Parametric Studies on the Synthesis of Amidoximated Adsorbent Resins

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ABSTRACT: The main goal of this study was to obtain acrylonitrile (AN)-divinylbenzene (DVB) copolymer beads that can serve as the matrix for preparation of amidoxime resins. AN-DVB amidoxime resin was synthesized via suspension polymerization and the effect of different parameters such as the speed of stirrer, the amounts of suspending agent, hydrophilic agent, diluent agent, and initiator on its properties was investigated by fractional factorial (Taguchi) experimental design method. This method gives much-reduced variance for the experiments with optimum control parameters setting and provides a set of minimum experiments compared to the conventional methods. The results showed that the most effective parameters on the amidoximation of resins were hydrophilic agent content, speed of stirrer, and the amount of suspending agent, respectively. Furthermore, anion-exchange capacity of the amidoxime resins was utilized as a criterion for the evaluation of amidoxime adsorbent groups and the adsorption potential of the synthesized resins was determined by cation-exchange capacity. The amount of methylacrylate as a hydrophilic agent had the most significant effect on the ion-exchange capacity of the final product. Swelling ratio was also measured to evaluate the adsorption capacity of the synthesized resin. The results showed that the amounts of hydrophilic and diluent agents had significant effects on swelling ratio of resin. Finally, cation-exchange capacity and swelling ratio of amidoxime resin were changed greatly because of alkaline treatment, but it had no significant effect on the anion-exchange capacity of the synthesized resin. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: amidoxime resin; adsorption; suspension polymerization; ion exchange; swelling ratio

INTRODUCTION

There are many methods available to remove heavy metal ions from waters and wastewaters. Among these methods, ion exchange is the most simple and efficient one. Recently, fibrous and granular chelating adsorbents containing amidoxime groups have been used in adsorption processes, especially in adsorption of radioactive components from seawater.[1–14]

It has been shown in the previous studies that the chelating amidoxime resin prepared from acrylonitrile (AN)-divinylbenzene (DVB) (10 mol %)-methylacrylate (MA) exhibits higher adsorption ability in comparison with other granular resins.[1–3] It has also been reported that swelling ratio and ion-exchange capacity of amidoxime resins can be a criterion for the adsorption potential of synthesized resins.[15,16]

Amidoxime adsorbent resins are usually synthesized via suspension polymerization method.[1–7] For investigating the adsorption behavior of this kind of resins, the evaluation of numerous combinations of mono and di-functional monomers together with the hydrophilic monomer, initiator, diluent agent, presents a significant experimental challenge. Surprisingly, little attention has been given to the parametric study on the synthesis of amidoximated adsorbent resins. Therefore, owing to the high adsorption potential of these resins, detailed parametric studies in the synthesis of the AN-DVB-MA adsorbent resins are necessary.

Therefore, the main aim of this study was parametric study with more details on the properties of the synthesized amidoxime AN-DVB-MA resins. Hence, AN-DVB-MA amidoxime resins were synthesized via suspension polymerization and a fractional factorial (Taguchi) experimental design was employed to investigate the parametric effects on the amidoximation, ion-exchange capacity, and swelling behavior of the resin. Finally, the effect of alkaline treatment on the properties of the resin was investigated.

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TABLE I
Materials Used

Materials	Molecular formula	Function	Supplier
Acrylonitrile (AN)	C_3H_3N	Monomer	Merck
Divinylbenzene (DVB)	$C_{10}H_{10}$	Crosslinking agent	Merck
Methylacrylate (MA)	$C_4H_6O_2$	Hydrophilic agent	Merck
Tri-calcium phosphate (TCP)	$Ca_3(PO_4)_2$	Suspending agent	Merck
Benzoylperoxide (BPO)	$C_{14}H_{10}O_3$	Initiator	Merck
Toluene	C_7H_8	Diluent	Merck
Hydroxylamine	NH_2OH	Amidoximation agent	Merck
Methanol	CH_3OH	Media	Merck
Sodium hydroxide	NaOH	Titration and alkaline treatment	Merck
Hydrochloric acid	HCl	Titration	Merck
Silver nitrate	$AgNO_3$	Titration	Merck
Fluorscein	$C_{20}H_{12}O_5$	Indicator	Merck
Methyl orange	$C_{14}H_{14}N_3O_3SNa$	Indicator	Merck

EXPERIMENTAL

Materials

The materials used in this study are summarized in Table I.

