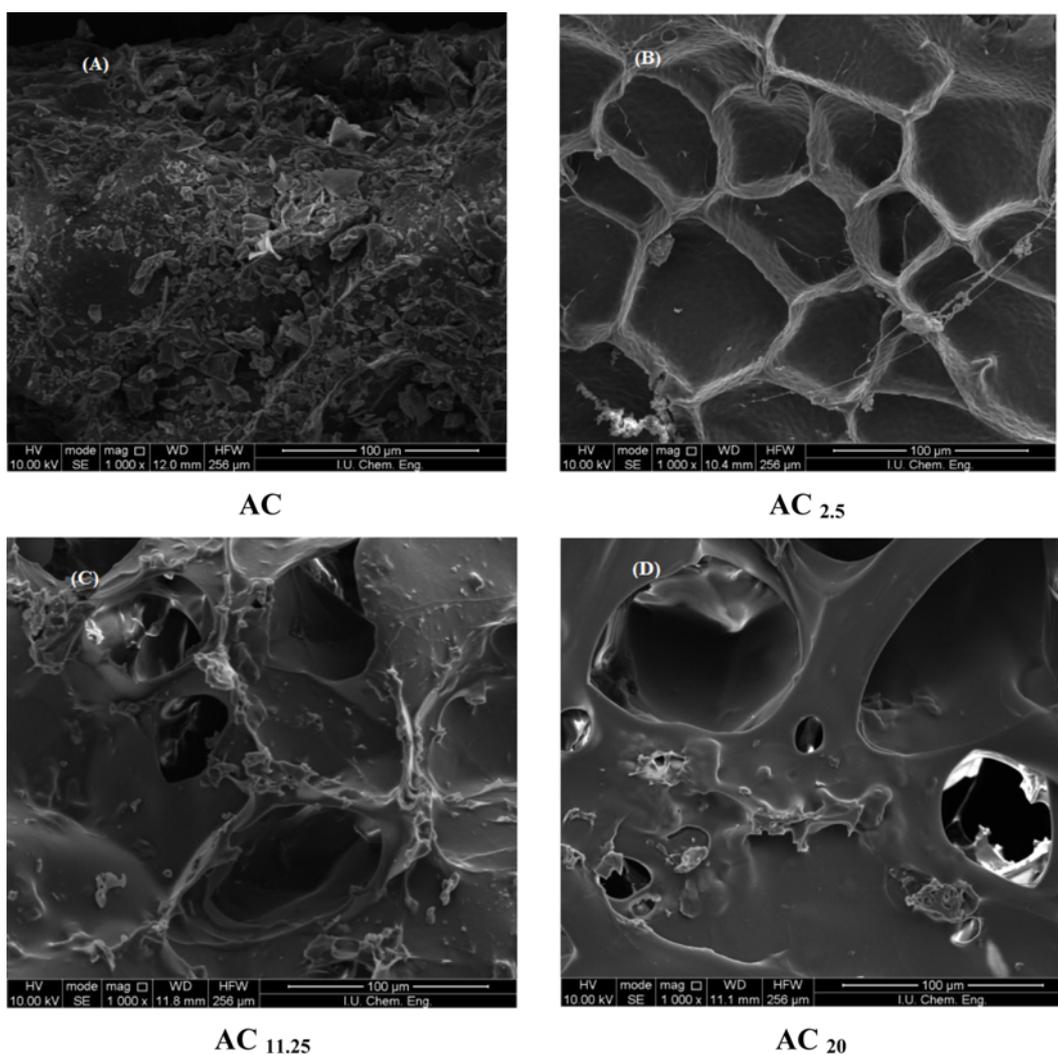


Fig. 2. SEM images of AC from pomegranate husk (A) and AC/PDMAEMA composite hydrogels containing 2.5 (B), 11.25 (C) and 20 (D) wt% of AC.

2. Surface Morphology of Adsorbent

The surface morphologies of AC from pomegranate husk and AC/PDMAEMA composite hydrogels containing 2.5, 10 and 20 wt% of AC analyzed by SEM, are shown in Figs. 2(A) to (D), respectively.

It is observed that the composites have similarly-sized porous structure and AC particles adhered on to the polymer surface to form a new composite system. However, the porosity of composite surfaces was decreased with increasing AC content. Higher amount of AC was trapped in network pores, and covered on the surface of the polymer.

