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# New copolymer of acrylamide with allyl methacrylate and its capacity for the removal of azo dyes

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## Abstract

The copolymerization reactions of Acrylamide (AA) with the different mole ratios of allyl methacrylate (AMA) such as 25/75, 50/50 and 75/25 were studied by radical polymerization under argon atmosphere using 2,2'-Azobis (isobutyronitrile) (AIBN) as initiator. The copolymers were characterized with Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TG). FTIR spectra showed that the C=O, C-N and N-H groups in copolymers remained during the copolymerization. It is concluded from the thermograms that Poly(AA-co-AMA) copolymers which contained different ratios of monomer and comonomer exhibit similar thermal behavior. Adsorption capacity, kinetic and isotherm studies of Direct Brown 2 onto the copolymers have been evaluated. Different factors such as the monomer ratio, pH, initial dye concentration, copolymer dosage and contact time affecting the removal process were studied. It was found that the adsorption process agreed with the Freundlich and Dubinin-Raduskevich model and the adsorption of Direct Brown 2 depended on the acrylamide content and pH of the solution. The standard Gibb's free energy was determined as - 14.7 kJ/mol, which means that adsorption occurred spontaneously and the process is feasible. Increasing the acrylamide content led to increased adsorption of Direct Brown 2 on the copolymer. Moreover, adsorption kinetic studies showed that the adsorption followed a pseudo-second-order kinetic model, indicating that the chemical adsorption was the rate-limiting step. These results show that Poly(AA-co-AMA) can be used as adsorbent for water pollutants such as Direct Brown 2 and has potential applications in related industrial and environmental areas.

**Keywords:** *acrylamide, allyl methacrylate, azo dye, adsorption isotherm, adsorption kinetics.*

## 1. Introduction

Dyes from waste effluents are widely generated in several industries such as textile, leather, paper, pharmaceutical, plastic, and food. The chemical oxidation, foam flotation, electrolysis, biodegradation, adsorption, chemical coagulation and photocatalysis are known as the most effective methods for removal of dye from industrial water of dyes. Adsorption is the effective and simple method to remove pollutants from wastewater. Several polymers and copolymers such as poly(N-vinylpyrrolidone-co-methacrylic acid), polystyrene-graft-poly(N,N-dimethylamino-2-ethyl methacrylate), aniline-formaldehyde polymer and so on as adsorbents were studied for their ability to remove metals or dyes<sup>[1-3]</sup>.

In recent years, many researchers have worked for development of new adsorbents having superior properties such as high adsorption capacity, fast adsorption rate, and mechanical strength. The several polymers having different functional groups have been also investigated in the preceding literature for this purpose. AA monomer has the amine and vinyl group. Because of their higher reactivities, bifunctional monomers containing two reactive groups can be used for the preparation of functional (co)polymers. In the related literature, AA monomer was copolymerized with different functional monomers in order to obtain useful synthetic adsorbents for dye removal of water. Solpan et al have studied the radiation-induced copolymerization of acrylamide and acrylic acid to uptake of some cationic dyes such as

Safranine and Magenta<sup>[4]</sup>. Poly(acrylamide-co-ethylene glycol dimethacrylate) was synthesized to remove catechins and caffeine by Lu et al.<sup>[5]</sup> There are also a lot of studies about poly(acrylamide) modification. Composite hydrogels based on polyacrylamide and chitosan were prepared to absorb of the anionic or cationic dyes<sup>[6]</sup>. Multiwalled carbon nanotubes have been grafted with poly(acrylamide) and with poly(N,N-dimethylacrylamide) to compare their adsorption capacities<sup>[7]</sup>. The cross linked poly (acrylic acid-co-acrylamide)/attapulgit (Poly(AA-co-AM)/ATP) composite to remove Methyl Violet (MV) cationic dye from aqueous solution have been reported by Wang et al.<sup>[8]</sup>. The studies have shown that acrylamide exhibits good adsorption capacity for the compounds since its amino and carbonyl groups may act as chelating sites.

