Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.807476

52 (2014) 5390–5400
August

Taylor & Francis
Taylor & Francis Group

Optimization of flocculation process by response surface methodology for diethyl phthalate removal using anionic polyacrylamide

Huaili Zheng[a], Jiangya Ma[a,*], Jun Zhai[a,*], Chuanjun Zhu[b], Xiaomin Tang[a], Yi Liao[a], Li Qian[c], Yongjun Sun[a]

[a]*Key Laboratory of the Three Gorges Reservoir Region's Eco-Environment, State Ministry of Education, Chongqing University, Chongqing 400045, China*
Tel. +86 02365120827; email: majiang_ya@126.com
Tel. +86 02365127812; email: zhaijun@cqu.edu.cn
[b]*China National Offshore Oil Corporation (CNOOC), Tianjin Chemical Research and Design Institute, Tianjin 300131, China*
[c]*School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400045, China*

Received 5 March 2013; Accepted 16 May 2013

ABSTRACT

Diethyl phthalate (DEP) are classified as endocrine disruptors in water. In the present study, response surface methodology (RSM) was employed for flocculation process optimization in DEP removal from water. Two different copolymers, anionic polyacrylamide (APAM), were used as flocculants in this flocculation process including $APAM_1$ and $APAM_2$. $APAM_1$ was polymerized by ultraviolet (UV) initiation, and $APAM_2$ was polymerized without UV-initiation. The analysis result of variance demonstrated that the model was highly significant and reliable. Optimization by RSM with $APAM_1$, the optimum conditions were dosage of 11.01 mg L^{-1}, pH of 8.93, and stirring time of 6.29 min. And the optimum conditions with $APAM_2$ were dosage of 13.68 mg L^{-1}, initial pH of 8.73, and stirring time of 6.80 min. DEP removal efficiency of 83.97% was achieved by using flocculants $APAM_1$ and 72.47% for $APAM_2$. Scanning electron microscopy images and spectrum from nuclear magnetic resonance spectrometer (^{1}H NMR) suggested that UV-initiation had played an important surface modification in APAM polymerization. In addition, the confirmation experiment results showed that the measured values had a good agreement with the predicted values, which demonstrated that RSM could be successfully used in flocculation process.

Keywords: Diethyl phthalate; Water treatment; Flocculation process; Anionic polyacrylamide; Response surface methodology

1. Introduction

In the modern industry, diethyl phthalate (DEP), as an important organic additive compound, has been widely used in plastic to improve the mechanical properties of the plastic resin, especially the flexibility [1–3]. To provide the required flexibility, DEP is not covalently bound to the resin and is therefore able to migrate into the environment [4,5]. Due to the large

*Corresponding authors.

This article was originally published with a mistake in Huaili Zheng's name. This version has been corrected. Please see Corrigendum [10.1080/19443994.2013.819163] production and utilization, DEP is leached out by water, thus turning into a ubiquitous aqueous persistent organic pollutant in the environment [6]. DEP have been detected in surface water, landfill leachate, sewage sludge, and sediment [7]. Specifically, DEP contributes a major proportion (53.4%) of micropollutants detected in the Han River which runs through Seoul in South Korea [8]. Furthermore, DEP can induce various etiological diseases in human, such as male reproductive tract disorders, breast and testicular cancers, dysfunction of neuroendocrine system etc. [9]. At present, four methods are used for DEP removal, which includes membrane treatment, adsorption, advanced oxidation, and biological degradation [10]. However, high cost of processing and complex operation limit the application of these methods in water treatment. Therefore, it is essential to research and develop an efficient approach with simple operation and low cost for controlling DEP pollution.

Flocculation process is an important treatment technology with a wide range of applications in drinking water and wastewater treatment facilities [11,12]. However, up to now, DEP removal using the flocculation process is a new approach. Therefore, this is a valuable research for enriching the theory of DEP contaminated wastewater treatment. For the flocculation process, the flocculation performance generally depends on species and properties of the flocculants. Recently, the application of high molecular organic compound as flocculants is becoming a research hotspot. Anionic polyacrylamide (APAM) compounds represent a class of typical organic flocculants. Due to containing the sulfonic acid, phosphoric acid or carboxylic acid functional groups, APAM shows electronegative [13]. In addition, the molecular chains of APAM stretch in water because of high charge density, which will increase the capacity of adsorption and bridging for organic particles removal [14]. Furthermore, the combination of flocculation with other appropriate physical-chemical treatment processes such as wastewater initial pH, flocculants dosage, and stirring conditions result in enhanced efficiency of the flocculation process [15,16]. In order to assess the flocculation efficiency, reasonable modeling with these influencing factors is necessary [17]. In recent years, response surface methodology (RSM) has been proved to be an efficient way to achieve the analyzing, modeling, and optimization. Therefore, RSM is employed to optimize the APAM flocculation performance for the DEP removal from water.

In this paper, the influence of APAM on the DEP removal was investigated. Furthermore, to improve the removal efficiency, influencing factors such as initial pH of simulation wastewater, APAM dosage, and stirring time were investigated. The $APAM_1$ polymerization reacted under the ultraviolet (UV) irradiation and $APAM_2$ polymerized without UV irradiation. Both $APAM_1$ and $APAM_2$ were synthesized by using acrylamide (AM), anionic monomers acrylic acid (AA), and 2-acylamido-2-methyl propane sulfonic acid (AMPS). In addition, $APAM_1$ and $APAM_2$ were compared for the DEP removal.

2. Materials and methods

2.1. Materials and instruments

All reagents used in this study were of analytical grade except AM and AMPS, which were of technical grade. The other reagents used in this study were AA, DEP, sodium hydroxide (NaOH), and hydrochloric acid (HCl). All aqueous solutions and standard solutions were prepared with ultrapure deionized water. The instruments used in the experimental set-up were as follows:

(1) ZR4–6 coagulation experiment blender from Zhongrun Water Industry Technology & Development Co., Ltd., China.
(2) VEGA II LMU scanning electron microscope (SEM) from TES-CAN Company, Czech.
(3) AVANCE 500 nuclear magnetic resonance (NMR) spectrometer from BRUKER Company, Germany.
(4) LC-10AT high-performance liquid chromatography from Shimadzu, Japan.
(5) HACH 2100Q turbidimeter supplied by HACH, USA.

2.2. Preparation of flocculants

Flocculants $APAM_1$ and $APAM_2$ used in this experiment were prepared in the laboratory. Firstly, 7.0 g AM, 1.0 g AA as well as 1.0 g AMPS were added into a reaction vessel. Then, deionized water was added to make the monomer ratio reach 40%. After complete mixing, 0.2% ammonium persulfate and sodium bisulfate as the initiator were added to the reaction vessel. The mixture was purged using nitrogen gas with agitation to remove oxygen for 20 min. Finally, $APAM_1$ was obtained from the polymerization under the UV irradiation for 1 h, while $APAM_2$ was obtained by polymerization in 30°C water bath for 2 h without UV irradiation.