This phenomenon serves to reduce polymer chain mobility which causes a decrease in the equilibrium swelling capability. The SEM image of raw AC is not exhibiting any porosity on its surface. Furthermore, AC_{2.5}/PDMAEMA composite consists of uniformly distributed pores separated by superficially porous walls. Consequently, appropriate amount of AC has created homogeneously dispersed numerous pores on the polymer matrix. Thus, interconnected pores improve water absorbency of composite adsorbents.

3. X-ray Powder Diffraction (XRD) Analysis of Adsorbent

Fig. 3 represents the XRD diffraction profiles of AC and PDMAEMA/AC composite hydrogel structures, respectively. The intensity of the crystalline sharp peaks of AC at around 30° and 40° is greatly reduced, while peak widths are broadened by introducing into gel matrix. It was confirmed that the AC particles were well dispersed inside the polymeric matrix. Furthermore, the major XRD peak was also detected in XRD profile of composite gel, but it was slightly shifted and sharpened. It might be attributed to the interaction between crystalline nature of AC particles and amorphous polymer chains.

4. Development of Regression Model Equation

Table 2 indicates the influence of pH (3-9), the initial solution concentration (20-100 ppm), and activated carbon (2.5-20%) wt on adsorption capacity (q_e) and the removal of 2,4-D (%).

The quadratic model for the 2,4-D removal was recommended by the software. Unlike the removal of 2,4-D, two factor interaction (2FI) was suggested for the adsorption capacity (q_e). The final equations in terms of actual factors are given in Eqs. (7) and (8),

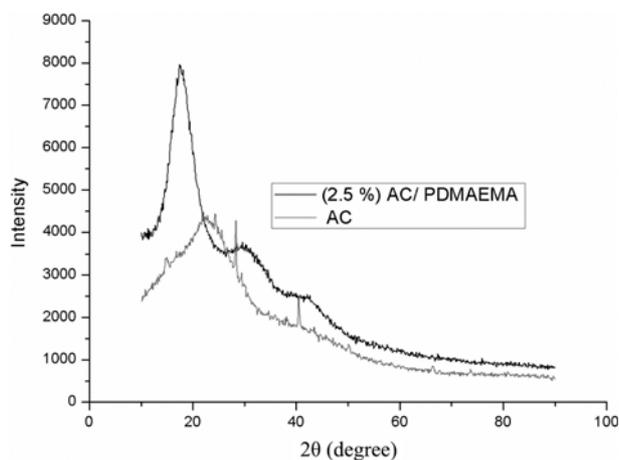


Fig. 3. XRD for pomegranate husk and AC/PDMAEMA composite hydrogels containing 2.5%.

Table 2. Design of RSM and actual responses

Run	pH	2,4-D conc. (mg/L)	Activated carbon (%)	Removal of 2,4-D (%)	Adsorption capacity (q_e (mg/g))
1	3	20	2.5	49.5430.042	13.2980.004
6	9	20	2.5	14.0520.009	3.7820.001
9	3	100	2.5	61.2080.052	68.4590.032
2	9	100	2.5	21.3120.016	20.6000.012
19	3	20	20	30.2580.021	8.1220.002
4	9	20	20	5.2240.002	1.4060.000
13	3	100	20	47.1190.023	51.6470.025
20	9	100	20	10.7410.009	11.1310.002
7	3	60	11.25	53.7010.033	38.3160.009
11	9	60	11.25	12.7340.007	8.8870.003
14	6	20	11.25	7.7590.004	2.0680.001
3	6	100	11.25	25.0970.013	39.0890.022
17	6	60	2.5	37.9000.019	28.0460.018
12	6	60	20	24.9870.021	19.9090.011
8	6	60	11.25	27.2640.024	21.0400.017
16	6	60	11.25	27.3460.018	21.0600.009
10	6	60	11.25	27.0020.009	20.9860.011
5	6	60	11.25	27.3490.015	21.0490.007
15	6	60	11.25	27.3370.011	21.2230.009
18	6	60	11.25	27.0480.014	21.0010.012

respectively.

$$\begin{aligned} \text{Removal of 2,4-D } (Y_1) = & 77.48202 - 15.27673X_1 + 0.95108X_2 \\ & - 2.81555X_3 - 0.016404X_1X_2 + 0.066539X_1X_3 \\ & + 1.23307E-003X_2X_3 + 0.79891X_1^2 \\ & - 5.99936E-003X_2^2 + 0.070739X_3^2 \end{aligned} \quad (7)$$

$$\begin{aligned} \text{Adsorption Capacity } (Y_2, q_e) = & 1.61418 - 0.50244X_1 + 0.93176X_2 \\ & - 0.36813X_3 - 0.075147X_1X_2 \\ & + 0.048301X_1X_3 - 6.68895E-003X_2X_3 \end{aligned} \quad (8)$$

The adequacy of the models was confirmed by means of variance analysis (ANOVA). ANOVA for the quadratic model for % removal of 2,4-D is given in Table 3, while ANOVA for the 2FI model for adsorption capacity is listed in Table 4.

