

γ -Radiation-Induced Preparation of Polyamidoxime Resins and Their Adsorption of Methyl Violet

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ABSTRACT: Poly(acrylic acid–amidoxime) [P(AA–AO)] and poly(maleic acid–amidoxime) [P(MA–AO)] resins were prepared by the γ -radiation-induced copolymerization of acrylonitrile with acrylic acid and maleic acid, respectively. The obtained resins were amidoximated by reaction with hydroxylamine. The prepared resins were used for the removal of methyl violet (MV) dye from aqueous solutions. Batch adsorption studies were made by the measurement of the effects of pH, the amount of adsorbent, the contact time, and the adsorbate concentration. The adsorption isotherm of MV onto P(AA–AO) and P(MA–AO) was determined at 25°C with initial MV dye concentrations of 10–70

mg/L. The equilibrium data were analyzed with the Langmuir and Freundlich isotherm models. The equilibrium process was described well by the Langmuir isotherm model with maximum adsorption capacities of 398.4 and 396.8 mg/L for P(AA–AO) and P(MA–AO), respectively. The kinetics of adsorption of MV onto P(AA–AO) and P(MA–AO) are discussed. The pseudo-second-order kinetic model described the adsorption of MV onto P(AA–AO) and P(MA–AO) very well. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1547–1554, 2011

Key words: adsorption; radiation; resins

INTRODUCTION

Wastewaters from industries such as dye manufacturing, textile dyeing, and paper and pulp mills, contain appreciable amounts of metal ions and/or colored matter. They must be treated to lower the level of pollutants before they are unloaded into receiving streams. The processes for color removal from industrial effluents include biological treatments, coagulation, flotation, adsorption, oxidation, and hyperfiltration. Among these treatments, adsorption has attracted considerable interest as a feasible procedure for removing color from effluents.^{1–3}

A number of articles have been published that describe the synthesis of macroreticular resins containing amidoxime groups because of their use in the adsorption of dye from wastewater.^{4,5} All studies of the synthesis of a sorbent with an amidoxime group mostly involved the incorporation of a nitrile group into a polymer matrix, followed by the conversion of this nitrile group into an amidoxime group by treatment with an alkaline solution of hydroxylamine (NH₂OH).

Egawa et al.⁶ prepared a macroreticular chelating resin containing amidoxime by reacting acrylonitrile

(AN)–divinyl benzene copolymer beads with NH₂OH. Kobuke et al.⁷ synthesized a polyacryloamidoxime resin from various copolymers of AN and crosslinking agents. Chelate-type resins with amidoxime and amidoxime/carboxylic acid groups were prepared by the radiation-induced polymerization of AN and AN–acrylic acid (AA) and by the subsequent amidoximation of cyano groups of polyacrylonitrile, respectively.⁸ Poly(*N*-vinyl 2-pyrrolidone)–AN polymer networks were synthesized with γ rays, which were amidoximated and used for the purpose of uranyl ion adsorption.⁹ A new type of adsorbent containing amidoxime and carboxyl groups was synthesized by γ rays.¹⁰

In this study, hydrophilic amidoxime resins were prepared by the γ -radiation-induced copolymerization of AN–maleic acid (MA) and AN–AA followed by the subsequent amidoximation of cyano groups of polyacrylonitrile. The hydrophilic amidoximes were characterized by Fourier transform infrared (FTIR) spectroscopy. The prepared resins were used for the adsorption of methyl violet (MV) dye from aqueous solutions.

EXPERIMENTAL

Materials and methods

AA and MA were obtained from Merck (Darmstadt, Germany). *N,N*-Methylenebisacrylamide (MBAM) was used as a crosslinking agent, and it was obtained from Aldrich (Germany); AN was obtained from Fluka

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(Switzerland). Acrylonitrile monomer was passed through a column filled with chromatographic-grade activated alumina to remove the inhibitor.

The hydrochloric acid and sodium hydroxide solutions that were used to adjust the pH of the medium were obtained from Merck, MV was obtained from Allied Chemical (New Jersey), hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) was obtained from Fluka, and methanol was obtained from Aldrich. The other chemicals that were used were analytical reagent grade.

γ cell

A cobalt-60 (Russia) γ cell (type MC-20, Russia) was used as the irradiation source, with a dose rate of 2 kGy/h.