Procedure

AN-DVB (10 mol %)-MA resin beads were synthesized via suspension polymerization in the presence of toluene and benzoylperoxide (BPO) as diluents and polymerization initiator, respectively. Polymerization was carried out in a glass reactor, immersed in a water bath at 80°C for 11 h. The product was filtered, washed with distilled water, and dried in a vacuum oven at 50°C for 96 h. Amidoxime groups were introduced to the synthesized resin by means of reaction with 3 vol % hydroxylamine solution in methanol/water in equal molar mixture (1:1) for 2 h at 80°C. For alkali treatment, the synthesized resin was treated with 0.1*M* NaOH solution at 30°C for 5 h.

Statistical survey of the resins synthesis

Experimental design is generally applied to determine the dependence of a target variable such as *N*-content, ion-exchange capacity, and swelling ratio on the rest of the variables. The effects of five variables at four levels (Table II) on the properties of the synthesized AN-DVB (10 mol %)-MA amidoxime resins were investigated.

To reduce the total number of experiments, a fractional factorial experimental design was employed. Taguchi developed a method for designing experiments to investigate how different parameters affect the mean and variance of a process performance characteristic that defines how well the process is functioning. The Taguchi statistical method involves reducing the variation in a process through robust design of experiments. This method is well suited to the study of a process that has many factors that need to be evaluated at several levels. By applying this technique, engineers, scientists, and researchers can significantly reduce the time required for experimental investigations.

An M_{16} (4^5) orthogonal array of experiments was chosen for the initial set of experiments (Table III). This M_{16} array can be used, in principle, to examine the effects of five variables at four levels on the target variables (i.e., *N*-content, ion-exchange capacity, and swelling ratio of the synthesized amidoxime resins) in only 16 experiments.

Characterization

To evaluate *N*-content of the synthesized resins, elemental analyses were performed on a CHNOS recorder instrument (Elementar Vario EL-III).

For the determination of the anion-exchange capacity, 0.5 g of the synthesized resin and 50 cm^3 of 0.1*M* HCl solution were shaken in a flask at 30°C for 15 h. The supernatant was titrated with 0.1*M* $AgNO_3$ solution in the presence of fluorescein as an

TABLE II
Different Levels of Variables Investigated

Variable	Level 1	Level 2	Level 3	Level 4
Speed of stirrer (rpm)	600	800	1000	1200
Suspending agent (wt %)	4	4.4	4.8	5.2
Hydrophilic agent (mol %)	0	15	30	45
Diluent (vol %)	60	90	120	150
Initiator (mmol/L of monomer)	60	80	100	120

TABLE III
M_{16} Orthogonal Array of Experiments

Exp. no.	Speed of stirrer	TCP	MA	Toluene	BPO
1	1	1	1	1	1
2	1	2	2	2	2
3	1	3	3	3	3
4	1	4	4	4	4
5	2	1	2	3	4
6	2	2	1	4	3
7	2	3	4	1	2
8	2	4	3	2	1
9	3	1	3	4	2
10	3	2	4	3	1
11	3	3	1	2	4
12	3	4	2	1	3
13	4	1	4	2	3
14	4	2	3	1	4
15	4	3	2	4	1
16	4	4	1	3	2

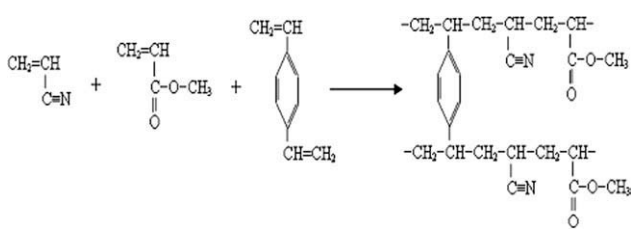
indicator to determine the concentration of Cl^- in the supernatant. The anion-exchange capacity of the synthesized resin was calculated by subtracting the amount of Cl^- in the initial solution from the amount in the supernatant.