According to Tables 3 and 4, both of the models were found significant ($p < 0.05$) to display the relationship between the response and independent variables. The values of correlation coefficient (R^2 , R_{adj}^2 and R_{pred}^2) were 0.9889, 0.9790 and 0.8968; 0.9920, 0.9883 and 0.9747 for the removal of 2,4-D and adsorption capacity, respectively. The Model F -values of 99.22 and 267.75 indicated that the models were significant. Furthermore, values of Prob>F less than 0.05 implied also that terms were significant. Under these conditions, X_1 , X_2 , X_3 , X_1X_2 , X_1X_3 , X_1^2 , X_2^2 , X_3^2 were significant because of lower p value ($p < 0.05$) for Y_1 . For Y_2 , X_1 , X_2 , X_3 , X_1X_2 , X_2X_3 were significant. The standard deviations of both models were 2.21 and 1.82, respectively. Besides, the coefficient of variation (CV) which means the ratio of standard error of predicting to the mean value of actual response explains the repeatability of the model. In general, lower standard deviation and lower CV (<10%) lead to higher

Table 3. ANOVA for the quadratic equations of design expert 8.0.7.1 for (%) the removal of 2,4-D using AC/PDMAEMA composite polymer gels

Source	Sum of squares	df	Mean square	F value	P-value prob>F	
Model	4365.74	9	485.08	99.22	<0.0001	Significant
X ₁	3160.03	1	3160.03	646.36	<0.0001	
X ₂	343.87	1	343.87	70.34	<0.0001	
X ₃	431.48	1	431.48	88.26	<0.0001	
X ₁ X ₂	31.00	1	31.00	6.34	0.0305	
X ₁ X ₃	24.41	1	24.41	4.99	0.0495	
X ₂ X ₃	1.49	1	1.49	0.30	0.5930	
X ₁ ²	142.17	1	142.17	29.08	0.0003	
X ₂ ²	253.39	1	253.39	51.83	<0.0001	
X ₃ ²	80.66	1	80.66	16.50	0.0023	
Residual	48.89	10	4.89			
Pure error	0.13	5	0.025			
Cor. total	4414.63	19				

Table 4. ANOVA for two-factor interactions of design expert 8.0.7.1 for the adsorption capacity of 2,4-D using AC/PDMAEMA composite polymer gels

Source	Sum of squares	df	Mean square	F value	P-value prob>F	
Model	5312.46	6	885.41	267.75	<0.0001	Significant
X ₁	1933.11	1	1796.57	543.29	<0.0001	
X ₂	2632.49	1	2632.49	796.07	<0.0001	
X ₃	176.15	1	176.15	53.27	<0.0001	
X ₁ X ₂	650.55	1	650.55	196.73	<0.0001	
X ₁ X ₃	12.86	1	12.86	3.09	0.0703	
X ₂ X ₃	43.85	1	43.85	13.26	0.0030	
Residual	42.99	13	3.31			
Pure error	0.036	5	7.18E-003			
Cor. total	5355.45	19				

reproducibility of a model [31]. Additionally, the root mean squared deviation for adsorption capacity (rmsd=0.328) is low enough to show its high accuracy.

5. Effects of Process Parameters on the Responses and Optimization

There are many papers that include adsorption of 2,4-D onto different adsorbents in the literature. Pavlovic et al. examined the adsorption of acidic pesticide 2,4-D on calcined hydrotalcite with different parameters comprised of time dependent, pH-dependent and concentration dependent via on factor at a time method (OFAT) [32]. They conducted their pH-dependent studies with pH values of 3, 6, 11. They found that similar amounts were adsorbed at all pH. When the concentration of solution was high, they got higher results. Cheah et al. studied the adsorption, desorption and mobility of four commonly used pesticides in Malaysian agricultural soils. They saw that temperature (20 °C-30 °C), pH did not affect the amount of adsorption of the pesticide [33].

In this study, various factors were investigated by using RSM instead of OFAT. Three-dimensional with contour plots were drawn according to the Eqs. (7)-(8) to evaluate the interaction among three factors and their corresponding effect on the responses.