Preparation of the resins

Poly(maleic acid–acrylonitrile) [P(MA–AN)] and poly(acrylic acid–acrylonitrile) [P(AA–AN)] were prepared by the γ -radiation-induced copolymerization of AN with AA and MA, respectively, in a water–methanol solution with MBAM as the crosslinking agent.^{11,12} Acrylonitrile (8 mL), AA (12 mL), and MBAM (1 g) were mixed with 100 mL of methanolic solution (methanol–water = 1 : 10). Acrylonitrile (8 mL), MA (12 g), and MBAM (1 g) were dissolved in 100 mL of methanolic solution (methanol–water = 1 : 10). The monomer mixtures were transferred into glass ampules, and nitrogen gas was purged into the ampules to remove air from the solutions. The glass ampules were sealed and then subjected to ^{60}Co γ -rays at a dose rate of 2 kGy/h. The obtained resins were cut into small pieces, precipitated in acetone for the removal of unreacted monomers, dried, and stored. The percentage conversion was determined gravimetrically and was about 90%.

Preparation of the NH_2OH solution

$\text{NH}_2\text{OH}\cdot\text{HCl}$ (42.1 g) was dissolved in 300 mL of methanolic solution (methanol–water = 5 : 1). The HCl of NH_2OH was neutralized by an NaOH solution, and the precipitate of NaCl was removed by filtration. The pH of the reaction solution was adjusted to pH 10 by the addition of NaOH solution. The reaction medium was maintained with a methanol–water ratio of 5 : 1.

Amidoximation of the prepared resins

The preparation of the resin containing amidoxime groups was based on the treatment of nitrile with NH_2OH .^{13,14} About 20.0 g of the prepared resin was placed into a two-necked flask, which was equipped with a mechanical stirrer, condenser, and thermo-

stated water bath. Then, the previously prepared NH_2OH solution was added to the flask, and the reaction was carried out at 70°C for 2 h duration. The resins were separated from the solution by filtration and washed several times with methanolic solution (methanol–water = 4 : 1). Then, the resin was treated with 200 mL of methanolic 0.1M HCl solution for at least 5 min. Finally, the resin was filtered and washed several times with methanolic solution (methanol–water = 4 : 1) and then dried at 50°C to a constant weight.

Qualitative test of the amidoxime functional group

About 0.2 g of wet resin was shaken with vanadium (V) ion in dilute hydrochloric acid solution, where a purple colored complex on the resin beads was observed.

FTIR analysis

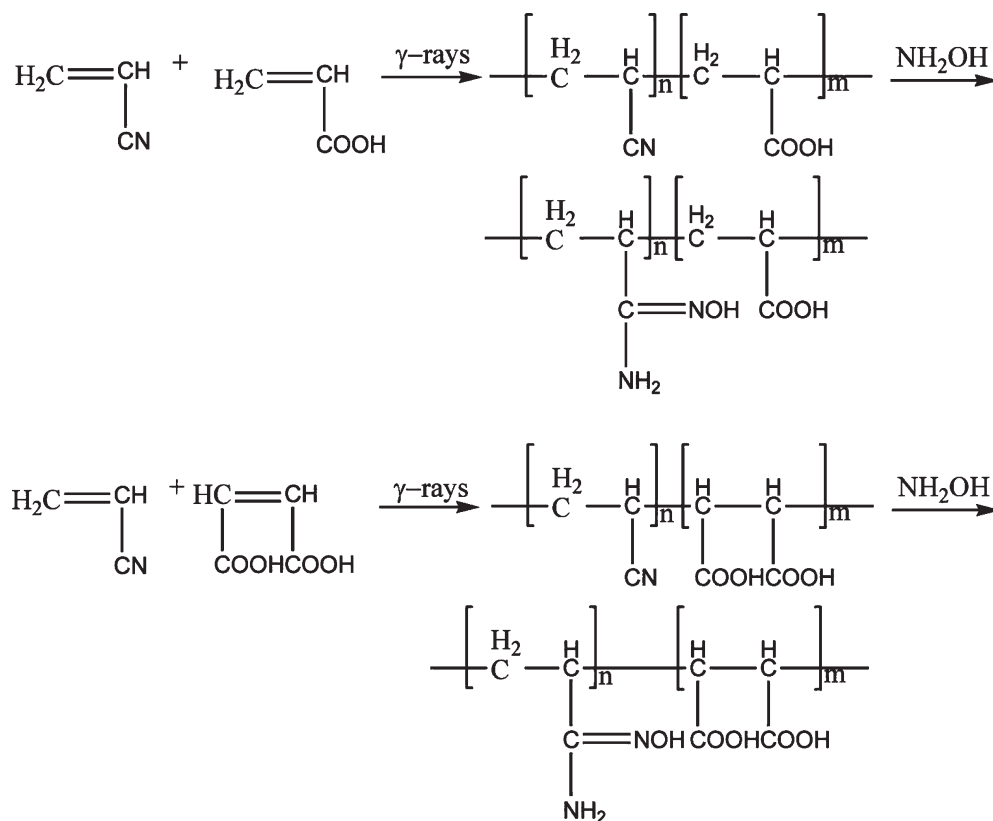
IR spectra of the polymer samples with KBr pellets were obtained with an FTIR spectrometer (Bomen, Hartman & Borunz spectrometer, model MB 157, Quebec, Canada).