Azo colorants have a coloring effect containing one or two azo groups (N=N double bonds) in their chemical structures. They are synthesized by coupling diazotized aromatic amines with other aromatic compounds. They are the largest group of synthetic colorants (60-70%) and can be used for the coloration of textile fibers, plastics, leather, cosmetics etc. Reductive cleavage of the azo linkage under anaerobic conditions has promoted concerns about the release of known carcinogens such as benzidine. These aromatic amines are biorefractory and highly toxic because they can react easily in the blood to convert hemoglobine into methahemoglobine and preventing oxygen uptake. It

is necessary to de-pollution of these azo dyes in order to avoid their dangerous environmental accumulation<sup>[9]</sup>. In order to remove these azo dyes from waste water, there are numbers of studies using polymers, hydrogels, natural polymer grafted synthetic polymers.

The object of the current study was to improve the adsorption capabilities of acrylamide for azo dyes. In this study, we attempt to prepare poly(acrylamide-co-allyl methacrylate) (Poly(AA-co-AMA) with different mole ratios by radicalic polymerization for removal of azo dyes from aqueous solution. The adsorption properties in azo dyes solution such as Direct Brown 2 of synthesized copolymers were investigated.

## 2. Experimental

### 2.1 Materials

The Acrylamide, AA (stated purity 98%) was purchased from Fluka, Allyl Methacrylate, AMA, (stated purity 98%) were purchased from Merck. The chemicals were used without any further purification.

### 2.2 Instrumentation

The FTIR (Fourier Transform Infrared Spectroscopy) spectra of the copolymers were obtained by using Perkin Elmer Spectrum 100 FT-IR Spectrometer by KBr pellet technique.

TG measurements of copolymers were obtained on Perkin–Elmer Diamond TA/TGA from 30 to 600°C at the 10°C min<sup>-1</sup> heating rate under constant flow of 100 mL/min of nitrogen atmosphere. The sample weights for all the experiments were taken in the range of 8-10 mg.

Spectrophotometrical measurements of Direct Brown 2 were obtained on UV/VIS Perkin-Elmer Spectrophotometer at 409nm.

### 2.3 Preparation of Poly(AA-co-AMA) copolymer in different AA/AMA ratio

Three different mole compositions of AA and AMA monomers such as 25/75, 50/50, and 75/25 and 0.0001 mmole of AIBN were placed into a pyrex flask. The polymerization was carried out at 60°C for 1 hour under argon atmosphere. At the end of the reaction period, the copolymers of Poly(AA-co-AMA) were washed with methanol. The copolymers were dried in vacuum oven at 50°C. The dried copolymer samples were then analyzed by using FTIR and TG.

### 2.4 Adsorption studies

#### 2.4.1 Determination the monomer ratio for dye removal

In order to determine the effect of monomer rate of copolymer for the most efficient dye removal, three different copolymers synthesized with different monomer ratios. These monomer ratios are 25% AA and 75% AMA (K1), 50% AA and 50% AMA (K2), and 75% AA and 25% AMA (K3). 50 mg different copolymers (K1, K2 and K3) incubated with 2 mL (1 mg/mL) dye solution for 2 hours in room temperature under constant shaking (240 rpm). At the end of the incubation

period, samples were centrifugated at 3000 rpm for 10 minutes in order to precipitate the copolymer. The dye amount of the upper phase was determined spectrophotometrically (409 nm). Dye removal efficiency was calculated using the following Equation 1<sup>[10]</sup>.

$$\% \text{ Dye removal} = \frac{\text{Initial dye amount (mg)} - \text{Remaining dye amount (mg)}}{\text{Initial dye amount (mg)}} \times 100 \quad (1)$$

#### 2.4.2 The effect of pH on dye removal

In order to investigate the effect of pH on dye removal of the copolymer, different buffer solutions prepared that pH ranges from 2-10 (pH 2 glycine/HCl buffer, pH 3-5 sodium acetate buffer, pH 6-8 phosphate buffer, pH 9-10 glycine/NaOH buffer). Concentration of the buffer solutions were chosen as 10 mM. 1 mg/mL dye solutions was prepared by using different pH buffers. 2 ml dye solutions with different pH added to 50 mg of copolymer and incubation was performed at room temperature for 2 hours. At the end of the incubation period, samples were centrifugated at 3000 rpm for 10 minutes in order to precipitate the copolymer and the dye amount of the upper phase were determined spectrophotometrically (409 nm)<sup>[11]</sup>.