Figs. 4(a) and 4(b) show the effect of interaction between pH

and initial concentration of 2, 4-D on % of removal 2,4-D and adsorption capacity.

It can be clearly seen in Figs. 4(a) and 4(b) that both responses increase with increasing initial concentration of 2,4-D. The initial concentration plays a crucial role as driving force to achieve all mass transfer resistance of 2,4-D between the aqueous and solid phases. Therefore, higher initial concentration of 2,4-D increases the equilibrium uptake capacity of the adsorbent and the adsorption rate. This phenomenon is explained by Fick's second Law [34]. Our results are in agreement with those of Aksu et al. [35], Gupta et al. [1], Amin [36], Salman and Al-Saad [15]. On the contrary, 2,4-D removal and adsorbent capacity both decrease with an increase in pH. This might be attributed to the fact that polymeric residue in the adsorbent has tertiary amine groups, which acquires positive charged at low pH, while a portion of surface functional groups (tertiary amine) tend to lose their charge above pH 6. At low pH value, 2,4-D with pKa of 2.64 is in the anionic form and activated carbon surface is positively charged by absorption of H⁺ ions. As mentioned above, due to the anion-cation attraction forces between the adsorbent surface and 2,4-D, the most effective pH was found to be the value of 3. Aksu et al. [14] investigated the effect of initial pH on 2,4-D adsorption. They used granular activated carbon

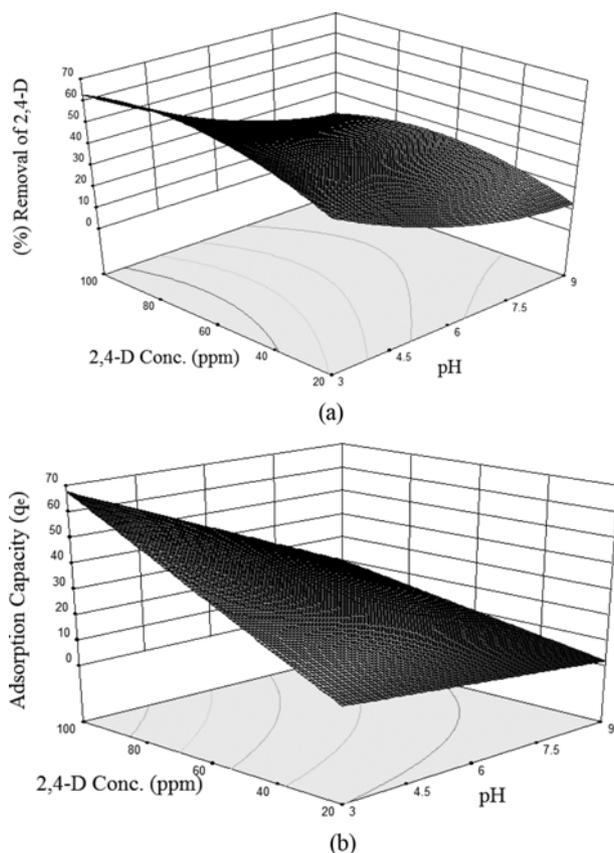


Fig. 4. Response surface plot for % of 2,4-D removal (a) and adsorption capacity of adsorbent (b) as a function of initial concentration of 2,4-D solution (mg/L) to pH (activated carbon =2.5%).

as adsorbent to adsorbate 2,4-D. They examined that adsorption capacity of 2,4-D decreased with increasing pH from 3 to 8. Hameed et al. [17] reported a similar result using activated carbon derived from data stones. Gupta et al. [1] studied the adsorption of 2,4-D using fertilizer and steel industry wastes. They showed that removal of 2,4-D decreases with increasing pH from 2 to 7.5. Kavaklı et al. [37] researched heavy metal ion adsorption using poly (N,N dimethylaminoethylmethacrylate) hydrogels. Maximum extent of swelling of the hydrogel occurred at pH 2, due to the protonization of ternary amine groups of DMAEMA. Zhu et al. [38] synthesized the Poly (N,N dimethylaminoethylmethacrylate) modification of commercial activated carbon to remove copper ions. They reported that the amount of the adsorption increased slightly from pH 2 to 5.5, and declined from pH 5.5 to 6 owing to the deprotonation of modified hydrogel. Amin [36] investigated the usage of pomegranate husk as adsorbent for adsorption of the blue dye from aqueous solution. They found that the surface of AC exist positive charged as a result of H^+ ion concentration at pH 2. Kim et al. [39] studied the adsorption behavior of 2,4-D onto various granular activated carbons (GACS). The adsorption capacity decreased with pH. Our results are consistent with those of the reports mentioned above.

