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Application of response surface methodology to optimize degradation of polyacrylamide in aqueous solution using heterogeneous Fenton process

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ABSTRACT

Response surface methodology was employed to investigate the individual and interaction effect of the independent variables on the degradation of polyacrylamide (PAM) in aqueous solution by heterogeneous Fenton process with Fe^{2+}–Al_2O_3 catalyst. pH, catalyst and H_2O_2 dosage were chosen as independent variables, and the degradation of PAM was chosen as the response value. A predictive polynomial quadratic equation model was developed by ANOVA as well as analysing the response surface plots and their corresponding contour plots. Response surface analysis results showed that the chosen variables had important correlation with the degradation of PAM in aqueous solution. The optimum conditions of heterogeneous Fenton process were determined to be pH of 4.80, 0.82 g L^{-1} catalyst and 20.64 mmol L^{-1} H_2O_2, under which the degradation ratio of PAM (initial concentration 1000 ppm) reached 95.68%. The adequacy of the model for predicting the optimum response values was verified by the experiment effectively. After five recycle, the Fe^{2+}–Al_2O_3 still maintain high catalysis activity.

Keywords: PAM; Heterogeneous Fenton; Response surface methodology

1. Introduction

Polyacrylamide (PAM) is a kind of linear water-soluble polymer. Based on its linear form, relatively high molecular weight and corresponding solubility, PAM is employed in a multitude of applications, such as water purification flocculants [1], soil-conditioning agents [2] and many biomedical applications [3]. In particular, it is extensively used to enhance oil recovery in tertiary oil extraction, called polymer flooding [4]. And recently, PAM is applied to coalbed methane developed as fracturing fluid [5]. In general, remarkable amounts of these polymers go through underground injection or discharge into the natural water body [6].

As a synthetic high polymer, PAM is absent in natural water. The discharge of sewage-containing PAM will not only change the physical and chemical properties of receiving waters, but also contribute to the chemical oxygen demand (COD), even though PAM is a safe material. Furthermore, the monomer acrylamide (acrylamide, AM) of PAM, who occurs naturally along with PAM degrading under some certain conditions, is neurotoxic [7,8]. Therefore, it is necessary to conduct studies on PAM degradation (or mineralization) effectively and rapidly.

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In recent years, researchers have made breakthroughs in treating PAM with a serials of methods [7,9–11]. Among them, Fenton agent has attracted attentions from many investigators [12–14]. It is sought after on account of rapid reaction, energy saving, simple operation and environment friendly, but, its shortcoming is also very obvious, narrow range of pH values, iron ion leaching, post-treatment of Fe-containing sludge [15,16]. For these reasons, heterogeneous Fenton can effectively overcome aforesaid deficiencies of traditional Fenton technique by employing solid catalyst fixed with iron ion or other catalytic ions [17–19].

The previous studies have demonstrated that, pH value, catalyst dosage, hydrogen peroxide (H_2O_2) dosage influence the reaction of heterogeneous Fenton more than other factors in existence of the same pollutant concentration [20–22]. In general case, such studies adopt conventional parameter optimization approach as follows: changing one variable each time while keeping all others invariable. This classical pattern is time consuming, labour and resources demanding and could not reflect the interactive effects of variables especially, which lead to process optimization results imprecision. As a solution, experimental design technique is suggested as a very useful tool. Response surface methodology (RSM), a coalition design technique of mathematical and statistical, can be used to evaluate, optimize the action process even in the presence of complex synergistic or antagonistic interactions between factors [23,24]. The most frequently-used design employed in RSM is the Box–Behnken design. Compared with other designs, Box–Behnken presents some advantages, i.e. requiring few experimental points for its application (three levels per factor) and high efficiency [25].

In the present paper, Box–Behnken design and RSM has been used to design experiments, build models and optimize the degradation of PAM by heterogeneous Fenton, in which Fe–Al_2O_3 as the catalyst. The impacts of three variables: pH value, catalyst dosage and H_2O_2 dosage were studied synchronously on a dependent variable, degradation of PAM. In addition, we expect this work could conduce to other researches, which their optimization method is single-factor test, to discover different aspects of heterogeneous Fenton process in PAM-containing effluents treatment practices.

2. Materials and methods

2.1. Chemicals

PAM (average molecular weight 3,000,000), ferrous sulphate ($FeSO_4·7H_2O$), activated alumina (γ-Al_2O_3), sodium acetate trihydrate ($C_2H_3NaO_2·3H_2O$), aluminium sulphate octadecahydrate ($Al_2(SO_4)_3·18H_2O$), acetic acid ($C_2H_4O_2$), bromine (Br), sodium formate ($CHNaO_2$), amylum ($(C_6H_{10}O_5)_n$), cadmium iodide (CdI_2), obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH) and titanium potassium oxalate ($K_2TiO(C_2O_4)_2$), anhydrous sodium acetate ($C_2H_3NaO_2$), purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. sulphuric acid (H_2SO_4), silver sulphate (Ag_2SO_4), mercury sulphate ($HgSO_4$), potassium dichromate ($K_2Cr_2O_7$), ammonium ferrous sulphate ($(NH_4)_2Fe(SO_4)_2•6H_2O$), potassium acid phthalate ($KC_6H_5O_4$), 1,10-phenanathroline monohydrate, Hydrogen peroxide (H_2O_2, 30%, w/w) procured from Shanghai Suyi Chemical Reagent Co., Ltd, and deionized water was used for all solutions preparation.

2.2. Preparation of the catalyst

Catalyst was synthesized using the modified version of Hu and Muthukumari [16,26]. Twenty grams of γ-Al_2O_3 was added to a certain amount of dilute sulphuric acid solution (25%), keeping stirring for 24 h, after that, cleaned, dried and set aside, which aims to clean up the surface impurity of γ-Al_2O_3. Then, 2.5 g of worked γ-Al_2O_3 and required concentration (4,000 ppm, measured in [Fe^{2+}]) $FeSO_4·7H_2O$ were added to 500 mL ethanol/water mixture (60:40). The suspension was stirred for 24 h under 300 rpm with adjustment the pH value to 4, and afterwards, resulting suspended solids was filtered, dried at 110℃ for 6 h, and then calcined at 550℃ for 5 h in a muffle furnace, the Fe–Al_2O_3 catalysts were obtained.