For the determination of the cation-exchange capacity, 0.5 g of the synthesized resin and 50 cm^3 of 0.1*M* NaOH solution were shaken in a flask at 30°C for 15 h. The supernatant was titrated with 0.1*M* HCl solution in the presence of methyl orange as an indicator to determine the concentration of Na^+ in the supernatant. The cation-exchange capacity of the synthesized resin was calculated by subtracting the amount of Na^+ in the initial solution from the amount in the supernatant.

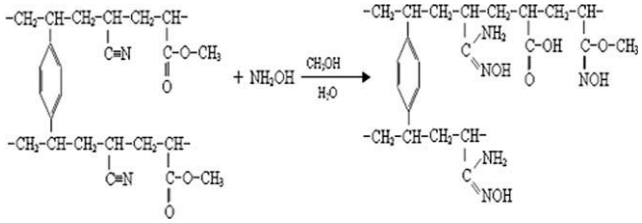
The swelling ratio of the synthesized resin was calculated as follows:

$$\text{Swelling ratio} = \frac{\text{Weight of wet resin}}{\text{Weight of dry resin}} \qquad (1)$$

For the determination of wet weight of the synthesized resin, 1.0 g of dry resin and 100 cm^3 of deionized water were shaken in a flask at 25°C for 24 h and then the weight of wet resin was measured.



Scheme 1 Schematic polymerization of AN-DVB-MA-synthesized resin.



Scheme 2 Schematic amidoximation reaction of the synthesized resin.

The porosity and pore size distribution of the dry resin was measured with mercury porosimetry (Pascal-140, Thermo Finnegan, Italy).

RESULTS AND DISCUSSION

Resins amidoximation

Polymerization of AN-DVB-MA resin and amidoximation of the synthesized resin are schematically shown in Schemes 1 and 2, respectively. As shown in Schemes 1 and 2, nitrile groups (C≡N) can convert to amidoxime groups after amidoximation of the resin beads. On the other hand, ester groups can be hydrolyzed to acidic groups such as hydroximic and carboxylic acid. Therefore, amidoximation of the synthesized resin was evaluated by *N*-content measurement.

Statistical analysis of the results using analysis of variance showed that the most affective parameters in the determination of the *N*-content of the synthesized resins were the amount of hydrophilic agent, speed of stirrer, and amount of suspending agent, respectively (Table IV).

Figure 1(a) shows the effect of methylacrylate (MA) on *N*-content of the synthesized resin after amidoximation. As shown in Figure 1(a), the effect of hydrophilic agent at low concentrations of MA is not considerable. However, at high amounts of MA, the *N*-content of the resin decreases dramatically by increasing hydrophilic agent content. This trend can be owing to the significant decrease of AN content of the resin.

Figure 1(b) shows the effect of stirrer speed on *N*-content of the synthesized resin after amidoximation. As shown in Figure 1(b), *N*-content of the synthesized resin decreases with an increase in the stirrer speed and reaches a minimum point at 800 rpm. Further increasing of stirrer speed results in an increase in *N*-content of the synthesized amidoxime resins. This trend can be explained by investigating porosity and particle size of resin beads.

Total porosity and pore size distribution of the synthesized beads were determined by mercury porosimetry (Fig. 2). It is clear that small dense particles were obtained at minimum point (800 rpm) at

TABLE IV
Statistical Analysis of *N*-Content Experimental Results

Variable	Degree of freedom	Sum of squares	Variance	Pure sum	Percent %
Speed of stirrer	3	14.922	4.974	14.922	18.634
Suspending agent	3	11.018	3.672	11.018	13.759
Hydrophilic agent	3	52.584	17.528	52.584	65.664
Diluent	3	1.110	0.370	1.110	1.386
Initiator	3	0.443	0.147	0.443	0.553
Total	15	80.080	–	–	100.000

which collision energy increases dramatically and overcomes to interfacial tension. Decreasing of porosity of resin beads results in a decrease of resin amidoximation, which is in a good agreement with *N*-content experimental results.