The effects of activated carbon content into the polymeric network and pH of the media are shown in Figs. 5(a) and 5(b) (concentration of 2,4-D=100 mg/L).

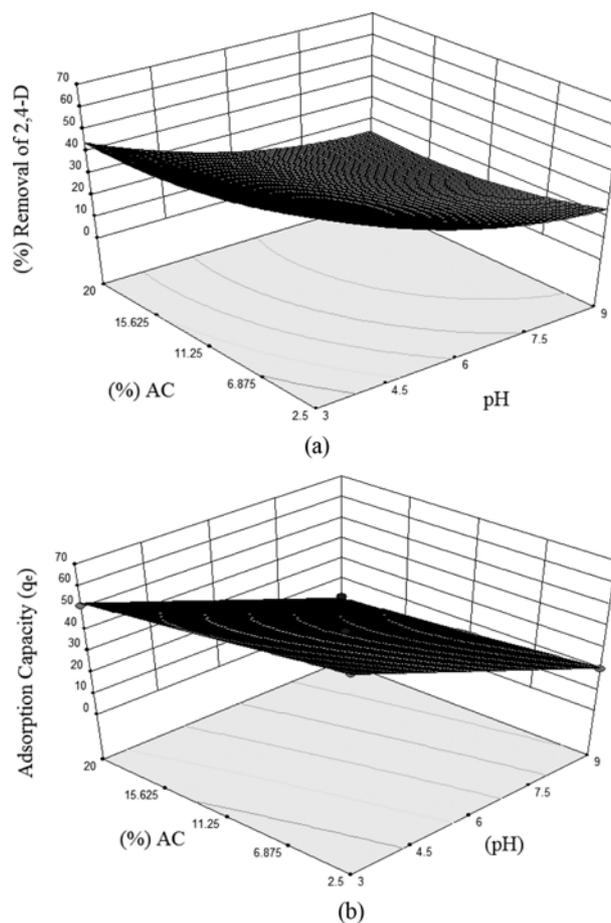


Fig. 5. Response surface plot for % of 2,4-D removal (a) and adsorption capacity of adsorbent (b) as a function of activated carbon (%) to pH (initial concentration of 2,4-D=100 (mg/L)).

Both responses had a tendency to decrease by increasing the activated carbon content. Increasing the content of AC in polymer matrix causes a decrease in porous structure. This result was also confirmed by SEM images (Figs. 2(A) to (D)). Increasing the AC content coated the surface of polymer, causing to hinder the electrostatic attraction with responses as stated above.

Figs. 6(a) and 6(b) exhibit the effects of the interaction between activated carbon content into the polymeric network and initial concentration of 2,4-D on responses.

High initial concentration and low activated carbon content had a positive effect on responses. As mentioned before, the effects of these two factors were widely discussed at the beginning of the section 3.4. Fig. 7 represents the correlation between the actual and predicted values.

The correlation coefficients of the models showed that the predicted data calculated from the models is in good agreement with the experimental data.

Table 5 shows the comparison of the results of the present study with those of the other reports on the adsorption of 2,4-D pesticide.

Our adsorption process reached equilibrium in a shorter time due to the properties of our adsorbent. This result is feasible from the economic point of view. Moreover, activated carbon was pre-