#### 2.4.3 The effect of initial dye concentration on dye removal efficiency

In order to determine the effect of dye concentration on dye removal yield, dye solutions prepared using 10 mM acetate buffer (pH 3.0) with varying concentrations from 0.2 to 0.01 mg/mL. Dye solutions with different concentrations were added onto copolymer and allowed to incubation for 2 hours at room temperature under constant shaking (240 rpm). At the end of the incubation period, samples were centrifugated at 3000 rpm for 10 minutes in order to precipitate the copolymer and the dye amount of the upper phase were determined spectrophotometrically (409 nm)<sup>[12]</sup>.

#### 2.4.4 Effect of copolymer dosage

In order to investigate the effect of varying the amount of copolymer, 5-400 mg copolymer weighted and 2 mL pH 3.0, 0.01 mg/mL dye solutions added. It was allowed to incubate at room temperature for 2 hours. At the end of the incubation period, samples were centrifugated at 3000 rpm for 10 minutes in order to precipitate the copolymer and the dye amount of the upper phase were determined spectrophotometrically (409 nm)<sup>[12]</sup>.

#### 2.4.5 Effect of contact time on dye removal

The batch system was established under optimum conditions and the removal of Direct Brown 2 was examined depending on time. For this purpose, 200 mg copolymer was treated with 50 mL (pH 3.0, 0.01 mg/mL concentration) dye solution. At pre-determined time intervals (5-120 minutes), the upper phase is collected to determine the amount of dye in the upper phase and dye removal time was estimated spectrophotometrically<sup>[11]</sup>.

#### 2.4.6 Direct Brown 2 desorption from copolymer

Batch system was set by using optimum copolymer amount and dye solution and system was incubated for 45 minutes. At the end of the incubation, pH of equilibrium

was pulled alkaline region from acidic region (3-10) and desorption behavior was examined under changing pH<sup>[12]</sup>.

#### 2.4.7 Adsorption isotherms and thermodynamic modelling

The experiments performed to observe the effect of concentration at constant pH and temperature. Copolymer was taken in tubes containing 2 mL each of different Direct Brown 2 concentrations. These tubes then constantly shaken at 25°C for 45 minutes. Then, samples centrifuged at 3,000 rpm and unadsorbed dye amount calculated.  $\Delta G$  of the adsorption calculated by using Langmuir constant  $Q_0$ . For all isotherm models dye concentration varied from 10-200  $\mu\text{g/mL}$ .

Adsorption isotherms of dye were studied. Dubinin-Radushkevich, Freundlich and Langmuir isotherms applied and constants calculated.

#### 2.4.8 Adsorption kinetics

The experiment performed to observe the effect of time at constant pH, concentration and temperature. 200 mg copolymer was taken in a flask containing 50 mL dye (0.01 mg/mL). The flask was constantly shaken at 25°C for 2 hours. Then, at predetermined time intervals 2 mL sample was taken from equilibrium and measured spectrophotometrically. After measurement the sample was poured back to the equilibrium. Adsorption change with time was estimated, kinetic models applied and kinetic constants were calculated.