2.3. Degradation of PAM by Fenton

The experiments were carried out in a batch reactor, which was made of borosil glass becherglas. In each batch, a magnetic stirrer was placed in 0.5 L of PAM solution with a certain concentration, for the maximum PAM content being 682.5 mg L^{-1} in the wastewater samples taken from Daqing oilfield, and also previous studies [10,15,27–29] mainly focusing on degradation of low concentration PAM, the level of model PAM solution used in this study was defined 1,000 mg L^{-1}. The dosages of Fe-Al_2O_3 catalyst at 0.25, 0.35, 0.5, 0.65, 0.75, 0.85 and 1 g L^{-1}, the initial pH values of reaction solution at 3, 4, 5, 6, 7, 8.35 (original pH value of PAM solution), and 10, the different concentrations of H_2O_2 at 15, 20, 25, 35, 50, 70 and 100 were added, respectively, and the suspension was stirred for 30 min. In reaction process, at the point 5, 10, 20, 30 min, successively, 10 mL reacting solution was pipetted for PAM residue measure. The percentage of PAM degradation efficiency ($\mathrm{DE_{PAM}}\%$) was calculated using the following formula:

$$\mathrm{DE_{PAM}}\ (\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

where C_0 and C_t represent the initial and remaining PAM concentrations at given time t, respectively.

2.4. Experimental design and statistical analysis

The three-level, three-factorial Box–Behnken experimental design was employed to investigate and validate the process parameters that affect the removal of PAM under the heterogeneous Fenton process. The design constituted by a total of 17 runs, including 12 factorial experiments and 5 replications at the centre point. On the basis of summarizing other research results and preliminary experiments, pH value, catalyst dosage and H_2O_2 dosage were selected as independent variables, which were labelled as X_1, X_2 and X_3, respectively, for the purpose of statistical computations and PAM degradation (Y) was considered as the dependent variable (response). Three levels of independent variable, (low, central and high, being designated as −1, 0 and +1), were assignment limited to the results of preliminary experiments. The experimental design matrix was generated with the help of the Design Expert 8.0.5 Trial software, and homologous experiments were implemented in duplicate. Data from the Box–Behnken design could be simply related by multiple regressions to fit linear or quadratic models. The most commonly used second-order polynomial equation can be written as follows:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j}^{k} \beta_{ij} X_i X_j + \varepsilon \tag{2}$$

where Y represents the predicted response, β_0 is the intercept parameter, β_i, β_i, β_{ij} is the linear coefficient, quadratic coefficient and interaction coefficient, distinguished. X_i X_j are the evaluated factors, k is the number of factors. ε, the random error. The results were analysed by applying the coefficient of determination (R^2), response plots and analysis of variance (ANOVA).

2.5. Analytical method

PAM concentration was measured by starch-cadmium iodide method [30], $\mathrm{COD_{Cr}}$ was determined with a potassium dichromate method base on ISO 6060–1989, colorimetric determination of iron concentration was performed with 1,10-phenanathroline monohydrate according to ISO 6332–1988. Hydrogen peroxide was analysed by a spectrophotometric method using titanium potassium oxalate [31].

3. Results and discussion

3.1. Preliminary experiments

Preliminary experiments were conducted following single-factor test method to determine the most influential experimental parameters affecting the Fenton degradation of PAM and to find out their ranges. The effect of initial pH on the Fe^{2+}–Al_2O_3 degradation efficiency of PAM was investigated and the results are shown in Fig. 1. It was observed that the increase in pH from 3 to 5 improves the extent of PAM dislodge, while the removal rate decreased with increase in pH from 5 to 10 yet. The possible reasons are as follows: the hydroxyl radical (HO·), pivotal active group of Fenton system, generate inversely with consistence of OH^- in liquor, so elevation of pH would restrain generation of HO·, in addition, H_2O_2 is labile thus to be effective at high-pH condition. On the other side, H_2O_2 being situated in low-pH circumstance would capture a proton to create H_3O^+, which is adverse to the repercussion H_2O_2 on catalyst, and that scavenging effect of hydrogen ion (H^+) to HO· could intensified at low pH, as indicated in the equation listed below:

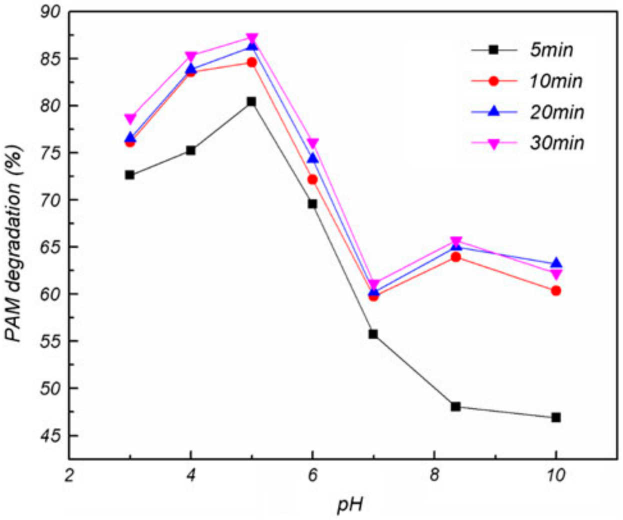

Fig. 1. Effect of initial pH for PAM degradation: PAM = 1,000 ppm, catalyst suspended = 0.65 g L^{-1}, H_2O_2 = 25 mmol L^{-1}, time: 5, 10, 20, 30 min.