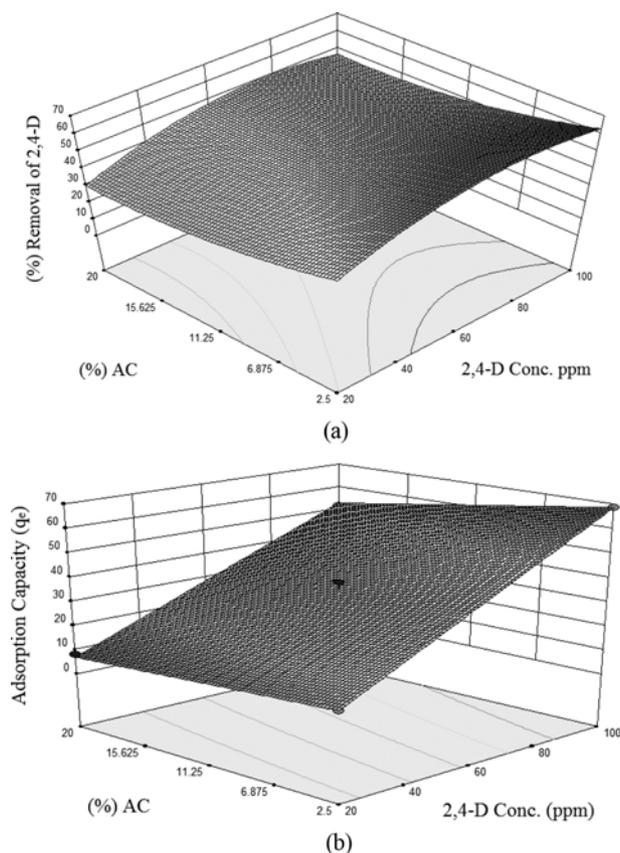


Fig. 6. Response surface plot for % of 2,4-D removal (a) and adsorption capacity of adsorbent (b) as a function of activated carbon (%) to initial concentration of 2,4-D (pH=3).

pared from pomegranate husk by microwave-assisted thermal treatment, providing reduced processing time with consequent reduction in energy consumption and elimination of the amount of gases without using any chemical material.

The optimal pH of the pesticide solution, activated carbon content into the polymeric network and initial concentration of 2,4-D were found to be 3, 2.5 wt% and 100 mg/L, respectively. 63.245 and

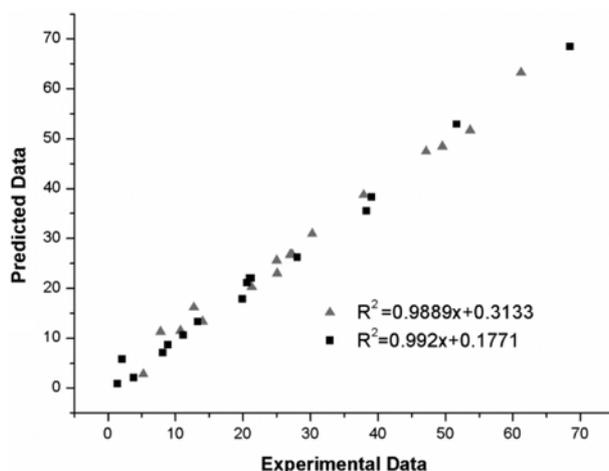


Fig. 7. The correlation experimentally between the values obtained versus calculated using model Eq. (7) and (8), respectively (% of 2,4-D removal=▲, adsorption capacity=■).

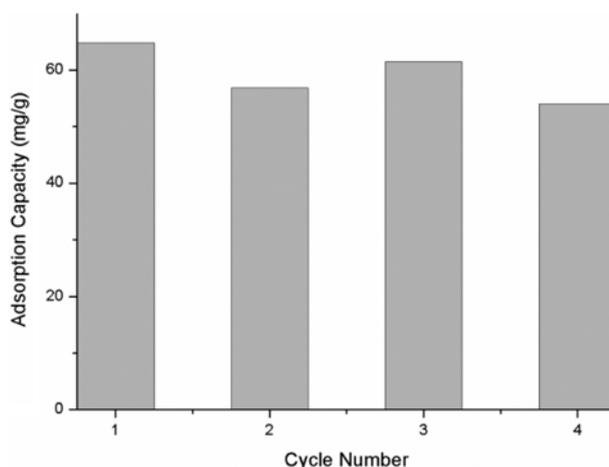


Fig. 8. Adsorption capacity of AC/PDMAEMA for 2,4-D in four adsorption-desorption cycles. Adsorption conditions: contact time, 90 min; initial concentration of 2,4-D, 100 mg/L; 100 rpm; solid/liquid ratio 10 mg/10 mL; pH, 3.0.

Table 5. Summary of the researches published on the adsorption of 2,4-D

Adsorbent	Operating conditions	Adsorption capacity $q_{e,exp}$ (mg/g)	Reference
Granular activated carbon	$C_0=100$ mg/L, 25 °C, 150 rpm, 7 days, pH: 2	98.1	[35]
Powdered activated carbon	$C_0=100$ mg/L, 25 °C, 150 rpm, 14 days, pH: 3	97.0	[14]
Pristine biomass	$C_0=50-300$ mg/L, 30 °C, 120 rpm, 24 h, pH: 3.8	88.4	[40]
BC	$C_0=10$ mg/L, 25 °C, 125 rpm, 30 h, pH: 1.25 and 5.90, respectively	174.2; 64.0	[41]
100TA-BC		97.4; 25.7	
300TA-BC		30.6; 6.1	
100GA-BC		166.0; 63.8	
300GA-BC		44.1; 59.8	
Granular activated carbon	$C_0=100$ mg/L, 30 °C, 120 rpm, 8 h, pH: 3	50.74	[9]
Data seed activated carbon	$C_0=100$ mg/L, 30 °C, 120 rpm, 30 h, without any pH adjustment	54.2	[15]
Pomegranate husk (2.5%wt)/PDMAEMA	$C_0=100$ mg/L, 25 °C, 100 rpm, 90 min, pH: 3	68.8	This study