2.3. Characterization of APAM

Flocculants samples $APAM_1$ and $APAM_2$ were dried at 60℃ in an oven for several days. After pretreatment with spray gold, the product morphology was determined using a SEM. In addition, the surface morphology of the sample was analyzed using fractal dimension. The SEM micrographs and analysis results are shown in Figs. 1 and 2, respectively. Furthermore, $APAM_1$ and $APAM_2$ were dissolved with deuterium oxide (D_2O) as the solvent before analyzes using ^1H NMR. Fig. 3 shows the ^1H NMR spectrum of APAM.

2.4. Wastewater sample

In order to determine the initial DEP concentration, the effect of DEP concentration on removal efficiency was investigated. We have conducted a series of experiments by using flocculants $APAM_1$. The result is shown in the following Table 1. It can be seen from the Table 1, DEP removal efficiency shows good stability when DEP initial concentration is set in the range of $1.00–15.0\,mg\,L^{-1}$. Furthermore, considering reduce experimental error and easy to detect, so we chose $10\,mg\,L^{-1}$ as the initial concentration of the prepared DEP wastewater sample.

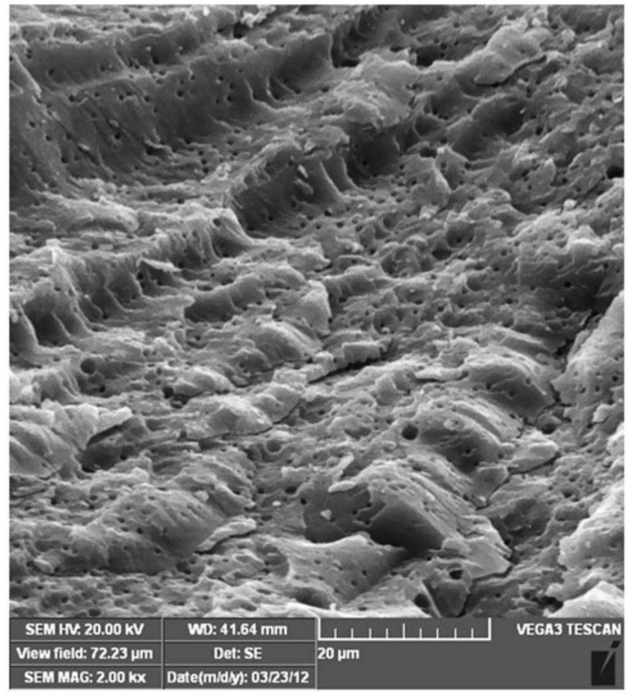
The simulation wastewater sample was prepared in the laboratory. Firstly, 1.0 g DEP was completely dissolved in chromatographically pure methanol. Then the solution was transferred to a 1 L volumetric flask to prepare a $1\,g\,L^{-1}$ DEP standard aqueous solution using ultrapure water. Finally, $10\,mg\,L^{-1}$ DEP simulation wastewater was accurately prepared through dilution with the ultrapure water.

2.5. Flocculation experiments

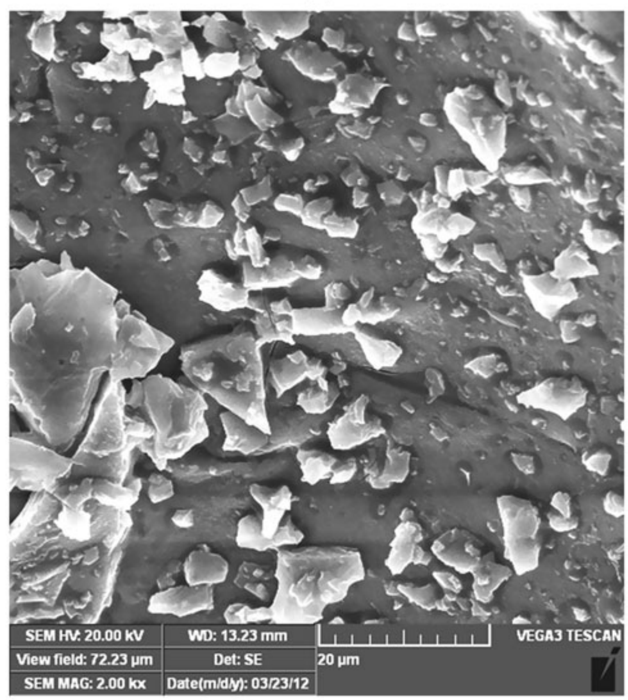
The flocculation experiments were carried out using a program-controlled jar test apparatus at ambient temperature. 500 mL of $10\,mg\,L^{-1}$ DEP simulation wastewater was transferred into a beaker and the initial pH was adjusted from original value 7.1 to the set value using $0.5\,mol\,L^{-1}$ HCl and NaOH. Initially, a certain amount of flocculants was added followed by rapid mixing at 300 rpm. After flocculation for several minutes and quiescent settling for 1 h, the clarified wastewater was extracted to measure the residual DEP using a high-performance liquid chromatography, and the removal efficiency was calculated using the following Eq. (1).

$$\text{Removal}\ (\%) = \frac{C_i - C_f}{C_i} \times 100\% \qquad (1)$$

where C_i and C_f are the initial and final concentration of DEP, respectively.



(a)



(b)

Fig. 1. SEM micrographs of (a) $APAM_1$ and (b) $APAM_2$.