$$HO^{\cdot} + H^+ + e^- \rightarrow H_2O \qquad (3)$$

The elimination of PAM with Fe^{2+}–Al_2O_3 at different H_2O_2 dosages was also studied. Fig. 2 displays removal efficiency of PAM with catalyst addition 0.65 g L^{-1} and the initial pH 5. It can be seen the efficiency of PAM degradation present to rise first and then fall along with increase in H_2O_2 dosages. It maybe because H_2O_2 contribute to productivity of HO·, which play the decisive role in the Fenton oxidation process. Low dosing of H_2O_2 create fewer HO· than system reacting required, but to excess, not only H_2O_2 itself would consume HO· hence decrease in removal efficiency but also hydroxyl radicals generated at high concentration dimerized to water, oxygen abiding by Eqs. (4–6) [32,33].

$$H_2O_2 + HO^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \qquad (4)$$

$$2HO^{\cdot} + 2HO^{\cdot} \rightarrow 2H_2O + O_2 \qquad (5)$$

$$HO_2^{\cdot} + HO^{\cdot} \rightarrow H_2O + O_2 \qquad (6)$$

In addition to initial pH and H_2O_2 consumption, catalyst dosage is another important factor for PAM degradation. Fe^{2+}–Al_2O_3 additions between 0.25 and 1.0 g L^{-1} with H_2O_2 concentration 25 mmol L^{-1}, initial PAM concentrations of 1000 ppm, and initial pH value 5 are investigated and represented in Fig. 3. Accompanying increment of Fe^{2+}–Al_2O_3 input from 0.25 g L^{-1} up to 0.75 g L^{-1}, removal ratio of PAM rises to 95.5% maximum, which indicated increase in catalyst dosage afford more active sites to expedite Fenton reaction. However, further added catalyst to 1 g L^{-1}, removal ratio dropped to 70% approximately, it maybe the interperturbance of catalyst particles and scavenging of HO· by excess iron species through reaction (7) [34].

$$HO^{\cdot} + Fe(II) \rightarrow OH^- + Fe(III) \qquad (7)$$

3.2. Statistical analysis

According to the preliminary experiments, the range and levels used in the experiments are selected and listed in Table 1. The design used for forecast and the responses observed in reality are depicted in Table 2, based on which, polynomial regression modelling was operated between the dependent variable and the three different independent variables. The results obtained were then analysed by ANOVA to estimate the "coincidence level". As shown in Table 3, the models of *F*-values are 23.24 and the corresponding *p*-values are 0.0002. This implies that the model is significant. There is only a 0.02% chance that a "Model *F*-value" this large could occur due to noise. The lack of fit (LOF) *F*-values of 0.17 was not

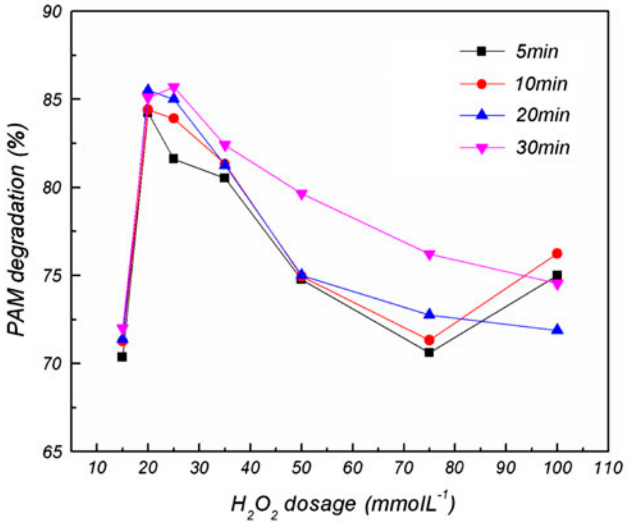

Fig. 2. Effect of H_2O_2 dosage for PAM degradation: PAM = 1,000 ppm, catalyst suspended = 0.65 g L^{-1}, initial pH = 5, time:5, 10, 20, 30 min.

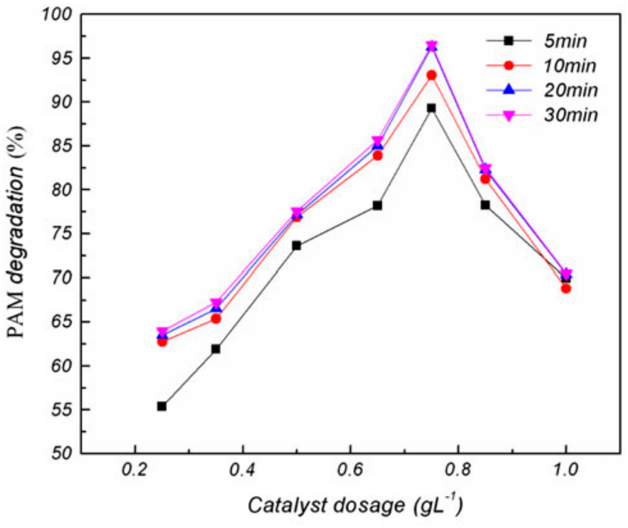

Fig. 3. Effect of catalyst dosage for PAM degradation: PAM = 1,000 ppm, H_2O_2 = 25 mmol L^{-1}, initial pH = 5, time:5, 10, 20, 30 min.

Table 1
Experimental range and levels of independent process variables

Independent variables	Symbol	Unit	Real values of coded levels		
			−1	0	+1
pH value	X_1	Dimensionless	4	5	6
Catalyst dosage	X_2	g L^{-1}	0.65	0.75	0.85
H_2O_2 dosage	X_3	mmol L^{-1}	15	20	25