68.805 (mg/g) for the removal of 2,4-D and adsorption capacity were obtained under these optimal conditions with relative errors 3.328% and 0.177%, respectively.

6. Desorption and Reusability Tests

Reusability of the adsorbent is vital because of the economic point of view in addition to anticipated higher adsorption capacity of adsorbent. Therefore, optimal conditions were applied to 2,4-D adsorption onto AC/PDMAEMA adsorbent exhibiting higher adsorption capacity. For desorption of adsorbed 2,4-D from the adsorbent surface, 0.5 N NaOH was used. Fig. 8 shows the adsorption-desorption cycle of the adsorbent. As seen in the figure, the adsorption capacity of AC/PDMAEMA for 2,4-D decreased at the fourth cycle.

CONCLUSION

A novel PDMAEMA/pomegranate husk composite hydrogel was prepared to evaluate the removal of 2,4-D and its adsorption capacity via RSM. The results of the RSM recommend that a pH of 3, 100 mg/L of initial concentration of 2,4-D and 2.5% of activated carbon were predicted as optimal factors in terms of maximum % removal of pesticide (63.245%) and adsorption capacity (68.805 mg/g). pH was found to be the most striking parameter because of the electrostatic attraction between polymer composite and adsorbate. Predicted data through RSM showed a good agreement with the actual data, which allows its application, modelling and optimization of adsorption. The present article is the first to examine the effects of not only the adsorption of 2,4-D from pomegranate husk/polymer composite hydrogel but also activated carbon incorporated into the PDMAEMA matrix on responses.

NOMENCLATURE

β_0	: constant coefficient
C_e	: final concentration of 2,4-D in the solution [mg/L]
C_i	: initial concentration of 2,4-D in the solution [mg/L]
k	: the number of factors
n_c	: the replicates in central points
M	: the mass of the dry adsorbent [g]
N	: the number of the experiments
$q_{e,i exp}$: adsorption capacity of the experiment i
$q_{e,i cal}$: calculated adsorption capacity value of the i
R_{adj}^2	: adjustment of correlation coefficient
R_{pred}^2	: predicted of correlation coefficient
X_1	: pH of the solution
X_2	: initial concentration of 2,4-D [mg/L]
X_3	: activated carbon content into the polymeric network [%]
V	: the volume of the solution [mL]
Y	: response
Y_1	: the percent pesticide removal [R %]
Y_2	: adsorption capacity