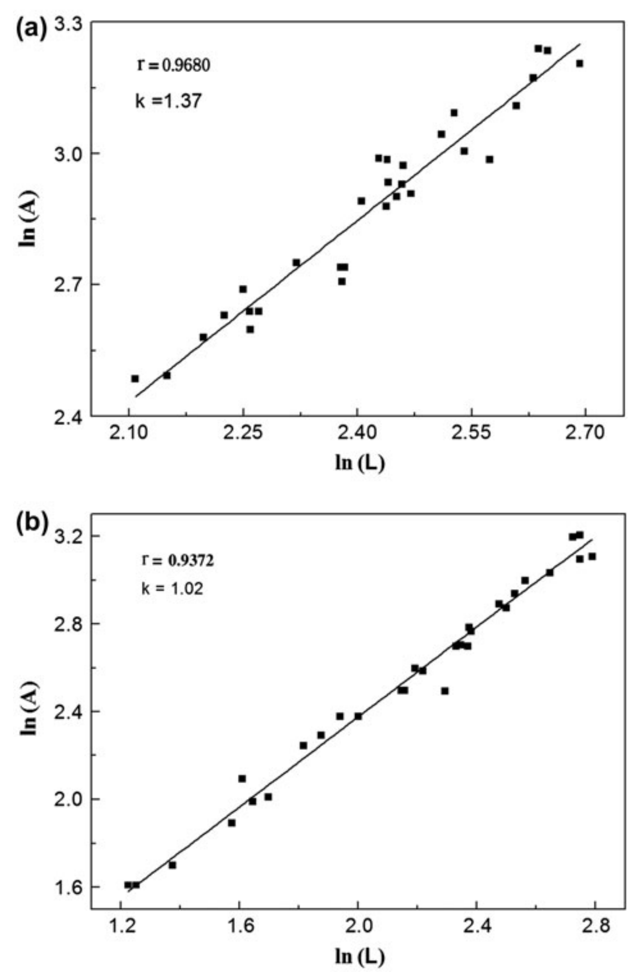


Fig. 2. Relationship between projected area and perimeter of (a) $APAM_1$ and (b) $APAM_2$.

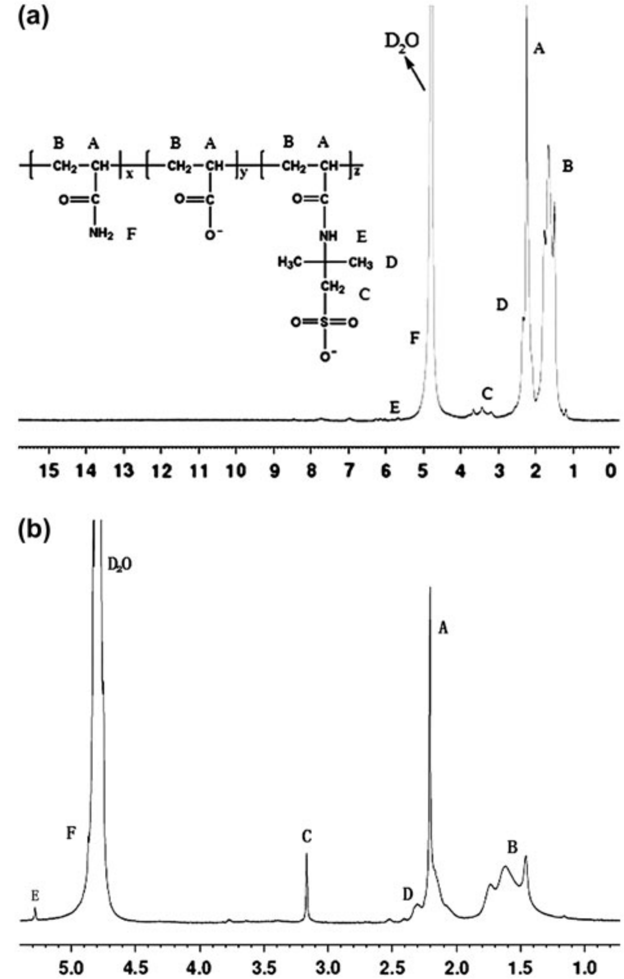


Fig. 3. ^{1}H NMR spectrum of (a) $APAM_1$ and (b) $APAM_2$.

2.6. RSM design

The relationship between the parameters APAM dosage, stirring time, and initial pH value was investigated to find the most suitable combination of these variables resulting in the optimal DEP removal efficiency by employing RSM. Central composite rotatable designs (CCRD) are widely used in statistical modeling to obtain response surface models that set the mathematical relationships between response and variables [18]. Based on CCRD, the three factors APAM dosage, stirring time, and initial pH value with three levels high (+1), low (−1), the center points (basic level, 0) were set up in the Expert Designer software. Table 2 shows experimental ranges and significant levels of factors. Table 3 shows the results obtained for DEP removal efficiency. In addition, the experimental design and results obtained from 17 experimental runs for DEP removal efficiency (as the response value) are presented in Table 2.

The quadratic equation models (Y_1 and Y_2) in terms of linear, quadratic and cross terms were constructed according to Eq. (2) [19].

$$Y = a_0 + \sum_{i=1}^{f} a_i X_i + \sum_{i=1}^{f} a_{ii} X_i^2 + \sum_{i}^{i<j} \sum_{j} a_{ij} X_i X_j + \varepsilon \qquad (2)$$

where Y is the response variable (DEP removal efficiency) to be modeled; X_i and X_j are the factors that influence the predicted response Y; a_i is the linear coefficient, a_{ii} is the squared coefficient for the factor I, and a_{ij} is the model coefficient for the interaction effect between factors I and J; f is the number of factors investigated in the experiment, and ε is the random error.

According to the response results of the model, analysis of variance (ANOVA) was applied to establish the feasibility of the quadratic equation model between the variables and the responses. In

Table 1
Effect of DEP concentration on removal efficiency

DEP concentration (mg L^{-1})	0.0250	0.050	0.100	0.500	1.00	5.00	10.0	15.0
Removal efficiency	41.1%	44.6%	48.8%	62.3%	74.7%	76.1%	76.5%	75.4%

Table 2
Experimental ranges and significant levels of factors

Factors	Ranges and levels		
	−1	0	1
$APAM_1$ dosage (mg L^{-1})	5	10	15
$APAM_2$ dosage (mg L^{-1})	5	10	15
Stirring time (min)	3	6	9
pH	8	9	10

order to check for the statistical significance of the quadratic equation model and test variables, F-test and p-values at 95% confidence level were used. Furthermore, based on the coefficient of determination R^2 and adjusted R^2, the modeling quality of the model was tested. Additionally, the interaction effect of the factors (dosage and pH, dosage and stirring time, and pH and stirring time) on the response value was analyzed using the three-dimensional plots. Finally, the predicted DEP removal efficiency and the measured value were compared to investigate the adequacy of the regression equations.

3. Results and discussion

3.1. SEM analysis

SEM instrument was used to analyze the structure and morphology of the flocculants $APAM_1$ and $APAM_2$. Fig. 1 shows the surface morphology of $APAM_1$ and $APAM_2$.

As shown in Fig. 1, tiered floccules with lots of holes were observed in the UV-initiated copolymers, $APAM_1$, whereas micrograph of $APAM_2$ shows looser and smaller floccules. The tiered floccules with lots of holes will be helpful for the bridging adsorption and enmeshment in DEP removal. In addition, the fractal dimension has been proved to be an appropriate approach to assess the flocculation efficiency [20–22].