Table 2
Experimental design for removal of PAM and results response

Run	pH value X_1	Catalyst dosage X_2(g L^{-1})	H_2O_2 dosage X_3(mmol L^{-1})	Degradation PAM (%)	
				Actual	Predicted
1	4.00	0.65	20	76.9418	77.01
2	6.00	0.65	20	70.726	71.79
3	4.00	0.85	20	92.4648	91.40
4	6.00	0.85	20	90.0838	90.01
5	4.00	0.75	15	75.2703	75.60
6	6.00	0.75	15	78.8497	78.19
7	4.00	0.75	25	87.91	88.57
8	6.00	0.75	25	79.69	79.36
9	5.00	0.65	15	65.76	65.35
10	5.00	0.85	15	86.9847	87.71
11	5.00	0.65	25	79.1932	78.47
12	5.00	0.85	25	88.3156	88.72
13	5.00	0.75	20	89.3136	93.19
14	5.00	0.75	20	95.7597	93.19
15	5.00	0.75	20	93.7419	93.19
16	5.00	0.75	20	90.8758	93.19
17	5.00	0.75	20	95.2391	93.19

significant as the p-value was 0.9129. The LOF F-values describes the variation of the data around the fitted model. Non-significant LOF is good for a model to be successfully used to predict. The coefficient of determination is used as a measure of degree of compliance of the model. In this case, the independent variables of the quadratic polynomial model catalyst dosage (X_2), and H_2O_2 dosage (X_3), the interaction between pH (X_1) and X_3, X_1X_3, the interaction between X_2 and X_3, X_2X_3, quadratic terms X_1^2, X_2^2 and X_3^2 are quite significant for the p-value is lower than 0.05. Judging by the F-values of the items in the regression model, the order in which the independent variables influence the degradation of PAM was, catalyst dosage (X_2) > H_2O_2 dosage (X_3) > initial pH (X_1). F-values greater than 0.1 indicated the model items are not significant, to modify regression model accuracy, the ultimate model equation in terms of coded factors after excluding the insignificant items [35,36] was obtained as follows:

Table 3
Analysis of variance regression model for PAM degradation by using Fenton process

Source	Sum of squares	df	Mean square	F value	p-value prob > F
Model	1265.77	9	140.64	23.24	0.0002
X_1	21.90	1	21.90	3.62	0.0988
X_2	531.83	1	531.83	87.89	<0.0001
X_3	99.72	1	99.72	16.48	0.0048
X_1X_2	3.68	1	3.68	0.61	0.4613
X_1X_3	34.81	1	34.81	5.75	0.0476
X_2X_3	36.62	1	36.62	6.05	0.0435
X_1^2	110.92	1	110.92	18.33	0.0036
X_2^2	127.33	1	127.33	21.04	0.0025
X_3^2	244.70	1	244.70	40.44	0.0004
Residual	42.36	7	6.05		
Lack of fit	4.73	3	1.58	0.17	0.9129
Pure error	37.63	4	9.41		
Cor. total	1308.13	16			

$$\begin{aligned}\text{Degradation PAM} = {} & +93.19 - 1.65X_1 + 8.15X_2 + 3.53X_3 \\ & - 2.95X_1X_3 - 3.03X_2X_3 - 5.13X_1^2 \\ & - 5.50X_2^2 - 7.62X_3^2 \qquad (8)\end{aligned}$$

In terms of actual factors, an empirical relationship has been expressed by the following quadratic equation:

$$\begin{aligned}\text{Degradation PAM} = {} & -683.20229 + 61.47120X_1 \\ & + 1027.44875X_2 + 20.39171X_3 \\ & - 0.58997X_1X_3 - 6.05115X_2X_3 \\ & - 5.13265X_1^2 - 549.92725X_2^2 \\ & - 0.30493X_3^2 \qquad (9)\end{aligned}$$

This model can be used to predict the removal of PAM within the restriction of experimental discussion. The coincidence level of the model was checked by the R^2 and adjusted R^2 then, both of them should be at least 0.80 for a preferable fit of a model [37] and approximate to one is desired. For this study, the values were 0.9648 and 0.9296, respectively, which means that predicted and actual degradation PAM efficiencies are accordance to a great extent. Moreover, the adjusted R^2 is closed to R^2, indicating that the sample size in this study and the number of terms in the model are rational and adequate. An adequate precision is a signal-to-noise ratio. It compares the range of the predicted values at the design points to the average prediction error. Ratios greater than four indicate adequate model discrimination [35,38]. The AP values obtained for the models of degradation PAM is 15.946, which demonstrates once again that the models could be used in predicting degradation PAM. Fig. 4(a) shows us the relationship of predicted value and experimental value. It manifests that the prediction model correspond to the experimental data in a specific range, and evident from its predict R^2 0.9067, the prediction of the destination object was quite satisfactory.

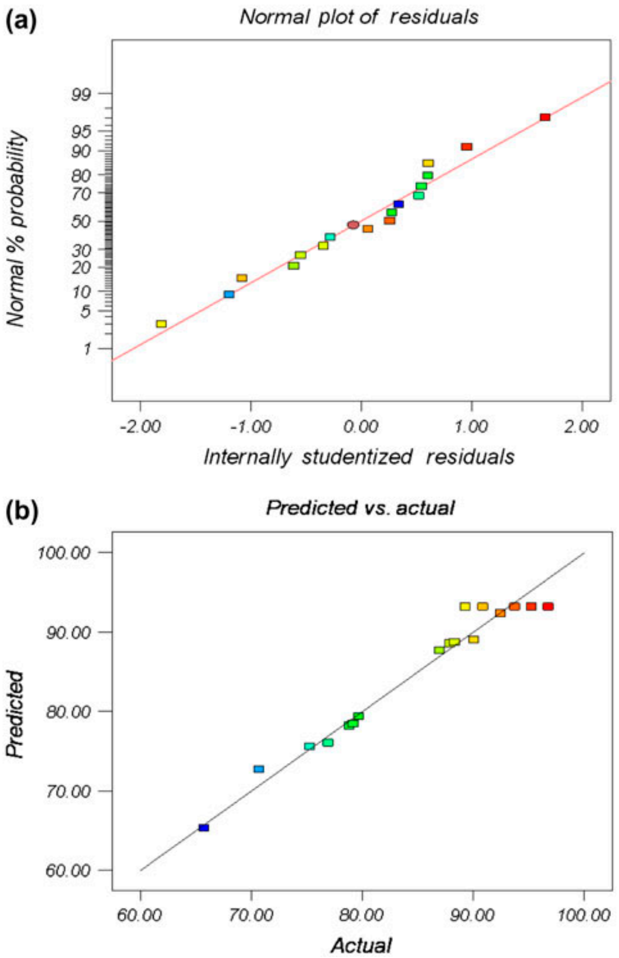

Fig. 4. Relationship of predicted and actual value (a) and residuals plots for the BBD (b).