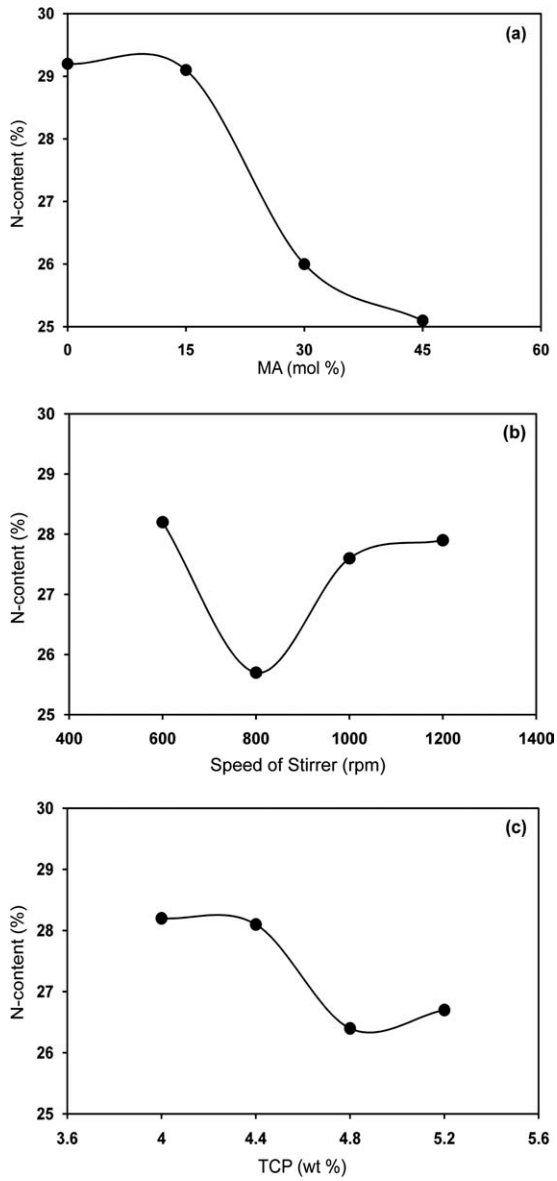


Figure 1 The main effects of (a) MA amount, (b) speed of stirrer, and (c) TCP amount on *N*-content of the synthesized resin.

As shown in Figure 1(c), by increasing of TCP amount, *N*-content of amidoxime resin decreases to reach a minimum and then increases slightly. As mentioned previously,[17] the effect of suspending agent on porosity and particle size of the synthesized resin beads is the same as speed of stirrer effect. Hence, the observed minimum point can be related to small particles with low porosity.

Ion-exchange capacity

Anion- and cation-exchange reactions are schematically shown in Schemes 3 and 4, respectively. As shown in Schemes 3 and 4, only amidoxime groups contribute to the anion-exchange reaction, whereas both acidic and amidoxime groups contribute to the cation-exchange reaction.