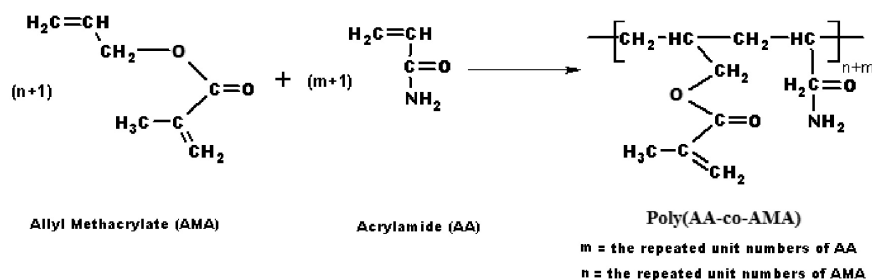
### 3. Results and Discussion

In this paper, the copolymers which contain different mole ratios (75/25, 50/50, 25/75 mmols) of the AA and AMA synthesized at the 60°C in the 1 hour under the argon atmosphere. Table 1 is demonstrated copolymerization yield and AA/AMA ratio. The copolymerization yield is given as the ratio of the weight of monomer to the weight of product. The proposed possible copolymerization reaction of the monomers is shown in Figure 1.

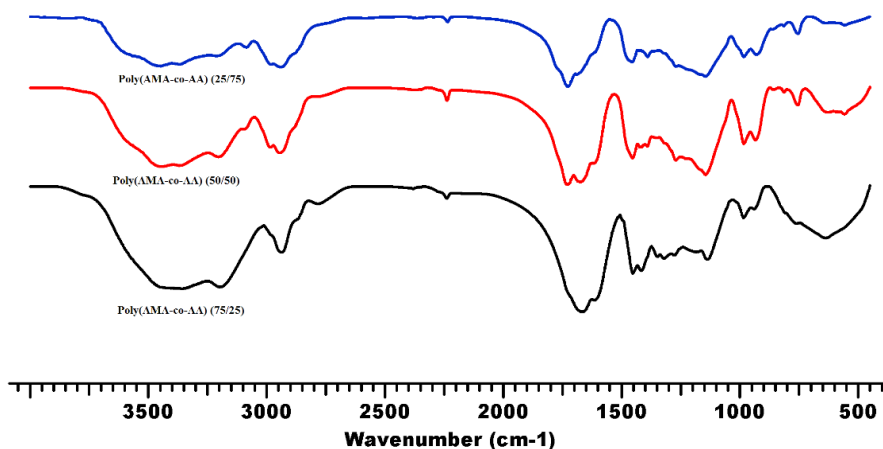
The FTIR spectra of Poly(AA-co-AMA) in three different compositions (AMA/AA mole ratios, 25/75, 50/50, and 75/25) are shown in Figures 2a, b and c. The peak assignment for the FTIR spectrum of the Poly(AA-co-AMA) is as follows: C-H in  $\text{CH}_3$  and C-H in  $\text{CH}_2$  between 2900-3100  $\text{cm}^{-1}$ ,  $\text{CH}_2$  at 1457  $\text{cm}^{-1}$ ;  $\text{CH}_3$  at 1389  $\text{cm}^{-1}$ ; C=C in allyl group around 1650  $\text{cm}^{-1}$ ;  $\text{CH}=\text{C}$  for allyl group around 980 and 929  $\text{cm}^{-1}$ . The absorption peak corresponding to allylic double bond at 980 and 929  $\text{cm}^{-1}$  still exists even with a reduced intensity

**Table 1.** The copolymerization yields of the Poly(AA-co-AMA) with different AA/AMA ratio.

AA/AMA mole ratio	Polymerization yields (%)
75/25	80
50/50	83
25/75	81



**Figure 1.** The proposed possible copolymerization reactions of the AA and AMA monomers.



**Figure 2.** The FTIR spectrum of the Poly(AA-co-AMA) with different AA/AMA ratio.

than that in the monomer spectrum. But the absorption peak of the vinyl group at  $800\text{ cm}^{-1}$  vanishes completely in copolymer spectrum which indicates that the copolymer does not contain any vinyl group. The FTIR absorption bands for C=O bond of the copolymers take place around  $1720\text{ cm}^{-1}$  and C-N band appear between  $2230\text{--}2240\text{ cm}^{-1}$ . As seen in Figure 2, the much broader absorption peaks around  $3400$  and  $3190\text{ cm}^{-1}$  due to the asymmetric and symmetric N-H stretching, respectively.