The normality test of the data can be run with the plots of residuals, which are an important diagnostic method to detect the homogeneity of variance, normal distribution and mutual independence of random errors. It is observed from the normal probability plot of the residuals shown in Fig. 4(b) that the points on the plot follow a straight line, demonstrating the correctness of normality hypothesis [39,40].

3.3. Interactive effect of process independent variables

To realize the interactive impact of any two factors on the degradation PAM within the experimental ranges, the surface response and contour plots were constructed in this section.

Three-dimensional and contour plots of the interaction of pH and catalyst dose on PAM removal efficiency are present in Fig. 5, with keeping constant H_2O_2 dose at 20 mmol L^{-1}. It is seen from Fig. 5(a) that at low value, about <0.75 g L^{-1}, the positive influence of catalyst dose on PAM removal efficiency is significant, while in case of the catalyst dose being above 0.75 g L^{-1}, the percentage of PAM removal will climb up 90 but no matter magnitude pH is, and that for a definite amount of catalyst, an optimum pH value exists around five. We deem the removal rate of PAM rise along with increase catalyst dosage roughly without regard to other operation condition as evident from Fig. 5(b).

In Fig. 6, the response curve and isogram are drawn as a function of H_2O_2 dose and pH value. Fig. 6(b) shows there is one site maximizing the degradation PAM with catalyst addition maintaining at 0.75 g L^{-1}. As seen from Fig. 6(a), in order to achieve satisfied removal efficiencies (>90%), the selected region being pH 4.0–5.5 and H_2O_2 dose 18–25 mmol L^{-1}. Furthermore, the importance of H_2O_2 dose appears relatively when pH value less than 5.5, the PAM removal rise from 80% corresponding increasing quantities of H_2O_2. Once pH leap up 5.5, adjustment of H_2O_2 transfusion in this investigate range is barely to gain high level removal ratio of PAM.

The effect of catalyst dose and H_2O_2 dose on PAM removal efficiency at constant pH of 5 is illustrated in Fig. 7. These two figures clearly display the PAM removal rate increase with the enhancement in both catalyst dose and H_2O_2 dose, and then remain almost invariant, above 90%. The H_2O_2 impact PAM removal percentage relatively insignificantly meanwhile the catalyst dose lies in extent 0.72–0.85 g L^{-1}.

3.4. Optimization and model validation

It is meaningful to seek the optimal conditions to maximize PAM degradation within defined

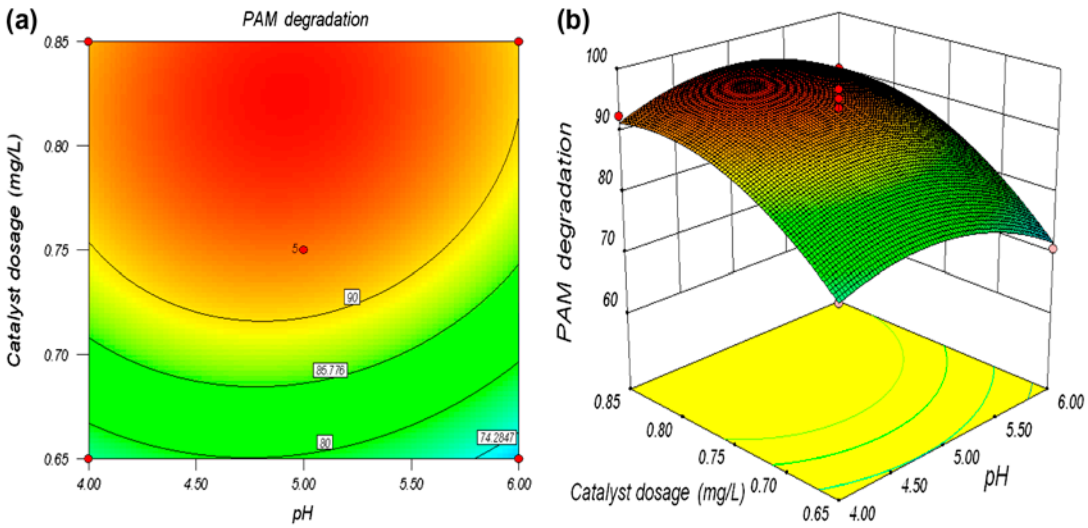

Fig. 5. Effects of catalytic dosage and pH on PAM degradation, H_2O_2 dose = 20 mmol L^{-1}.

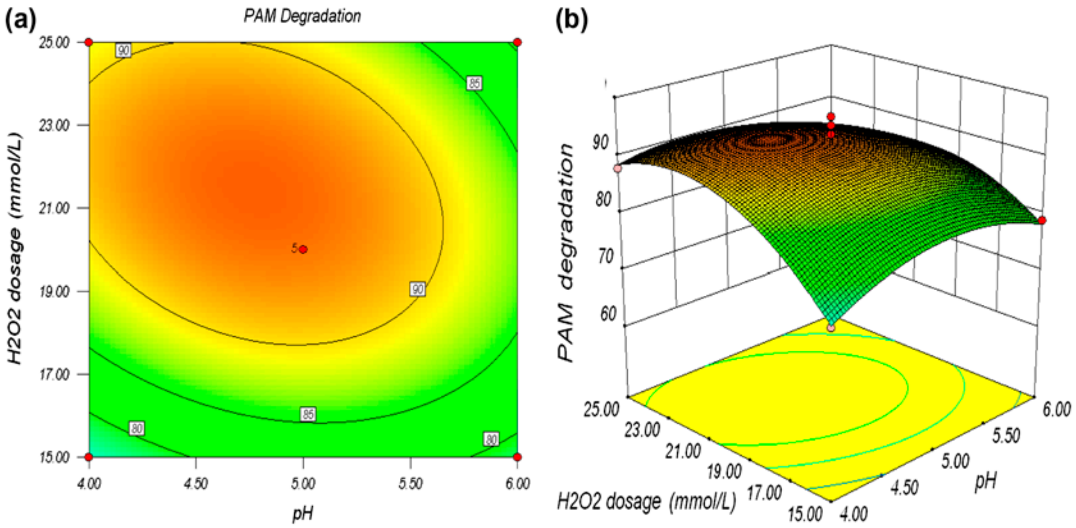

Fig. 6. Effects of H_2O_2 dosage and pH on PAM degradation, catalyst dose = 0.75 g L^{-1}.