Adsorption studies

Adsorption experiments were carried out at 25°C in magnetically stirred (180 rpm) cylindrical glass vessels with batch conditions. The samples (10 mg) of resin were mixed with dye solution (20 mL) with a concentration of 200 mg/L. The amount of residual dye in the solution was determined by a spectrophotometric method after 2 h. In these experiments, samples were stirred with dye solutions under the experimental conditions described previously, and the residual dye concentrations were determined at regular time intervals. The adsorption capacity (q) of the polymer was determined in the pH range 3–7 for cationic MV dye. The pH values of the initial solutions were adjusted with dilute HCl or NaOH solutions. The dependence of the q values on the time was determined, and the adsorption kinetics were investigated in detail. Furthermore, adsorption isotherms were obtained by the stirring of the polymers with dye solutions with various initial concentrations (C_i 's) for a period of time equal to the respective equilibrium times. All of experiments were done in triplicate, and the q value (mg of dye/g of polymer) of the polymers was calculated with the following expression:

$$q(\text{mg/g}) = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations of the dye (mg/L), respectively; V is the volume of the solution added (L); and m is the amount of polymer (g).



Scheme 1 Preparation of P(AA-AO) and P(MA-AO).

RESULTS AND DISCUSSION

FTIR

The resins, P(AA-AN) and P(MA-AN), were prepared by irradiation of the monomer solutions of AA and MA in AN, respectively, at a 20-kGy dose. The conversion of nitrile to amidoxime groups was carried out by the treatment of the resins with NH₂OH in an alkaline medium. The resins were prepared with the following experimental conditions: copolymer-NH₂OH ratio = 1 : 1, reaction period = 2 h, temperature = 70°C, reaction medium = methanol-water (ratio = 5 : 1), and pH = 10. The reaction

mechanism for the synthesis of the amidoximated resins is shown in Scheme 1.

The FTIR spectra of poly(acrylic acid-amidoxime) [P(AA-AO)] and poly(maleic acid-amidoxime) [P(MA-AO)] are shown in Figures 1 and 2, respectively. New absorption peaks appeared at 2247 and 1744 cm⁻¹; these were attributed to contributions of cyano groups (-CN) and carboxyl (-COOH) groups of AN of AA, respectively, as shown in Figure 1(a). The presence of these peaks verified the polymerization of AN and AA by γ radiation. After the amidoximation reaction of P(AA-AO), the carboxyl peak remained unchanged, the cyano peak vanished, and

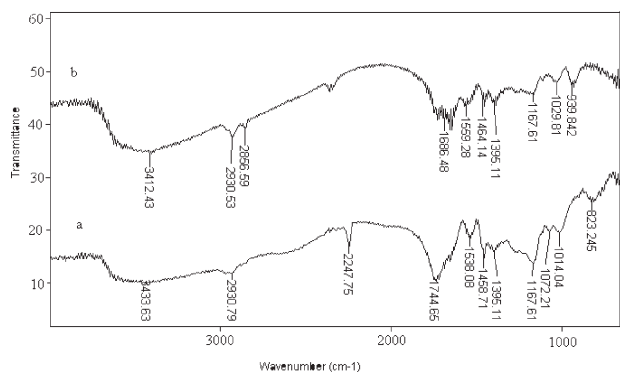


Figure 1 FTIR of (a) P(AA-AN) and (b) P(AA-AO).