### 3.1 Thermogravimetric analysis of the copolymers

Thermogravimetric analysis (TG) was used to investigate the thermal stability. The TG thermograms of the Poly(AA-co-AMA) in three different compositions (AA/AMA mole ratios, 25/75, 50/50, and 75/25) are shown in Figure 3a. To determine the thermal stability of the copolymers, the temperature for the maximum weight loss ( $T_{\max}$ ) and the temperature for half-life ( $T_{1/2}$ ) were found directly from its dynamic thermograms given in Figure 3b.

It is shown in Figure 3 that there is only one decomposition stage for the K1 copolymer. The temperature for maximum weight loss of the copolymer is  $T_{\max} = 424^\circ\text{C}$  and  $T_{1/2} = 413^\circ\text{C}$ . On the other hand, there are two decomposition stages for those of 50/50 and 75/25 mole ratio of the copolymers. Very weak peaks with  $T_{\max} = 305^\circ\text{C}$  and  $T_{\max} = 310^\circ\text{C}$  are observed in the DTG curves of K2 and K3 copolymers, respectively over the temperature range  $200$  to  $330^\circ\text{C}$  with the weight losses of 9% for K2 and 13% for K3 copolymers. These very

weak peaks in the DTG curves of K2 and K3 copolymers may be due to branching structure in the copolymers from the tip of AMA monomer. The  $T_{\max}$  and  $T_{1/2}$  are  $421$  and  $409^\circ\text{C}$  for K2, and  $412$  and  $404^\circ\text{C}$  for K3 copolymers. The K3 copolymer also gives 10% residue over  $600^\circ\text{C}$ . The TG results show that thermal decomposition temperatures increase with rising AA content.  $T_{\max}$  for Poly(acrylamide) (PAA) is  $396^\circ\text{C}$  and  $T_{1/2}$  is  $418^\circ\text{C}$ . PAA gives 25% residue at  $600^\circ\text{C}$ <sup>[13]</sup>.  $T_{\max}$  and  $T_{1/2}$  are given as  $409^\circ\text{C}$  and  $400^\circ\text{C}$  for Poly(allylmethacrylate) (PAMA) homopolymer in the literature, respectively<sup>[14,15]</sup>. Consequently, it is understood that the thermal stability and the temperature for maximum weight loss of Poly(AA-co-AMA) copolymers are between those of PAA and PAMA homopolymers indicating that thermal stabilities of PAMA, PAA and Poly(AA-co-AMA) are found to be rather similar.

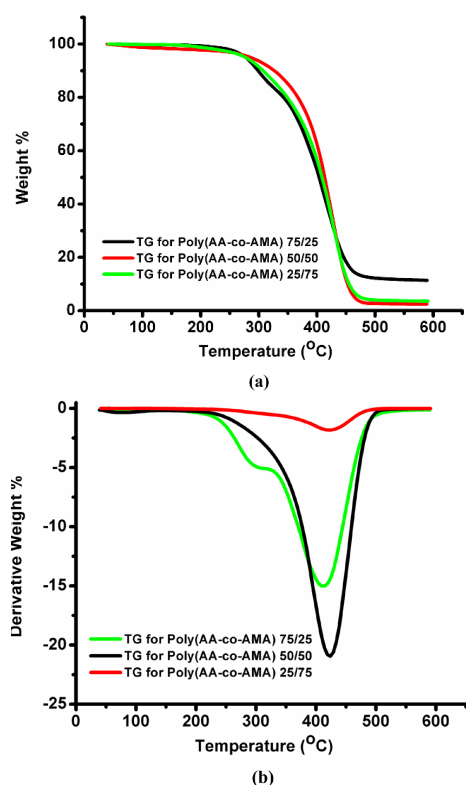
### 3.2 Determination the monomer ratio for dye removal