experimental range using appropriate mathematical model. Operating the Design Expert software optimization choices, keeping the goal selection of each arguments (pH value, catalyst dosage, and H_2O_2 dosage) "in range", response (degradation PAM) being "maximize" meanwhile to obtain the optimal conditions for degradation PAM using heterogeneous Fenton in batch process, which reveal as follow: initial pH of 4.80, catalyst dose of 0.82 g L^{-1} and H_2O_2 dose of 20.64 mmol L^{-1}. At these conditions, 96.4561% removal was calculated by the regression equation (7), and then the result was tested and verified experimentally (95.98% PAM degradation), which was very close to the predicted value.

3.5. Catalyst stability and reusability

The stability and reusability of Fe^{2+}/Al_2O_3 were performed at the above-optimized conditions, i.e. PAM solution of 1,000 mg L^{-1} (COD_{Cr} was 873 mg L^{-1}), initial pH of 4.80, catalyst addition of 0.82 g L^{-1} and H_2O_2 dose of 20.64 mmol L^{-1}. The catalyst was separated by filtration and then rinsed by deionized water for three times and dried at 110°C for 12 h before the next batch experiment. Fig. 8 displays the degradation efficiency of PAM, the removal of COD_{Cr} and leaching of iron ions in five consecutive runs. It can be seen both PAM and COD_{Cr} removal efficiency reduce slightly during five successive runs, the reason for this

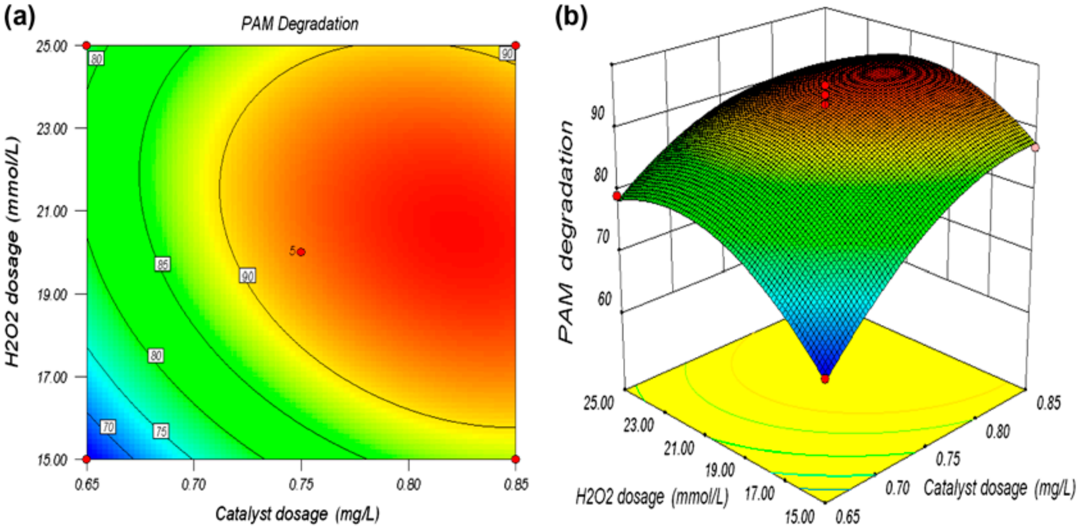

Fig. 7. Effects of H_2O_2 dosage and catalyst dosage on PAM degradation, pH = 5.

profile may was the loss of iron from the catalyst surface [41], or poisoning of catalyst for adsorbing organic species [42]. Lower removal rate of COD_{Cr} compared with PAM may be due to the formation of intermediates of propionamide and acetamide. In addition, as shown in Fig. 8, in all of the runs, the leaching of iron ions remained below 1 mg L^{-1}, the high catalyst stability could be ascribed to employ at higher pH [43] and proper calcination [44]. It should be noticed, after five times reuse, nearly 90% of PAM and 85% of COD_{Cr} could be removal steadily, with the residual 113 and 146 mg L^{-1}, respectively, which were exceeding the limit established by specific industry organization in China, including SY/T 5329–2012 and GB 20426–2006. Considering the synthetic solution contained more amount than actual effluent, laboratory finding was acceptable.

3.6. Changes of pH with reaction time

The change of pH value in reaction process were investigated with PAM concentration of 1,000 ppm, catalyst dose of 0.5 g L^{-1}, H_2O_2 dose of 25 mmol L^{-1} and initial pH value of 3, 5, 7, 8.35, the result was graphed to Fig. 9. It is obvious that at the initial stage, the pH value varied fast and then, after 20 min,

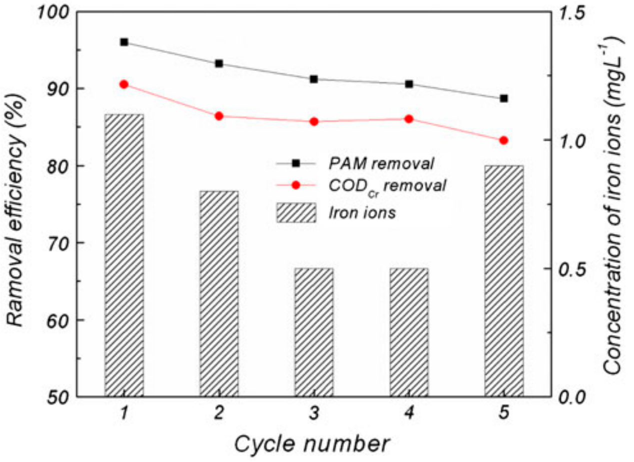

Fig. 8. Removal efficiency of PAM and COD_{Cr}, leaching iron ion in recycle experiment.