REFERENCES

1. V. K. Gupta, I. Ali and V. K. Suhas Saini, *J. Colloid Interface Sci.*, **299**, 556 (2006).

- D. J. Lapworth, N. Baran, M. E. Stuart and R. S. Ward, *Environ. Pollut.*, **163**, 287 (2012).
- A. Agrawal, R. S. Pandey and B. Sharma, *Journal of Water Resource and Protection*, **2**, 432 (2010).
- K. R. Munkittrick, M. R. Servos, J. L. Parrott, V. Martin, J. H. Carey, P. A. Flett, G. Potashnik and A. Porath, *J. Occup. Env. Med.*, **37**, 1287 (2005).
- Q. Wang, J. Li, Y. Song and X. Wang, *Chem. Asian J.*, **8**, 225 (2013).
- G. Zhao, L. Jiang, Y. He, J. Li, H. Dong, X. Wang and W. Hu, *Adv. Mater.*, **23**, 3959 (2011).
- Y. Sun, S. Yang, G. Zhao, Q. Wang and X. Wang, *Chem. Asian J.*, **8**, 2755 (2013).
- B. H. Hameed, J. M. Salman and A. L. Ahmad, *J. Hazard. Mater.*, **163**, 121 (2009).
- J. M. Salman and B. H. Hameed, *Desalination*, **256**, 129 (2010).
- E. Piera, J. C. Calpe, E. Brillas, X. Domènech and J. Peral, *Appl. Catal. B-Environ.*, **27**, 169 (2010).
- E. Brillas, J. C. Calpe and J. Casado, *Water Res.*, **34**, 2253 (2000).
- C. Zipper, C. Bolliger, T. Fleischmann, M. J-F Suter, W. Angst, M. D. Müller and H.-P. E. Kohler, *Biodegradation*, **10**, 271 (1999).
- A. L. Ahmad, L. S. Tan and S. R. A. Shukur, *J. Hazard. Mater.*, **151**, 71 (2008).
- Z. Aksu and E. Kabasakal, *J. Environ. Sci. Health B.*, **40**, 545 (2005).
- J. M. Salman and K. A. Al-Saad, *Int. J. Chem. Sci.*, **10**, 677 (2012).
- V. K. Gupta, A. Mittal, V. Gajbe and J. Mittal, *Ind. Eng. Chem. Res.*, **45**, 1446 (2006).
- B. H. Hameed and A. A. Rahman, *J. Hazard. Mater.*, **160**, 576 (2008).
- M. Kumar and R. Tamilarasan, *J. Chem. Eng. Data*, **58**, 517 (2013).
- U. K. Garg, M. P. Kaur, V. K. Garg and D. Sud, *Bioresour. Technol.*, **99**, 1325 (2008).
- N. Seeram, R. Lee, M. Hardy and D. Heber, *Sep. Purif. Technol.*, **41**, 49 (2005).
- G. Kyriakopoulou, D. Doulia and E. Anagnostopoulos, *Chem. Eng. Sci.*, **60**, 1177 (2005).
- C.-F. Chang, C.-Y. Chang, K.-E. Hsu and S.-C. Lee, W. Höll, *J. Hazard. Mater.*, **155**, 295 (2008).
- E. Bojemueller, A. Nennemann and G. Lagaly, *Appl. Clay Sci.*, **18**, 277 (2001).
- Y. Liu, Y. Zheng and A. Wang, *J. Env. Sci.*, **22**, 486 (2010).
- M. Dalaran, S. Emik, G. Güçlü, T. B. Iyim and S. Özgümüş, *Poly. Bull.*, **63**, 159 (2009).
- H. Tokuyama and N. Ishihara, *React Funct Polym.*, **70**, 610 (2010).
- A. S. Franca, L. S. Oliveira, A. A. Nunes, C. C. O. Alves, *Bioresour. Technol.*, **101**, 1068 (2010).
- M. Mahramanlioğlu, İ. Kizilcikci, İ. Ö. Biçer and M. Tunçay, *J. Environ. Sci. Health, Part B*, **35**, 187 (2000).
- D. C. Montgomery, *Design and Analysis of Experiments*, 4th Ed., John Wiley and Sons. New York, NY (1997).
- J. Neter, M. H. Kutner, C. J. Nachtsheim and W. Wasserman, *Applied Linear Statistical Models*, (4th Ed.) McGraw-Hill, Chicago (1996).
- Q. Beg, V. Sahai and R. Gupta, *Process Biochem.*, **39**, 203 (2003).
- I. Pavlovic, C. Barriga, M. C. Hermosin, J. Cornejo and M. A. Ullbarri, *Appl. Clay Sci.*, **30**, 125 (2005).
- U.-B. Cheah, R. C. Kirkwoodb and K.-Y. Luma, *Pestic. Sci.*, **50**, 53 (1997).

34. G. M. Walker, L. Hansen, J.-A. Hanna and S. J. Allen, *Water Res.*, **37**, 2081 (2003).
35. Z. Aksu and E. Kabasakal, *Sep. Purif. Technol.*, **35**, 223 (2004).
36. N. K. Amin, *J. Hazard. Mater.*, **165**, 52 (2009).
37. P. A. Kavaklı, Z. Yilmaz and M. Şen, *Sep. Sci.*, **42**, 1245 (2007).
38. S. Zhu, N. Yang and D. Zhang, *Mater. Chem. Phys.*, **113**, 784 (2009).
39. S. J. Kim, T. Y. Kim, S. J. Kim and S. Y. Cho, *Korean J. Chem. Eng.*, **19**, 1050 (2002).
40. S. Deng, R. Ma, Q. Yu, J. Huang and G. Yu, *J. Hazard. Mater.*, **165**, 408 (2009).
41. Y. Qui, X. Xiao, H. Cheng, Z. Zhou and G. D. Sheng, *Environ. Sci. Technol.*, **43**, 4973 (2009).