Table 3
Experimental design and results obtained for DEP removal efficiency

Run	Experimental design			Results (DEP removal efficiency %)			
				$APAM_1$		$APAM_2$	
	Dosage	Stirring time	pH	Exp.[a]	Pred.[b]	Exp.	Pred.
1	5	6	8	77.32	77.46	69.53	69.38
2	15	6	8	80.97	80.55	71.54	71.59
3	10	6	9	84.54	83.85	72.37	72.09
4	5	9	9	79.36	78.91	69.56	69.62
5	10	6	9	83.91	83.86	71.84	72.09
6	10	3	10	80.70	80.45	69.13	69.04
7	5	3	9	79.32	79.22	69.48	69.62
8	10	6	9	84.11	83.84	72.37	72.09
9	10	6	9	83.74	83.80	71.29	72.09
10	15	9	9	81.38	81.48	71.87	71.73
11	10	6	9	83.10	83.86	72.57	72.09
12	5	6	10	77.91	78.26	69.21	69.16
13	10	3	8	79.82	79.76	69.51	69.52
14	15	3	9	80.20	80.59	70.59	70.53
15	10	9	8	80.85	81.05	70.46	70.55
16	10	9	10	79.72	79.74	69.22	69.21
17	15	6	10	79.27	79.13	69.83	69.98

[a]Exp. is the measured DEP removal efficiency.
[b]Pred. is the predicted DEP removal efficiency.

The fractal dimension can be calculated by image-pro Plus 6.0 Software. Fig. 2 presents the linear correlation of the logarithm of perimeter (L) and area (A).

The previous studies have shown that UV-initiation as a new research technique in the synthesis of the APAM has been recognized to be an efficient approach for surface modification [23,24]. The result shows the correlation coefficient (r) values were 0.9680 and 0.9907, respectively, which indicates a strong correlation between ln(L) and ln(A). Most important is the fractal dimension of $APAM_1$ and $APAM_2$ as 1.37 and 1.02, respectively. This big difference in morphological structure shows the specific surface area of $APAM_1$ is bigger than $APAM_2$, indicating that UV played an important role in the polymerization of $APAM_1$. As a result, the adsorption and enmeshment capacity of surface modified flocculants $APAM_1$ will be greatly enhanced. Therefore, we can predict $APAM_1$ will play a better performance in DEP removal than $APAM_2$.

3.2. ^{1}H NMR analysis

It can be seen from Fig. 3(a) and Fig. 3(b) that, $APAM_1$ and $APAM_2$ generally have a similar ^{1}H NMR spectrum. The resonance peak at $\delta = 4.75$ ppm was attributed to the solvent D_2O. In addition, the peaks at $\delta = 2.24$ and $\delta = 1.65$ ppm were derived from the proton at the methane group and methylene group of –CH_2–CH– in the AM, AA, and AMPS [13,25]. Furthermore, the resonance peak at $\delta = 3.25$ and $\delta = 2.33$ ppm were ascribed to the proton at the methylene group and methyl group –C$(CH_3)_2CH_2SO_3^-$ in the AMPS.

However, the resonance peak shows a difference between $APAM_1$ and $APAM_2$ at $\delta = 3.25$ ppm. This structural difference indicates $APAM_1$ have a good adsorption and bridging ability as a result of UV-initiation. Moreover, the peak at $\delta = 5.75$ ppm resulted from the proton of –NH– in the AMPS, but it has a low proportion in the copolymer according the integral of the area of the resonance spectrum.

3.3. Model fitting

The responses (DEP removal efficiency) of $APAM_1$ and $APAM_2$ were correlated with three factors APAM dosage, X_1, initial pH, X_2, and stirring time, X_3, by using the second-order polynomial according to Eq. (2). From the experimental data (Table 2), the following quadratic regression models were generated for DEP removal efficiency.

$$Y_1 = 83.86 + 0.99X_1 - 0.16X_2 + 0.14X_3 - 0.55X_1X_2 + 0.30X_1X_3 - 0.50X_2X_3 - 2.61X_1^2 - 2.41X_2^2 - 1.20X_3^2 \ (R^2 = 0.9765,\ \text{Adj. } R^2 = 0.9464) \tag{3}$$

$$Y_2 = 72.09 + 0.76X_1 - 0.46X_2 + 0.30X_3 - 0.35X_1X_2 + 0.30X_1X_3 - 0.21X_2X_3 - 0.63X_1^2 - 1.43X_2^2 - 1.08X_3^2 \ (R^2 = 0.9537,\ \text{Adj. } R^2 = 0.8941) \tag{4}$$

Eqs. (3) and (4) are the quadratic regression models for DEP removal using $APAM_1$ and $APAM_2$, respectively.

3.4. Statistical analysis

The responses were analyzed by employing ANOVA to estimate the goodness of fit; the result of which are presented in Table 4.

Table 4 shows the p-value of regression less than 0.05 (<0.0001 and 0.0007), which implies the models for $APAM_1$ and $APAM_2$ are significant at 95% confidence level. On the contrary, the p-value of 0.5012 and 0.9330 for lack of fit are greater than 0.05, indicating the lack of fit is not significant. Therefore, for the two models, the second-order polynomial model fitted the experimental results well.

Secondly, in order to ensure a satisfactory adjustment of the quadratic model, a higher R^2 coefficient is desirable [26]. For $APAM_1$, the R^2 value of 97.65% indicates the model could not explain 2.35% of the total variations. However, for $APAM_2$, the R^2 value of 95.37% implies the model could not explain 4.63% of the total variations. Fig. 4 shows the diagnostic plots of DEP removal efficiency for $APAM_1$ and $APAM_2$. The actual values are distributed near to a straight line although there are a few points showing discrepancy with predicted values for $APAM_2$. It can be seen from Fig. 4 that the correlation coefficient for $APAM_1$ is 0.9742 and 0.9013 for $APAM_2$. This is attributed to the models corresponding well with the measured value [27]. Therefore, these two plots show a sufficient agreement between the actual values obtained from the models and real data.

3.5. Mutual effect of parameters

The response surface contour plots were used to investigate the interaction effect of the three factors APAM dosage, initial pH, and stirring time. The two-dimensional contour plots are shown in Figs. 5 and 6.