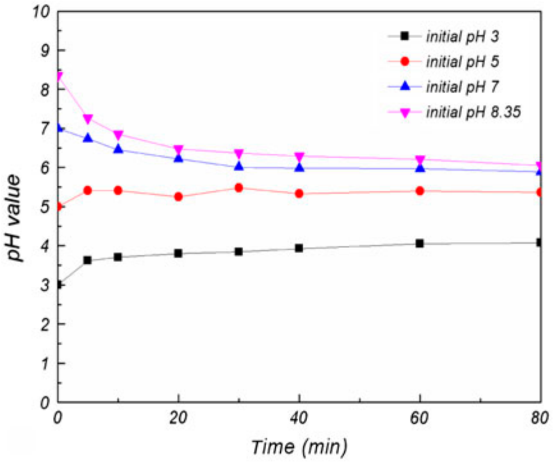

Fig. 9. pH variation over reaction time.

swings between 4 and 6 slightly, which explained partly the influence of pH value on PAM removal was smallest among three factors we chose, this verdict is slightly different from homogeneous Fenton process. We inferred that heterogeneous Fenton system was relaxed in pH, for another, the accumulation of degradation products, designating, acetic acid and ammonium acetate, which two buffer pH situating 3.757–5.757.

4. Conclusions

The effects of three variables: pH value, catalyst dose and H_2O_2 dose on the PAM degradation with heterogeneous Fenton using Fe^{2+}–Al_2O_3 catalyst were studied by conducting Box–Behnken experimental design and RSM. The results displayed in the present study revealed that the response surface model developed for predicting PAM removal efficiency was sufficiently adaptive, as confirmed by a high coefficient of determination value R^2 of 0.9648.

The optimum conditions calculated by the modificatory regression equation and RSM were 4.80 pH value, 0.82 g L^{-1} catalyst and 20.64 mmol L^{-1} H_2O_2, at the point, 95.68% removal ratio achieves, which fitted well to the predicted value.

In all five consecutive runs, the Fe^{2+}–Al_2O_3 catalyst is good activity.

The outcomes of this research indicated that heterogeneous Fenton had great possibilities to degrade the polymer-bearing effluents.

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References

[1] J. Ji, J. Qiu, N. Wai, Influence of organic and inorganic flocculants on physical-chemical properties of biomass and membrane-fouling rate, Water Res. 44 (2010) 1627–1635.

[2] K. Yang, Z. Tang, Effectiveness of fly ash and polyacrylamide as a sand-fixing agent for wind erosion control, Water Air Soil Pollut. 223 (2012) 4065–4074.

[3] N. Dave, M.Y. Chan, P.J. Huang, Regenerable DNA-functionalized hydrogels for ultrasensitive, instrument-free mercury(II) detection and removal in water, J. Am. Chem. Soc. 132 (2010) 12668–12673.

[4] M. Wu, S.F. Deng, F.L. Wei, Q.B. Wang, Y.K. Li, Polyacrylamide synthesis technology and its application in oil field development, Adv. Fine Petrochem. 12 (2011) 1–4 (in Chinese).

[5] H. Zhao, C.L. Dai, L. Liang, X. Wang, F.L. Zhao, Research on nonionic polyacrylamide zirconium gel fracturing fluids in coalbed methane gas wells, Pet. Drill. Tech. 40 (2012) 64–68 (in Chinese).

[6] Q.X. Wen, Z.Q. Chen, Y. Zhao, H.C. Zhang, Y.J. Feng, Performance and microbial characteristics of bioaugmentation systems for polyacrylamide degradation, J. Polym. Environ. 19 (2011) 125–132.

[7] M.J. Caulfield, X.J. Hao, G.G. Qiao, D.H. Solomon, Degradation on polyacrylamides. Part I. Linear polyacrylamide, Polymer 44 (2003) 1331–1337.

[8] R.W. Tyl, M.A. Friedman, Effects of acrylamide on rodent reproductive performance, Reprod. Toxicol. 17 (2003) 1–13.

[9] M.T. Bao, Q.G. Chen, Y.M. Li, G.C. Jiang, Biodegradation of partially hydrolyzed polyacrylamide by bacteria isolated from production water after polymer flooding in an oil field, J. Hazard. Mater. 184 (2010) 105–110.

[10] S.P. Vijayalakshmi, G. Madras, Photocatalytic degradation of poly (ethylene oxide) and polyacrylamide, J. Appl. Polym. Sci. 100 (2006) 3997–4003.

[11] Y.Q. Zhang, B.Y. Gao, L. Lu, B.C. Cao, Effect of produced wastewater from polymer flooding in Shengli oilfield treated by the coagulation method, J. Shandong Univ. (Eng. Sci.) 40 (2010) 98–102 (in Chinese).

[12] J.L. Wang, L.J. Xu, Advanced oxidation processes for wastewater treatment: Formation of hydroxyl radical and application, Crit. Rev. Env. Sci. Technol. 42 (2011) 251–325.

[13] J. Wang, Z.F. Yang, Application of Fenton oxidation technology in wastewater, Environ. Sci. Technol. 34 (2011) 104–108 (in Chinese).

[14] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Env. Sci. Technol. 36 (2006) 1–84.

[15] T. Liu, H. You, Q.W. Chen, Heterogeneous photo-Fenton degradation of polyacrylamide in aqueous solution over Fe(III)–SiO_2 catalyst, J. Hazard. Mater. 162 (2009) 860–865.

[16] Y. Hu, S.X. Lv, Y.L. Qiu, Effect of preparation process for Fe_2O_3/Al_2O_3 catalyst on the catalytic activity for degradation of wastewater containing polyacrylamide, J. Tianjin Univ. Sci. Technol. 25 (2010) 39–42 (in Chinese).

[17] E.G. Garrido-Ramirez, B. Theng, M.L. Mora, Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions—A review, Appl. Clay Sci. 47 (2010) 182–192.