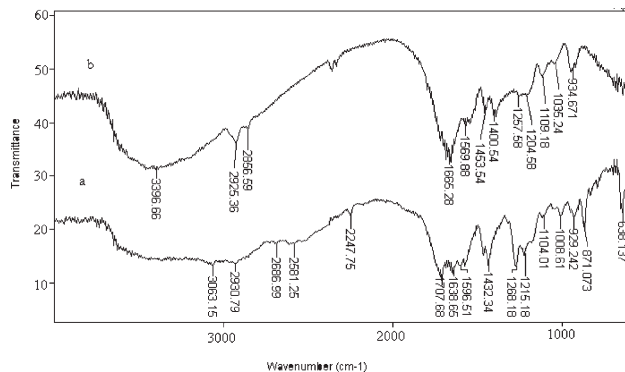


Figure 2 FTIR of (a) P(MA-AN) and (b) P(MA-AO).

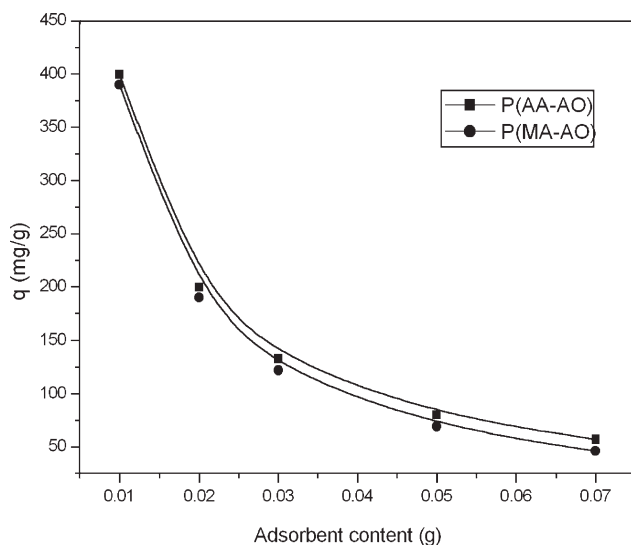


Figure 3 Adsorption of MV dye by P(AA-AO) and P(MA-AO) at different adsorbent.

a new strong peak attributed to —C=N stretching vibrations at 1659 cm^{-1} and the amide II band of N—H at 1559 cm^{-1} , respectively, appeared, as shown in Figure 1(b). This showed that the cyano groups reacted with hydroxyl amine and that —C=N double bonds were produced.

The FTIR spectrum of P(MA-AN) prepared by γ radiation is presented in Figure 2(a); the characteristic absorption peaks at 2247 and 1707 cm^{-1} were attributed to cyano groups (—CN) of AN and carboxyl groups (—COOH) of MA, respectively. After amidoximation, the CN band (2247 cm^{-1}) disappeared, a new band of amidoxime groups formed at 1665 cm^{-1} , and the amide II band of NH formed at 1569 cm^{-1} ; these are shown in Figure 2(b). This proved the conversion of cyano groups to amidoxime.

Effect of the adsorbent content

The adsorbent content is an important parameter because it determines the capacity of an adsorbent for a given C_i of the adsorbate.

The adsorption amount (mg/g) of MV dye at different doses of P(AA-AO) and P(MA-AO), with all other experimental conditions kept constant, are shown in Figure 3. The q value of P(AA-AO) and P(MA-AO) decreased from 398 to 60 mg/g with the dose of P(AA-AO) and P(MA-AO) increasing from 0.01 to 0.07 g. This was because the adsorption sites remained unsaturated during the adsorption reaction. Thus, with increasing adsorbent dose, the amount of MV adsorbed per unit mass of adsorbents was reduced; this caused a decrease in the q value.

Effect of the solution pH on the dye uptake

The effect of pH on q of MV by P(AA-AO) and P(MA-AO) was studied within the pH range 2–8.

The q values (mg/g) of the prepared resins were calculated, and the results are given in Figure 4. According to the protonation of the carboxylic and amidoxime groups of resins and amine groups of the dye, MV could be adsorbed more or less into P(AA-AO) and P(MA-AO) in basic and acidic media, respectively. The equilibrium sorption capacity was 376 mg/g at pH 2.7 and increased up to 394 and 396 mg/g at pH 5 for P(AA-AO) and P(MA-AO), respectively.