As can be seen from Figs. 5 and 6, the DEP removal efficiency increases as the stirring time

Table 4
ANOVA results for response parameters

Source model	$APAM_1$					$APAM_2$				
	SS	DF	MS	*F*-value	*p*-value	SS	DF	MS	*F*-value	*p*-value
Regression	75.98	9	8.44	32.37	<0.0001	24.73	9	2.75	16.01	0.0007
Dosage	7.82	1	7.82	29.99	0.0009	4.58	1	4.58	26.66	0.0013
pH	0.20	1	0.20	0.75	0.4155	1.67	1	1.67	9.70	0.0170
Time	0.17	1	0.17	0.64	0.4483	0.72	1	0.72	4.19	0.0798
Dosage × pH	1.22	1	1.22	4.68	0.0672	0.48	1	0.48	2.81	0.1373
Dosage × Time	0.36	1	0.36	1.38	0.2784	0.36	1	0.36	2.10	0.1908
Time × pH	1.00	1	1.00	3.38	0.0911	0.18	1	0.18	1.08	0.3338
Dosage × Dosage	28.60	1	28.60	109.67	<0.0001	1.69	1	1.69	9.82	0.0165
pH × pH	24.38	1	24.38	93.48	<0.0001	8.58	1	8.58	50.00	0.0002
Time × Time	6.10	1	6.10	23.39	0.0019	4.91	1	4.91	28.63	0.0011
Residual	1.83	7	0.26			1.20	7	0.17		
Lack of fit	0.75	3	0.25	0.94	0.5012	0.11	3	0.037	0.14	0.9330
Pure error	1.07	4	0.27			1.09	4	0.27		

increased from 6.5–7.0 min, and then decreases while increasing the APAM dosage and initial pH value. The greatest influence on the DEP removal efficiency came from the APAM dosage compared to the initial pH value. Therefore, APAM dosage is the predominant significant factor for DEP removal. However, at initial pH value close to 8.0 or 10.0 and APAM dosage near 5.0 or 15.0 mg L^{-1}, the changes in stirring time have no effect on DEP removal efficiency. This is attributed to the flocculation hydrolysis, which can inhibit the bridging and enmeshment [28–30]. On the other hand, flocculation is not enough at low dosages, whereas flocs can lose stability under excessive dosage [23,31,32].

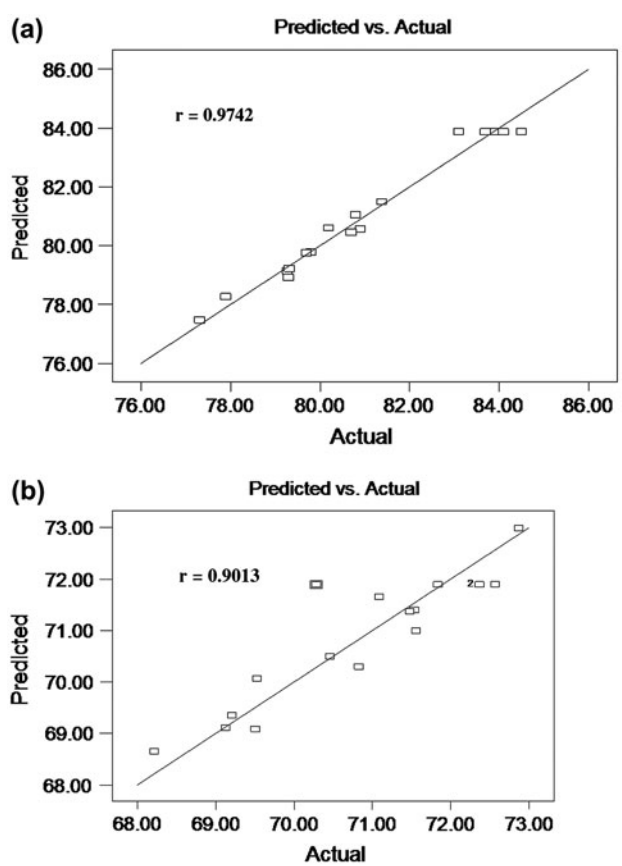


Fig. 4. Diagnostic plots: predicted vs. actual values plots for DEP removal efficiency by using flocculants (a) $APAM_1$ and (b) $APAM_2$.

3.6. Optimization analysis

Figs. 7 and 8 illustrates the three-dimensional (3D) surface plots for $APAM_1$ and $APAM_2$.

For $APAM_1$ and $APAM_2$, the response surface plots are approximately symmetrical in shape with circular contours clearly showing peaks, which are located inside the design boundary. This implies the optimum conditions for maximum DEP removal and are influences by flocculants dosage, initial pH, and stirring time. Combined the 3D surface plots with regression Eq. (3), the optimal conditions for the DEP removal were as follows: dosage of 11.01 mg L^{-1}, initial pH of 8.93, stirring time of 6.29 min for $APAM_1$ whereas for $APAM_2$ its dosage of 13.68 mg L^{-1}, initial pH of 8.73, stirring time of 6.80 min. Under the optimal conditions, the maximum DEP removal efficiency using $APAM_1$ and $APAM_2$ were 83.97 and 72.47%, respectively. The difference of the result also confirms the modification by UV-initiation in the polymerization.

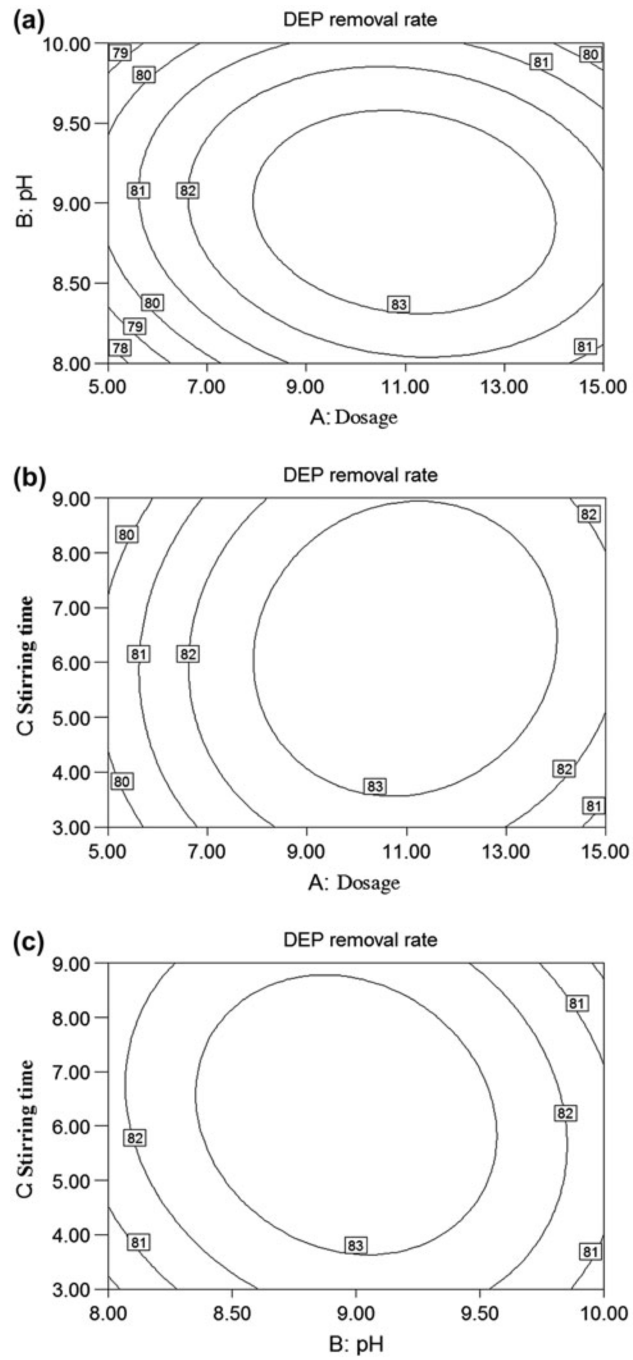


Fig. 5. Two-dimensional contour plots for DEP removal efficiency showing the interaction effect of variables: (a) dosage-pH, (b) dosage-stirring time and (c) pH-stirring time by using $APAM_1$.