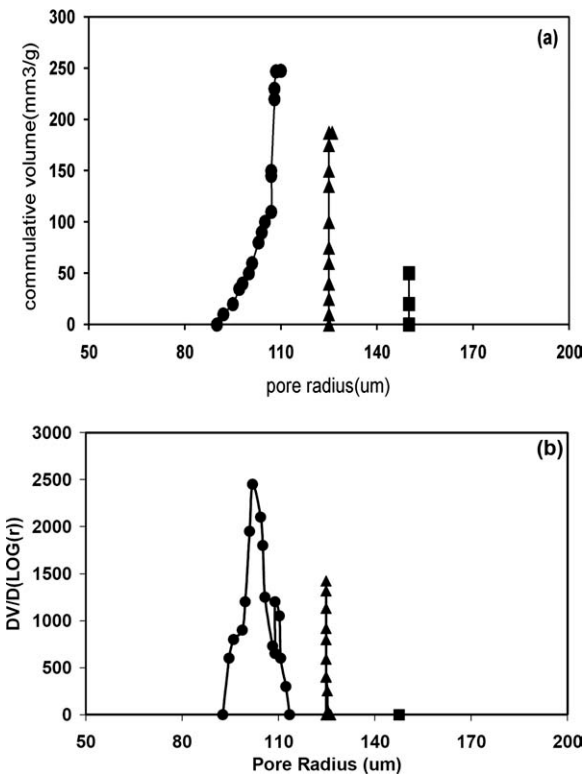
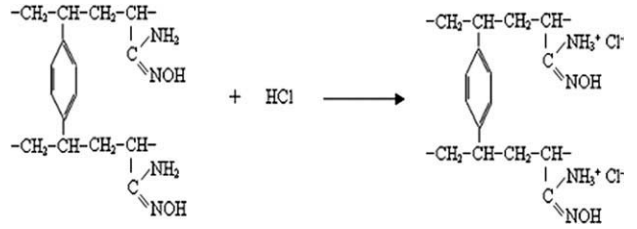
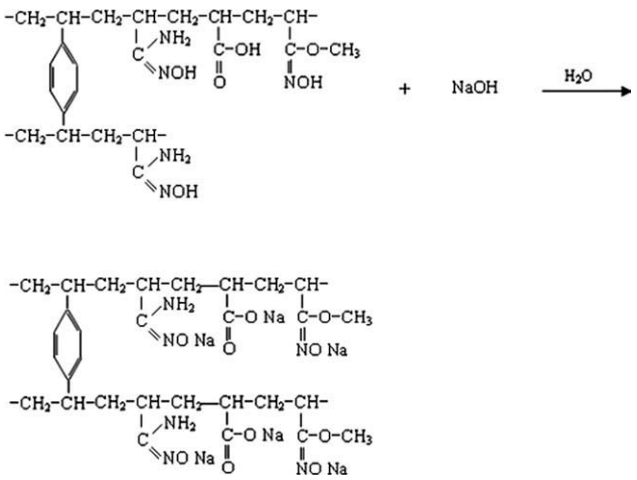


Figure 2 (a) Cumulative volume and (b) pore size distribution of the synthesized resin (▲) RPM: 600 TCP: 4 wt % porosity: 15.5%; (■) RPM: 800 TCP: 4.8 wt % porosity: 5%; and (●) RPM: 1200, TCP: 4 wt %, porosity: 19.8%.



Scheme 3 Schematic anion-exchange capacity of amidoxime resin.



Scheme 4 Schematic cation-exchange capacity of amidoxime resin.

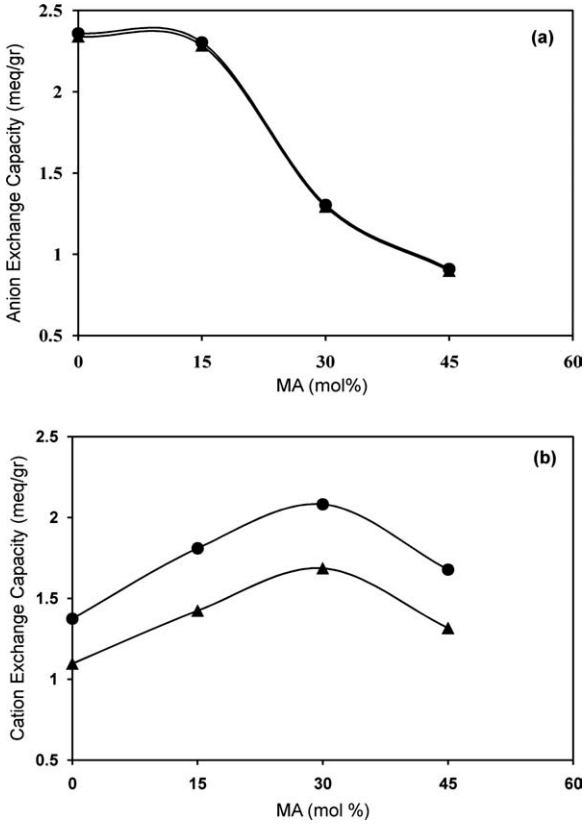


Figure 3 The main effects of MA on (a) anion- and (b) cation-exchange capacity (▲) nontreated resin and (●) alkaline-treated resin.