Hwang and Chen¹⁵ reported that both adsorbate and adsorbent might have chemical characteristics that are affected by the concentration of hydrogen ions ($[\text{H}^+]$'s) in the solution. Some adsorbents have affinities for H^+ or OH^- ions; this can directly affect the solution pH. Therefore, the solubility and amount adsorbed (q ; milligrams per gram) may change. The presence of the carboxylic COOH and NH_2OH groups in adsorbent materials affect the amount of dye adsorbed (milligrams per gram). Free carboxylic acid and amidoxime groups have the tendency to form salts with dye cations. The change in the dye absorption with increasing pH is due to the number and strength of these acidic groups.¹⁶

Other types of interaction between resins and dye may be hydrophobic and hydrogen bonding. Hydrophobic effects are specifically aqueous solution interactions, which in this case, involved the aromatic rings and the methyl groups on the dye molecules and the methine groups on the resins. Hydrogen bonding was expected to occur between the amine group's nitrogen atom on the dye molecules with the carbonyl groups on the monomer unit of the resins.¹⁷ However, electrostatic interactions between dye molecules and the resins were dominant because of the hydrophobic and hydrogen bonds.¹⁸

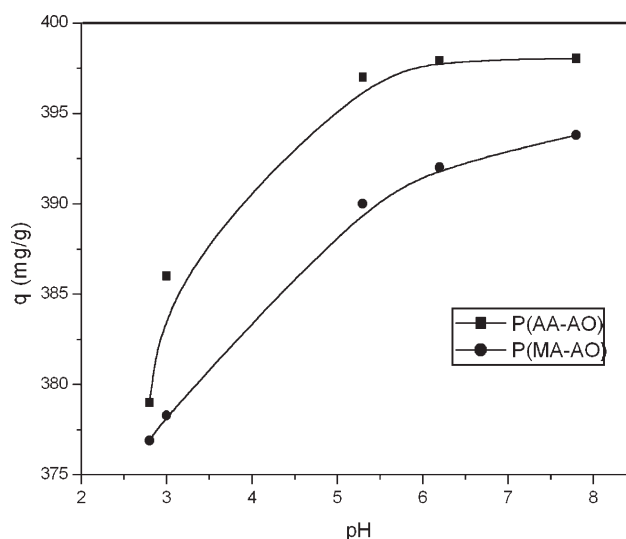


Figure 4 Effect of pH on q of MV onto P(AA-AO) and P(MA-AO).

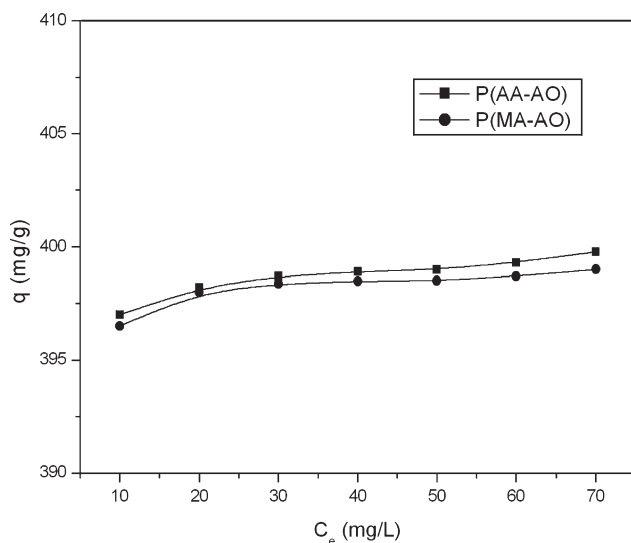


Figure 5 Equilibrium adsorption of MV onto P(AA-AO) and P(MA-AO).