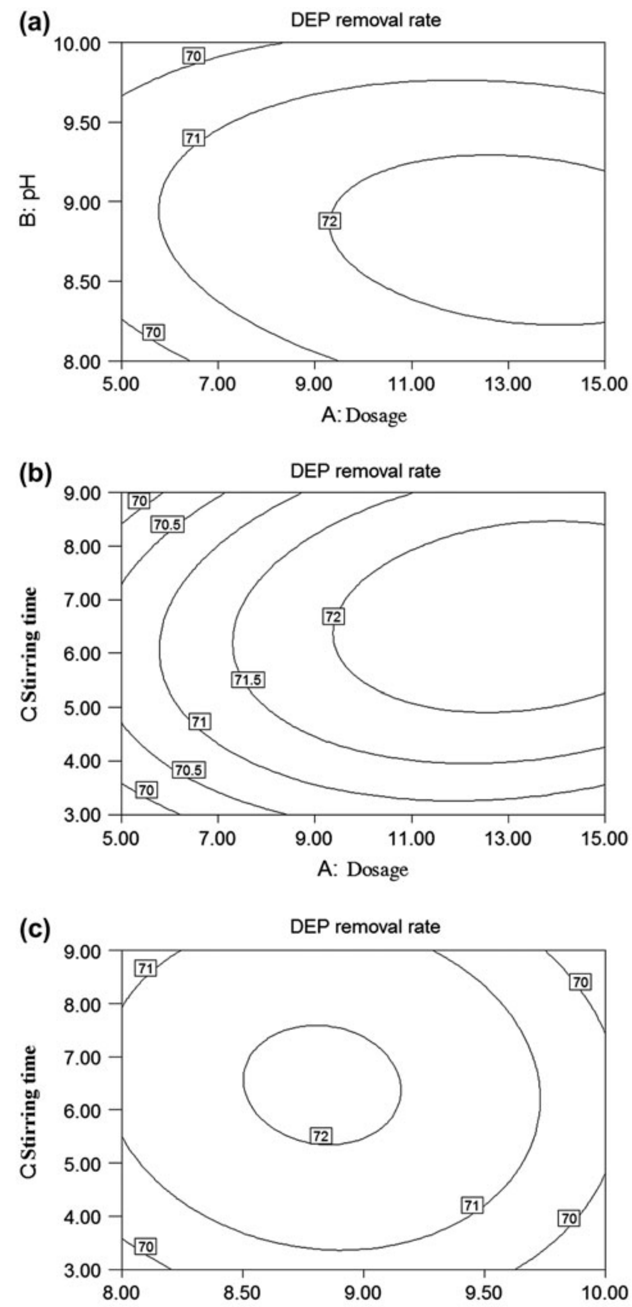


Fig. 6. Two-dimensional contour plots for DEP removal efficiency showing the interaction effect of variables: (a) dosage-pH, (b) dosage-stirring time and (c) pH-stirring time by using $APAM_2$.

3.7. Model validation

Model validation is essential for RSM. Therefore, three runs of additional experiments for each flocculants were conducted to confirm the validity of the model. According to the practical situation, the optimal conditions were modified as follows: dosage of 11.0 mg L^{-1}, pH of 8.9, stirring time of 6.3 min for $APAM_1$ and dosage of 13.7 mg L^{-1}, initial pH of 8.7, stirring time of 6.8 min for $APAM_2$. The confirmation experimental results are shown in Table 5.

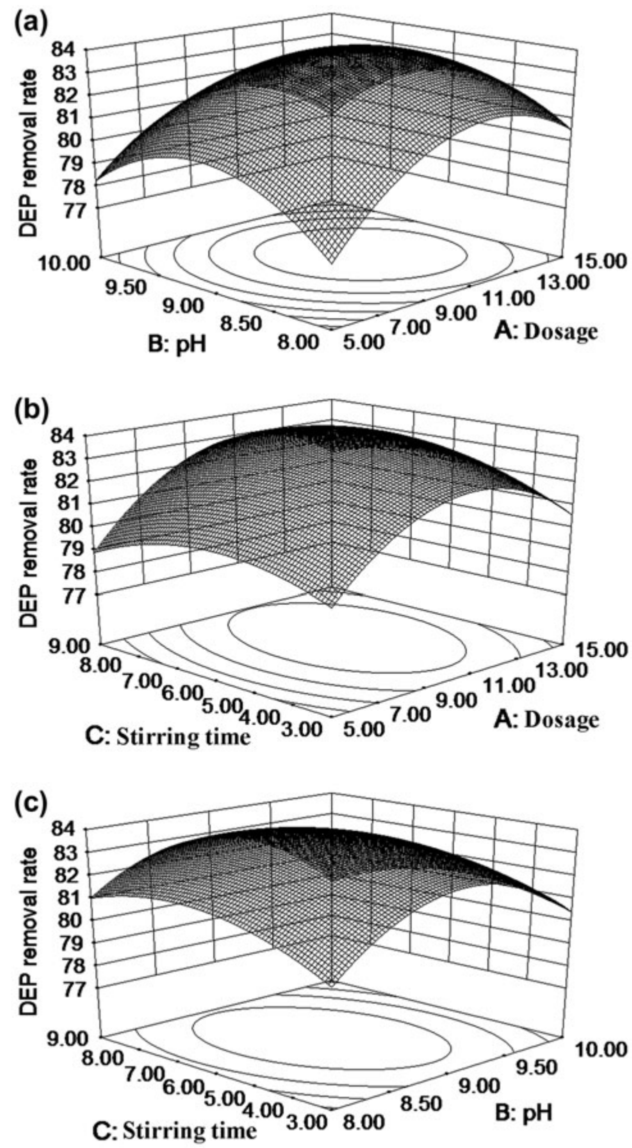


Fig. 7. 3D surface plots for $APAM_1$.