[18] S. Navalon, M. Alvaro, H. Garcia, Heterogeneous Fenton catalysts based on clays, silicas and zeolites, Appl. Catal., B 99 (2010) 1–26.

[19] A.N. Soon, B.H. Hameed, Heterogeneous catalytic treatment of synthetic dyes in aqueous media using Fenton and photo-assisted Fenton process, Desalination 269 (2011) 1–16.

[20] J.H. Ramirez, F.J. Maldonado-Hodar, A.F. Perez-Cadenas, C. Moreno-Castilla, C.A. Costa, L.M. Madeira, Azo-dye orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts, Appl. Catal., B 75 (2007) 312–323.

[21] X.L. Liang, Y.H. Zhong, S.Y. Zhu, J.X. Zhu, P. Yuan, H.P. He, J. Zhang, The decolorization of acid orange II

in non-homogeneous Fenton reaction catalyzed by natural vanadium-titanium magnetite, J. Hazard. Mater. 181 (2010) 112–120.

[22] S. Shafieiyoun, T. Ebadi, M. Nikazar, Treatment of landfill leachate by Fenton process with nano sized zero valent iron particles, Int. J. Environ. Res. 6 (2012) 119–128.

[23] S. Chatterjee, A. Kumar, S. Basu, S. Dutta, Application of response surface methodology for Methylene Blue dye removal from aqueous solution using low cost adsorbent, Chem. Eng. J. 181 (2012) 289–299.

[24] B. Kayan, B. Gozmen, Degradation of acid red 274 using H_2O_2 in subcritical water: Application of response surface methodology, J. Hazard. Mater. 201 (2012) 100–106.

[25] G.E.P. Box, D.W. Behnken, Some new three level designs for the study of quantitative variables, Technometrics 2 (1960) 455–475.

[26] B. Muthukumari, K. Selvam, I. Muthuvel, M. Swaminathan, Photoassisted hetero-Fenton mineralisation of azo dyes by Fe(II)–Al_2O_3 catalyst, Chem. Eng. J. 153 (2009) 9–15.

[27] S. Deng, R. Bai, J.P. Chen, Z. Jiang, G. Yu, F. Zhou, Z. Chen, Produced water from polymer flooding process in crude oil extraction: Characterization and treatment by a novel crossflow oil—water separator, Sep. Purif. Technol. 29 (2002) 207–216.

[28] G.M. Ren, D.Z. Sun, J.S. Chung, Kinetics study on photochemical oxidation of polyacrylamide by ozone combined with hydrogen peroxide and ultraviolet radiation, J. Environ. Sci. (China) 18 (2006) 660–664.

[29] Q.X. Wen, Z.Q. Chen, Y. Zhao, H.C. Zhang, Y.J. Feng, Biodegradation of polyacrylamide by bacteria isolated from activated sludge and oil-contaminated soil, J. Hazard. Mater. 175 (2010) 955–959.

[30] M.W. Scoggins, J.W. Miller, Determination of water-soluble polymers containing primary amide groups using the starch-triiodide method, Old SPE Journal 19 (1979) 151–154.

[31] J. De Laat, H.E. Gallard, Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: Mechanism and kinetic modeling, Environ. Sci. Technol. 33 (1999) 2726–2732.

[32] M. Neamtu, C. Catrineseu, A. Kettrup, Effect of dealumination of iron(III)-exchanged Y zeolites on oxidation of Reactive Yellow 84 azo dye in the presence of hydrogen peroxide, Appl. Catal., B 51 (2004) 149–157.

[33] R. Andreozzi, V. Caprio, R. Marotta, Iron(III) (hydr) oxide-mediated photooxidation of 2-aminophenol in aqueous solution: A kinetic study, Water Res. 37 (2003) 3682–3688.

[34] L.J. Xu, J.L. Wang, Fenton-like degradation of 2,4-dichlorophenol using Fe_3O_4 magnetic nanoparticles, Appl. Catal., B 123 (2012) 117–126.

[35] H. Zhang, Y.L. Li, X.G. Wu, Statistical experiment design approach for the treatment of landfill leachate by photoelectro-Fenton process, J. Environ. Eng.Asce 138 (2012) 278–285.

[36] I. Arslan-Alaton, G. Tureli, T. Olmez-Hanci, Treatment of azo dye production wastewaters using photo-Fenton-like advanced oxidation processes: Optimization by response surface methodology, J. Photochem. Photobiol., A 202 (2009) 142–153.

[37] A.M. Joglekar, A.T. May, Product excellence through design of experiments. Cereal Foods World 32 (1987) 857–868.

[38] S. Ghafari, H.A. Aziz, M.H. Isa, A.A. Zinatizadeh, Application of response surface methodology (RSM) to optimize, coagulation-flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum, J. Hazard. Mater. 163 (2009) 650–656.

[39] H. Zhang, X.N. Ran, X.G. Wu, D.B. Zhang, Evaluation of electro-oxidation of biologically treated landfill leachate using response surface methodology, J. Hazard. Mater. 188 (2011) 261–268.

[40] S. Mohajeri, H.A. Aziz, M.H. Isa, M.A. Zahed, M.N. Adlan, Statistical optimization of process parameters for landfill leachate treatment using electro-Fenton technique, J. Hazard. Mater. 176 (2010) 749–758.

[41] H. Hassan, B.H. Hameed, Fe–clay as effective heterogeneous Fenton catalyst for the decolorization of Reactive Blue 4, Chem. Eng. J. 171 (2011) 912–918.

[42] J. Guo, M. Al-Dahhan, Activity and stability of iron-containing pillared clay catalysts for wet air oxidation of phenol, Appl. Catal., A 299 (2006) 175–184.

[43] J. Herney-Ramirez, M.A. Vicente, L.M. Madeira, Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review, Appl. Catal., B 98 (2010) 10–26.

[44] T. Luenloi, B. Chalermsinsuwan, T. Sreethawong, N. Hinchiranan, Photodegradation of phenol catalyzed by TiO_2 coated on acrylic sheets: Kinetics and factorial design analysis, Desalination 274 (2011) 192–199.