Adsorption isotherm

q of an adsorbent is dependent on the concentration of the adsorbed molecule and other process parameters. To investigate the effect of the initial dye concentration on q , experiments were carried out at various initial dye concentrations (10–70 mg/L) at 25°C for 2 h, as described in the Experimental part. The adsorption isotherms given in Figure 5 show that the dye q increased with increasing initial dye concentration until saturation. The results obtained from the adsorption isotherms were evaluated by means of Langmuir and Freundlich adsorption models.^{19,20}

The basic assumption of the Langmuir adsorption model is that sorption takes place at specific homogeneous sites within the adsorbent. The Langmuir isotherm is represented by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}} \tag{2}$$

where q_e (mg/g) is the amount of the adsorbed dye molecules per unit weight of adsorbent at the final equilibrium concentration of the dye molecules solution (C_e ; mg/L). q_{max} signifies the maximum adsorption capacity (mg/g), and b is related to the energy of adsorption (L mg). The essential characteristic of the Langmuir equation can be expressed in terms of the dimensionless separation factor (R_L), which is defined as follows:

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where C_0 is the highest initial dye concentration (mg/L) and b is the Langmuir constant. The value of R_L indicates the type of the isotherm either to be

unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

The Freundlich isotherm model can be represented by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where K_F and n are Freundlich constants that are related to q and the intensity of adsorption, respectively.

The isotherm data were fitted with the Langmuir isotherm model for both P(AA-AO) and P(MA-AO). The Langmuir isotherms for the adsorption of MV onto P(AA-AO) and P(MA-AO) are represented in Figure 6. The Langmuir and Freundlich constants are given in Table I. As shown in the table, the correlation coefficient (R^2) of Langmuir was 0.999 for both resins. The q_{max} values calculated from the equation were close to the experimental results. The low value of RL indicated favorable adsorption. When the Freundlich isotherm model was applied to the experimental data, a good fit was not obtained because the R^2 values were 0.857 and 0.811 for P(AA-AO) and P(MA-AO), respectively.

q values and kinetics

The adsorption dependence of MV dye onto P(AA-AO) and P(MA-AO) was investigated through the initial dye concentration, time, and properties of the samples. The contact time is one important parameter in the adsorption process. Additionally, rapid adsorption and a high capacity are desirable properties for a sorbent. To investigate this property, P(AA-AO) and P(MA-AO) samples were left in dye solutions, and their capacities were determined at

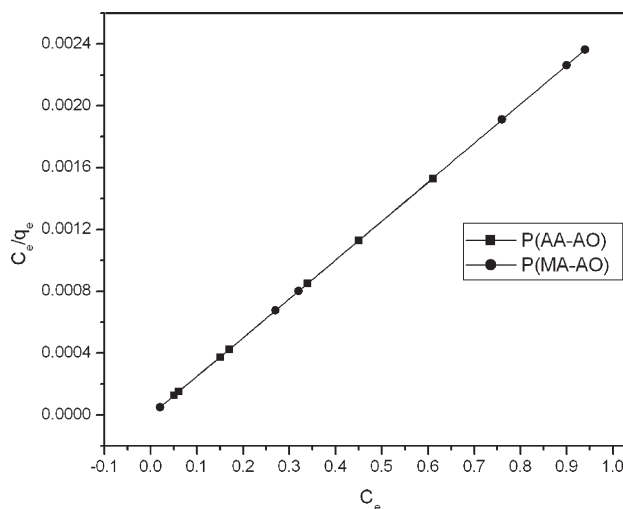


Figure 6 Langmuir isotherms for MV by P(AA-AO) and P(MA-AO).

TABLE I
Langmuir and Freundlich Constants for the Adsorption of MV
onto P(AA-AO) and P(MA-AO)

	Freundlich constants			Langmuir constants			
	K_F	n	R^2	q_{\max}	b	R_L	R^2
P(AA-AO)	3.98×10^2	1000	0.857	398.4	3.7×10^3	1.3×10^{-6}	0.999
P(MA-AO)	3.98×10^2	1000	0.811	396.8	1×10^3	4.8×10^{-6}	0.999

specified time intervals. Changes in the q values of the samples with time are given in Figure 7. Clearly, the P(AA-AO) resin had quite high q values; also, the capacity of P(MA-AO) increased with contact time. The interactions between the cationic groups of the dye and the hydrophilic groups of the polymer were ion-ion interactions. These may have occurred between the negative charge of the carboxyl and amidoxime groups on the polymer and the positive charge on the tertiary nitrogen of the dye. Furthermore, hydrophobic interactions between the aromatic rings of the dye and the hydrophobic groups on the polymer may have been present.