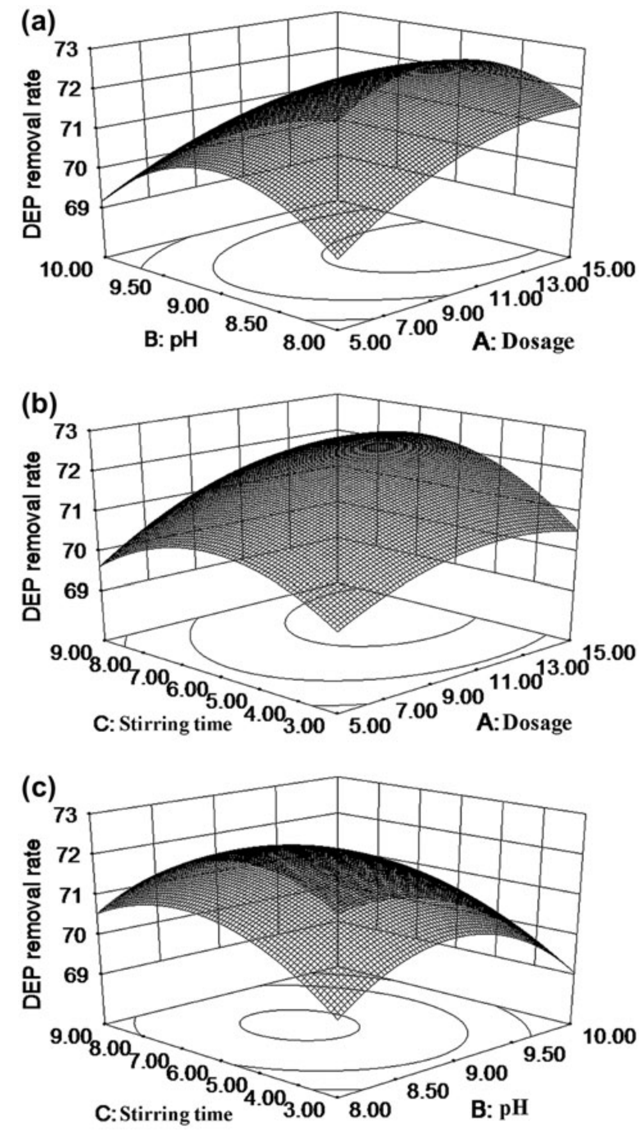


Fig. 8. 3D surface plots for $APAM_2$.

As shown in Table 5, the error between measured DEP removal efficiency and the corresponding predicted value ranges between 0.49–0.73% using $APAM_1$, as well as 0.43–0.84% using $APAM_2$. Confirmation experiments show the measured value is very close to the predicted values using the regression models. As a result, RSM approach was proved to be successfully applied for modeling and optimizing the flocculation process in DEP removal [33–34].

Table 5
Measured and predicted values of DEP removal efficiency for the confirmation experiments

Flocculants	Conditions			DEP removal efficiency (%)	
	Dosage ($mg\,L^{-1}$)	pH value	Stirring time (min)	Measured	Predicted
$APAM_1$	11.0	8.9	6.3	83.46 ± 0.10	83.97
$APAM_2$	13.7	8.7	6.8	72.93 ± 0.15	72.47

4. Conclusions

In this paper, the flocculation process with flocculants $APAM_1$ and $APAM_2$ was used for the DEP removal from wastewater. To maximize the DEP removal efficiency, RSM was employed to optimize the factors of dosage, initial pH value, and stirring time. Using $APAM_1$, the optimization results show the DEP removal efficiency of 83.97% can be achieved under the dosage of $11.01\,mg\,L^{-1}$, initial pH of 8.93, stirring time of 6.29 min, which is better than 72.47% achieved by using $APAM_2$ at dosage of $13.68\,mg\,L^{-1}$, initial pH of 8.73, stirring time of 6.80 min. Moreover, SEM images and ^1H NMR demonstrated that UV-initiation can result in the surface modification during flocculants polymerization which is helpful for DEP removal. Finally, the confirmation experiments result showed RSM was an effective method for the optimization of experimental parameters in the treatment of DEP wastewater.

Acknowledgments

The authors are grateful for the financial support provided by the National Natural Science Foundation of China (Project No. 21177164; 51078366).

Abbreviations

DEP	—	Diethyl phthalate
APAM	—	Anionic polyacrylamide
RSM	—	Response surface methodology
AM	—	Acrylamide
AA	—	Acrylic acid
AMPS	—	2-Acylamido-2-methyl propane sulfonic acid
UV	—	Ultraviolet
CCRD	—	Central composite rotatable designs
ANOVA	—	Analysis of variance
SEM	—	Scanning electron microscopy
NMR	—	Nuclear magnetic resonance spectrometer

References

[1] T.F.D. Oliveira, O. Chedeville, H. Fauduet, B. Cagnon, Use of ozone/activated carbon coupling to remove diethyl phthalate from water: Influence of activated carbon textural and chemical properties, Desalination 276 (2011) 359–365.

[2] H. Maruyama, H. Seki, Y. Matsukawa, A. Suzuki, N. Inoue, Adsorption behavior of bisphenol-A and diethyl phthalate onto bubble surface in nonfoaming adsorptive bubble separation, Chem. Eng. J. 141 (2008) 112–118.

[3] Y. Lu, F. Tang, Y. Wang, J.H. Zhao, X. Zeng, Q.F. Luo, L. Wang, Biodegradation of dimethyl phthalate, diethyl phthalate and di-n-butyl phthalate by Rhodococcus sp. L4 isolated from activated sludge, J. Hazard. Mater. 168 (2009) 938–943.

[4] Y. Wang, Y. Fan, J.D. Gu, Microbial degradation of the endocrine disrupting chemicals phthalic acid and dimethyl phthalate ester under aerobic conditions, Bull. Environ. Contam. Toxicol. 71(4) (2003) 810–818.

[5] S. Tlili, E.G. Alvarez, S. Gligorovski, H. Wortham, Adsorption behavior of two model airborne organic contaminants on wafer surfaces, Chem. Eng. J. 187 (2012) 239–247.

[6] G.P. Yang, X.K. Zhao, X.J. Sun, X.L. Lu, Oxidative degradation of diethyl phthalate by photo chemically – enhanced Fenton reaction, J. Hazard. Mater. 126 (2005) 112–118.

[7] H.H.P. Fang, D.W. Liang, T. Zhang, Aerobic degradation of diethyl phthalate by Sphingomonas sp, Bioresour. Technol. 98 (2007) 717–720.

[8] S.M. Na, Y.G.Y. Ahn, M.C. Cui, J.Y. Khim, Significant diethyl phthalate (DEP) de gradation by combined advanced oxidation process in aqueous solution, J. Environ. Manage. 101 (2012) 104–110.