Statistical analysis of the ion-exchange capacity results revealed that only the effects of hydrophilic agent and diluent amounts on the anion- and cation-exchange capacity are significant (Table V), but the effect of hydrophilic agent (MA) is more significant than the latter.

As shown in Figure 3(a), by increasing of the amount of MA, anion-exchange capacity decreases. This can be attributed to a significant decrease of amidoxime groups by increasing MA. Furthermore, the anion-exchange capacity is not affected by alkaline treatment, because amidoxime groups are hardly hydrolyzed by a weak alkaline solution.[1–6] In addition, Figure 3(b) shows that the cation-exchange capacity increases with an increase of MA to reach a maximum point. Further increasing of MA amount resulted in a decrease in cation-exchange capacity of the synthesized amidoxime resin. This trend can be explained by decreasing of AN content and increasing of hydrophilicity in copolymer beads by the formation of hydroximic and carboxylic groups. The obtained results confirm the significant effect of alkaline treatment on the cation-exchange capacity of the synthesized resins.

Figure 4 shows a linear increasing of ion-exchange capacity of the synthesized resin by increasing of toluene volume percent. This behavior could be related to increasing porosity of amidoxime resin beads.

TABLE V
Statistical Analysis of Ion-Exchange Capacity Experimental Results

	Degree of freedom		Sum of squares		Variance		Percent %	
Variable	Anion Ex. Ca	Cation Ex. Ca	Anion Ex. Ca	Cation Ex. Ca	Anion Ex. Ca	Cation Ex. Ca	Anion Ex. Ca	Cation Ex. Ca
Speed of stirrer	3	3	0.932	0.128	0.310	0.042	0.455	0.400
Suspending agent	3	3	0.308	0.111	0.102	0.037	0.150	0.346
Hydrophilic agent	3	3	195.729	28.835	65.243	9.611	95.603	89.674
Diluent	3	3	7.367	2.536	2.455	0.845	3.598	7.887
Initiator	3	3	0.392	0.543	0.130	0.181	0.191	1.689
Total	15	15	204.730	204.730			100.000	100.000

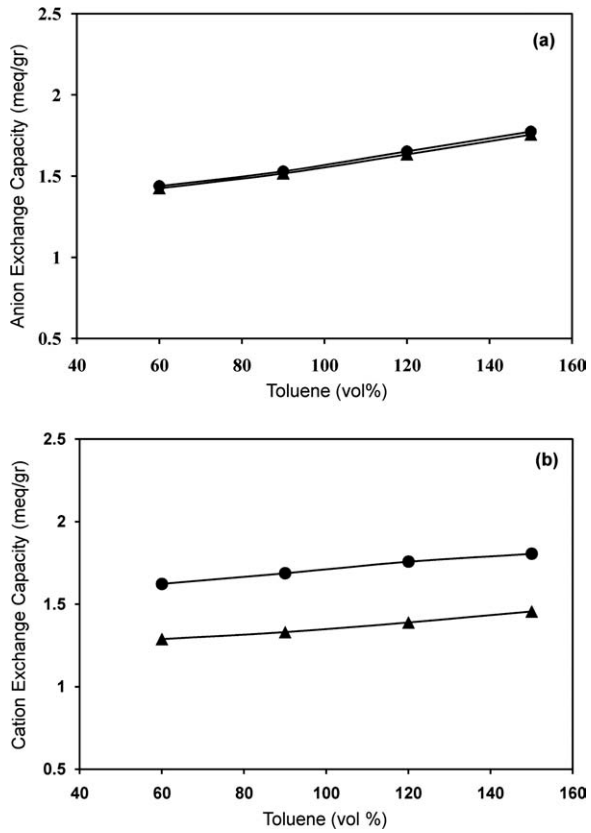


Figure 4 The main effects of toluene on (a) anion- and (b) cation-exchange capacity (▲) nontreated resin and (●) alkaline-treated resin.