Figure 7 shows the effect of the contact time on the adsorption of MV dye by the prepared resins. The capacity increased rapidly during the initial adsorption stage, and then, it continued to increase at a relatively slow speed with contact time and reached an equilibrium point after 6 and 12 h for P(AA-AO) and P(MA-AO), respectively. The adsorption of MV dye on the resins was a fast process, where more than 90% of the adsorption took place within the first 100 min. In the literature, various polymeric sorbents showed different properties with respect to dye adsorption from aqueous solutions within a range of 2 h to 5 days.²¹⁻²⁴ Furthermore, it was reported that equilibrium times changed between 12 h and 2 days for various sorbents used for MV removal.¹² The quite high q and higher adsorption rates of P(AA-AO) and P(MA-AO) will provide an important advantage for the use of these materials in cationic dye solutions.

To express the mechanism of the adsorption process of MV on P(AA-AO) and P(MA-AO), kinetic data were analyzed by pseudo-first-order and the pseudo-second-order equations.

The adsorption kinetic data were described by the Lagergren pseudo-first-order model,²⁵ which is the earliest known equation describing the adsorption rate on the basis of q . The differential equation is generally expressed as follows:

$$\frac{dq_e}{dt} = k_1(q_e - q_t) \quad (5)$$

where q_e and q_t refer to the amounts adsorbed (mg/g) at equilibrium and at a given time (t ; min),

respectively, and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). The integration of eq. (5) for the boundary conditions (from $t = 0$ and $q_t = 0$ to t and q_t) gives the following equation:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303}t \quad (6)$$

which is the integrated rate law for a pseudo-first-order reaction. Equation (6) can be linearized as the following form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (7)$$

k_1 and theoretical maximum amount adsorbed (q_e) can be determined from the slope of the straight-line plots of $\log(q_e - q_t)$ against t and the intercept.

The adsorption kinetics may be described by the pseudo-second-order model.²⁶ The differential equation is generally given as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (8)$$

where k_2 is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). The integration of eq. (8)

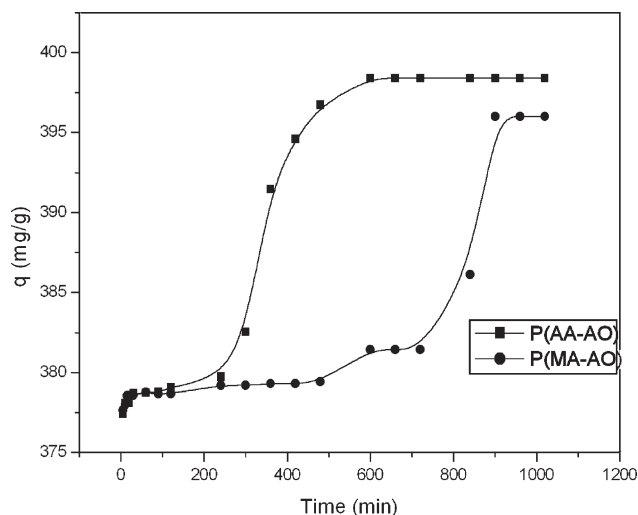


Figure 7 Plots of the adsorbed MV dye amounts by P(AA-AO) and P(MA-AO) samples versus time.

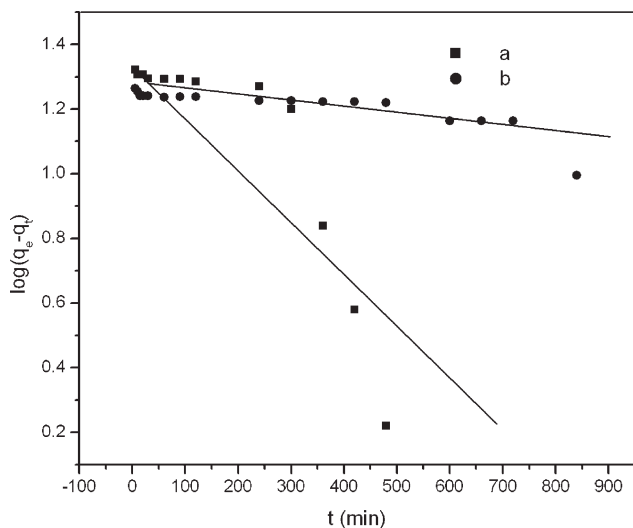


Figure 8 Adsorption kinetics of MV onto (a) P(AA-AO) and (b) P(MA-AO) according to the pseudo-first-order model.