[9] B. Xu, N.Y. Gao, X.F. Sun, S.J. Xia, M. Rui, M.O. Simonnot, C. Causserand, J.F. Zhao, Photochemical degradation of diethyl phthalate with UV/H_2O_2, J. Hazard. Mater. 139 (2007) 132–139.

[10] S.M. Na, J.H. Cai, M.C. Cui, J.Y. Khim, Sonophotolytic diethyl phthalate (DEP) degradation with UVC or VUV irradiation, Ultrason. Sonochem. 19 (2012) 1094–1098.

[11] H. Zheng, G.C. Zhu, S.J. Jiang, T. Tshukudu, X.Y. Xiang, P. Zhang, Q. He, Investigations of coagulation–flocculation process by performance optimization, model prediction and fractal structure of flocs, Desalination 269 (2011) 148–156.

[12] G.C. Zhu, H. Zheng, W.Y. Chen, W. Fan, P. Zhang, T. Tshukudu, Preparation of a composite coagulant: Polymeric aluminum ferric sulfate (PAFS) for wastewater treatment, Desalination 285 (2012) 315–323.

[13] H. Song, S.F. Zhang, X.C. Ma, D.Z. Wang, J.Z. Yang, Synthesis and application of starch-graft-poly (AM-co-AMPS) by using a complex initiation system of CS-APS, Carbohydr. Polym. 69 (2007) 189–195.

[14] A. Pourjavadi, S. Barzegar, F. Zeidabadi, Synthesis and properties of biodegradable hydrogels of К-carrageenan grafted acrylic acid-co-2-acrylamido-2-methylpropanesulfonic acid as candidates for drug delivery systems, React. Funct. Polym. 67 (2007) 644–654.

[15] X.J. Yang, L. Ni, Synthesis of hybrid hydrogel of poly(AM co DADMAC)/silica sol and removal of methyl orange from aqueous solutions, Chem. Eng. J. 209 (2012) 194–200.

[16] A.W. Zularisam, A.F. Ismail, M.R. Salim, M. Sakinah, T. Matsuura, Application of coagulation-ultra filtration hybrid process for drinking water treatment: optimization of operating conditions using experimental design, Sep. Purif. Technol. 65(2) (2009) 193–210.

[17] W. Brostow, S. Pal, R.P. Singh, A model of flocculation, Mater. Lett. 61(22) (2007) 4381–4384.

[18] C. Cojocaru, G. Zakrzewska-Trznadel, Response surface modeling and optimization of copper removal from aqua solutions using polymer assisted ultra filtration, J. Membr. Sci. 298 (2007) 56–70.

[19] J.P. Wang, Y.Z. Chen, X.W. Ge, H.Q. Yu, Optimization of coagulation–flocculation process for a paper-recycling wastewater treatment using response surface methodology, Colloids Surf. A 302 (2007) 204–210.

[20] O.M. Bruno, R. de Oliveira Plotze, M. Falvo, M. de Castro, Fractal dimension applied to plant identification, Inf. Sci. (Ny) 178(12) (2008) 2722–2733.

[21] J.U. Baer, T.F. Kent, S.H. Anderson, Image analysis and fractal geometry to characterize soil desiccation cracks, Geoderma 154(1–2) (2009) 153–163.

[22] J. Li, Q. Du, C. Sun, An improved box-counting method for image fractal dimension estimation, Pattern Recognit. 42(11) (2009) 2460–2469.

[23] H. Song, S.F. Zhang, X.C. Ma, D.Z. Wang, J.Z. Yang, Synthesis and application of starch-graft-poly (AM-co-AMPS) by using a complex initiation system of CS-APS, Carbohydr. Polym. 69 (2007) 189–193.

[24] A. Mostak, B.K. Mohammad, A.K. Mubarak, M. Shamsul Alam, H.K. Anwar, Sulfonation of polyester fabrics by gaseous sulfur oxide activated by UV irradiation, J. Power Sources 196 (2011) 614–617.

[25] Z. Abdollahi, M. Frounchi, S. Dadbin, Synthesis, characterization and comparison of PAM, cationic PDMC and P(AM- co - DMC) based on solution polymerization, J. Ind. Eng. Chem. 17 (2011) 580–586.

[26] V. Jaikumar, V. Ramamurthi, Statistical analysis and optimization of acid dye biosorption by brewery waste biomass using response surface methodology, J. Modern Appl. Sci. 3(4) (2009) 71.

[27] J.M. Gonzalea-Saiz, C. Pizarro, Polyacrylamide gels as support for enzyme immobilization by entrapment, effect of polyelectrolyte carrier, pH and temperature on enzyme action and kinetics parameters, Eur. Polym. J. 37 (2011) 435–444.

[28] G.C. Zhu, H. Zheng, Z. Zhang, T. Tshukudu, P. Zhang, X.Y. Xiang, Characterization and coagulation–flocculation behavior of polymeric aluminum ferric sulfate (PAFS), Chem. Eng. J. 178 (2011) 50–59.

[29] H.Q. Zhang, Z.X. Zhong, W.H. Xing, Application of ceramic membranes in the treatment of oilfield-produced water: Effects of polyacrylamide and inorganic salts, Desalination 309 (2013) 84–89.

[30] F.Q. An, X.Q. Feng, B.J. Gao, Adsorption of aniline from aqueous solution using novel adsorbent PAM/SiO_2, Chem. Eng. J. 151 (2009) 183–187.

[31] H.L. Wang, J.Y. Cui, W.F. Jiang, Synthesis, characterization and flocculation activity of novel Fe $(OH)_3$–polyacrylamide hybrid polymer, Mater. Chem. Phys. 130 (2011) 993–999.

[32] J.P. Wang, Q. Wang, A.Q. Wang, Synthesis and characterization of chitosan- g -poly(acrylic acid)/attapulgite superabsorbent composites, Carbohydr. Polym. 68 (2007) 367–374.

[33] A.M.M. Vargas, A.C. Martins, V.C. Almeida, Ternary adsorption of acid dyes onto activated carbon from flamboyant pods (Delonix regia): Analysis by derivative spectrophotometry and response surface methodology, Chem. Eng. J. 195–196 (2012) 173–179.

[34] X.S. Yi, W.X. Shi, S.L. Yu, C. Ma, N. Sun, S. Wang, L.M. Jin, L.P. Sun, Optimization of complex conditions by response surface methodology for APAM–oil/water emulsion removal from aqua solutions using nano-sized TiO_2/Al_2 O_3 PVDF ultrafiltration membrane, J. Hazard. Mater. 193 (2011) 37–44.