Swelling behavior

Statistical analysis of the swelling results revealed that the effects of the investigated variables on the swelling ratio are significant (Table VI). Furthermore, the hydrophilic agent (MA) had the most appreciable effect on swelling ratio of the synthesized resin.

The effect of hydrophilic agent on swelling ratio is shown in Figure 5(a). By increasing MA content, the hydrophilicity and average polymer chain length between chemical crosslinking (junctions) increases significantly, this can result in increasing water uptake of the final polymeric network. Further increasing of MA resulted in a decrease in the swelling ratio of the synthesized resin, which can be owing to decrease of amidoxime content.

As shown in Figure 5(b), by increasing toluene amounts, swelling ratio of the synthesized resin increases to reach a maximum point owing to the pore-forming role of the diluent agents in the synthesis of polymeric resin via suspension polymerization method. However, swelling ratio decreases at higher contents of toluene. This trend can be related to the reverse effect of highly macroporous structures on the swelling ratio. Initiator amount showed the same effect as toluene content [Fig. 5(c)]. This trend can be related to decreasing of polymer chains length between chemical crosslinking at high contents of initiator. Further increasing of BPO amount can result in the synthesis of very short polymeric chains that cannot have strong role in the formation of polymeric networks. In addition, with increasing of stirrer speed and suspending agent amount, swelling ratio increases initially and then decreases [Fig. 5(d,e)]. This trend can be owing to the presence of copolymer beads with tiny size and high-specific surface area at the maximum point.

As shown in Figure 5, alkaline treatment increases the swelling ratio. This behavior can be owing to increasing of the synthesized resin hydrophilicity based on the formation of carboxylic and hydroximic groups.

CONCLUSION

The amidoxime adsorbent resin was synthesized via suspension polymerization. The effects of stirrer speed, suspending agent, hydrophilic agent diluent, and initiator amounts on the amidoximation, ion-exchange capacity, and swelling ratio of the synthesized resin were investigated by using fractional–factorial (Taguchi) experimental design method. The hydrophilic and suspending agents and speed of stirrer were found to be the most effective parameters on the amidoximation of the resin, whereas the effect of hydrophilic agent (MA) was more significant than the other variables. The trend of speed of stirrer and suspending agent effects on the amidoximation of the synthesized resin was confirmed by

TABLE VI
Statistical Analysis of Swelling Ratio Experimental Results

Variable	Degree of freedom	Sum of squares	Variance	Percent %
Speed of stirrer	3	0.091	0.030	4.438
Suspending agent	3	0.348	0.116	16.890
Hydrophilic agent	3	1.343	0.447	65.168
Diluent	3	0.165	0.055	8.021
Initiator	3	0.112	0.037	5.476
Total	15	2.062	–	100.000