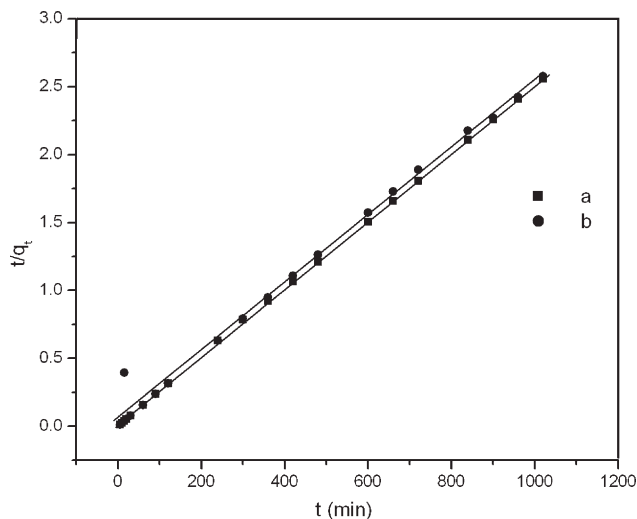


Figure 9 Adsorption kinetics of MV onto (a) P(AA-AO) and (b) P(MA-AO) according to the pseudo-second-order model.

for the boundary conditions gives the following equation:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{9}$$

which is the integrated rate law for a pseudo-second-order reaction. Equation (9) can be linearized to the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{10}$$

The values of k_2 , q_e , and the initial adsorption rate ($h = k_2 q_e^2$, mg g/min) can be obtained from the slope and intercept of the plot of t/q_t against t .

The validity of these two models can be checked by analysis of the linearized plots. Figures 8 and 9 illustrate the fitted results. The rate constants, calculated amounts of the q_e values, and R^2 values are given in Table II. The pseudo-second-order kinetic model fit better than the data obtained from the first-order model for the adsorption of MV onto P(AA-AO) and P(MA-AO) as the R_2^2 values were closer to 1 than those of the first-order kinetics (R_1^2). Moreover, the q_e values for the second-order kinetics

were close to the q_e values obtained experimentally [experimental q_e values = 400 and 401 mg/g for P(AA-AO) and P(MA-AO), respectively]. The adsorption rate was related to the concentration of the active sites on the adsorbent surface. Dye adsorption onto the resins could have been a rate-controlling process that involved valency forces through the associated electrons between the dye cation and adsorbent.

CONCLUSIONS

P(AA-AO) and P(MA-AO) resins were prepared by the γ -radiation-induced copolymerization of AN with AA and MA, respectively. The obtained resins were amidoximated by reaction with NH_2OH .

This study revealed that P(AA-AO) and P(MA-AO) resins could be used as potential adsorbents for the removal of MV cationic dye. The adsorption of the cationic dye was studied by a batch technique, and more than 90% of dye removal was achieved with 0.01 g of the resins for an initial dye concentration of 200 mg/L. The q values increased with the pH value of the solution and the initial dye concentration but decreased with the adsorbent content. The q values of the resins at $\text{pH} > 5$ provided a

TABLE II
 k_1 and k_2 Values for MV Dye Onto the Polymer

	q_e (experimental)	Pseudo-first-order kinetics			Pseudo-second-order kinetics			
		k_1	q_e (calculated)	R_1^2	k_2	q_e (calculated)	h	R_2^2
P(AA-AO)	398.4	5.59×10^{-3}	18	0.762	6×10^{-4}	400	96	0.999
P(MA-AO)	396	5.85×10^{-3}	17	0.683	1×10^{-4}	401	18	0.992

great advantage in utilization of these resins systems for the treatment of cationic textile dye from wastewater. The experimental data were best correlated by a generalized isotherm. The data obtained from the adsorption isotherms were fitted to the Langmuir model. The kinetic study of MV on the P(AA-AO) and P(MA-AO) resins was performed on the basis of the pseudo-first-order and pseudo-second-order kinetic models. The data indicate that the adsorption kinetics followed the pseudo-second-order kinetic model. The R_L values showed that the P(AA-AO) and P(MA-AO) resins were favorable for the adsorption of MV.

The results of this study indicate that P(AA-AO) and P(MA-AO) resins can be successfully used for the adsorption of MV cationic dye from wastewaters.

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