The result of the attempt to dye removal with K1 copolymer, copolymer dissolution in dye solution was observed and is not able to remove any dye from equilibrium. This dissolution was observed based on the  $-\text{NH}_2$  groups of AA monomer. Because of this  $-\text{NH}_2$  residues copolymer gains hydrophilic character and becomes soluble in water. Copolymer K2 is not dissolved in dye solution but yet it was not able to remove any dye from equilibrium. The copolymer K2 may become more insoluble due to the decreased number of  $-\text{NH}_2$  residues. Therefore the copolymer did not dissolve in equilibrium. However, it still cannot adsorb the dye because dye cannot compete with water. But the experiment with copolymer K3 gave 50% percent dye removal yield. In consequence of dye removal rate is higher of K3 compared with other copolymers under unoptimized conditions, it is decided to continue with copolymer which contains 25% allyl methacrylate and 75% acrylamide monomers for dye removal study.

### 3.3 The effect of pH on dye removal

In order to determine the optimum pH where dye can be maximum adsorbed, dye removal yield was measured under varying pHs. Dye is not soluble at pH 2 which is why the pH range chosen as 3 to 10. The most dye removal was observed at pH 3 with 100% and as seen in Figure 4 the yield was decreased with increasing pH<sup>[16]</sup>.

It is thought that at pH 3 carboxyl and sulfonyl groups of dye is negatively charged and the copolymer is positively charged, consequently, dye removal yield is higher compared with other pHs. The carboxyl and sulfonyl groups of dye lose their negative charge with increasing pH. On the other hand, the copolymer is positively charged at this pH due to its  $-\text{NH}_2$  residues. The negative charge of dye and positive charge of copolymer's AA monomer promoted the adsorption process. P. Senthil Kumar and co-workers removed Congo Red dye by using cashew nut shell. In their study, the adsorbate was an anionic dye and the adsorbent had positively charged character. The adsorption yield of Congo Red was decreased with increasing pH as in our study. Their finding is compatible with our finding<sup>[17]</sup>.



**Figure 3.** a) The TG thermograms of the Poly(AA-co-AMA) with different AA/AMA ratio. b) The DTG thermograms of the Poly(AA-co-AMA) with different AA/AMA ratio.



### 3.4 The effect of initial dye concentration on dye removal efficiency

It is aimed to estimate the dye concentration effect on dye removal yield. For this purpose, the dye concentration range chosen as 0.01 to 0.2 mg/mL. An adsorbent has limited binding site for adsorbate molecules which become saturated at a certain concentration. Consequently, with increasing dye concentration dye removal yield is decreases. As can be seen in Figure 5 copolymer is saturated with increasing dye concentration and it results with a decrease in dye removal yield. Chowdhury S. and coworkers removed Basic Green 4 by using *Ananascomosus* leaf powder. They used initial dye concentration range as 0.02 mg/mL to 0.1 mg/mL which is 2 fold lower in our study. They found the similar results as in our study. It seemed that our results are compatible with their results<sup>[18]</sup>.

### 3.5 Effect of copolymer dosage

Adsorbent dosage is an important parameter which influences the sorption capacity of an adsorbent. Figure 6 shows the adsorption profile of Direct Brown 2 versus different copolymer concentration in the range of 0.005-0.4 g. It can be seen that the adsorption increased with increasing adsorbent dosage and after 0.2 g adsorbent dosage there was no significant change in dye removal yield. The positive correlation between copolymer dosage and dye removal can be explained with increased adsorbent surface area and availability of more binding sites.

### 3.6 Effect of contact time on dye removal

The uptake of Direct Brown 2 on copolymer was rapidly occurred in first 30 minutes and reached 70% sorption yield as seen in Figure 7. This increase was continued until 45 minutes and 93% of dye adsorbed at that time. After 45 minutes adsorption slowed down and reached to the equilibrium with a 100% dye removal yield. It is thought that the optimum contact time is 45 minutes because the sorption after that time was really slower also no significant dye removal yield occurred. Mittal A. used fen heathers to remove Brilliant Blue FCF. In his study, sorption comes to equilibrium after 200 minutes<sup>[19]</sup>. However we reached equilibrium after 45 minutes which indicates that our study showed better removal time compared with Mittal A.'s study. The reason for this time shift may be due to the positive charge of copolymer which is accelerates the rate of adsorption.