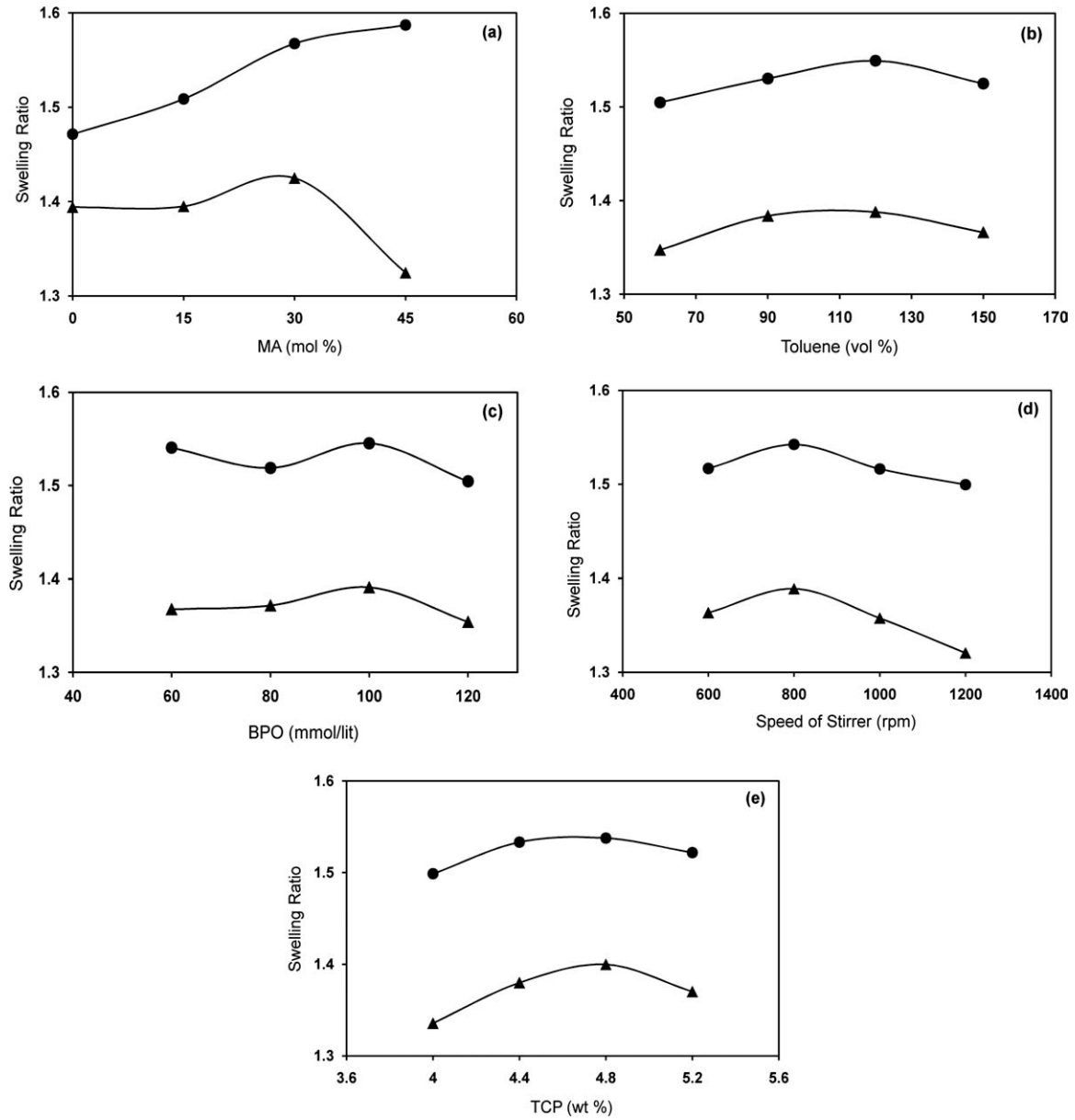


Figure 5 The main effects of (a) MA, (b) toluene, (c) BPO, (d) speed of stirrer, and (e) TCP on the swelling ratio (▲) nontreated resin and (●) alkaline-treated resin.

the measurement of porosity and pore size distribution of the resin beads.

It was found that the formation of hydroximic and carboxylic groups affected the ion-exchange capacity of amidoxime resin. The results showed that the amounts of hydrophilic and diluent agents have significant effects on the anion- and cation-exchange capacity of AN-DVB-MA adsorbent resins. In addition, the cation-exchange capacity of the synthesized resins was greatly enhanced because of alkaline treatment.

The statistical analysis of experimental results of swelling ratio showed that the hydrophilic agent has the most significant effect on the swelling ratio of the synthesized amidoxime resins. In addition, the swelling ratio of the resin was greatly enhanced because of alkaline treatment.

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