The positive charge of copolymer and negative charge of dye drives the adsorption in a chemical nature which will be discussed in further sections.

### 3.7 Direct Brown 2 desorption from copolymer

Desorption is an important parameter for re-usage of adsorbents in industry. For this reason it is important to establish desorption yield. As seen in Figure 8, desorption increased with increased pH. Owing to the increasing pH, carboxyl and sulfonyl groups of dye protonated and lost their negative charge and it is similar for the copolymer. Ionic interactions between anionic dye and positively charged copolymer were broken with increasing pH. In our study, copolymer released 63% of adsorbed dye in alkaline conditions means that copolymer has potential for re-usage.

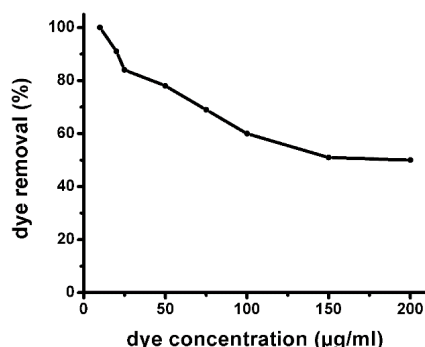


Figure 5. Initial dye concentration effect on adsorption yield.

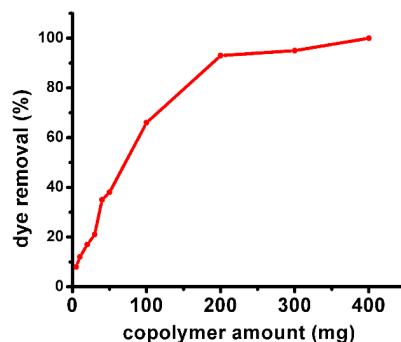


Figure 6. Dye adsorption with varying copolymer amounts.

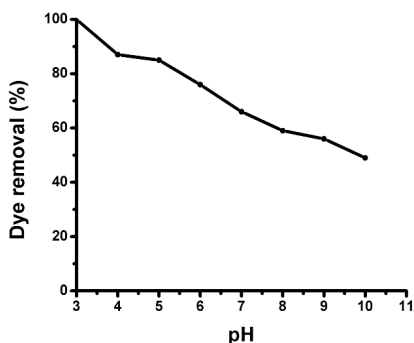


Figure 4. pH effect on dye removal.

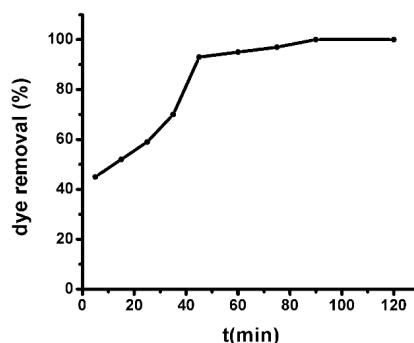


Figure 7. Contact time effect on adsorption removal yield.

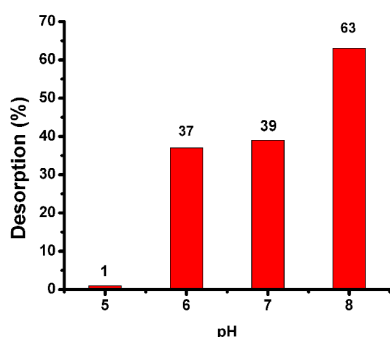


Figure 8. Desorption yield in different pH values.

### 3.8 Adsorption isotherms and thermodynamic modelling

Adsorption process can not be explained with just one adsorption model. Therefore, a few adsorption model should be applied for an equilibrium. Due to this necessity we studied Langmuir, Freundlich and Dubinin-Raduskevich isotherms, and calculated the related constants. Isotherm models were given below.

Langmuir adsorption isotherm explains the monolayer coverage of the sorbate on a sorbent surface at a constant temperature. The assumption is that the forces exerted by chemically unsaturated surface atoms do not extend further than diameter of one sorbed molecule<sup>[20]</sup>. The linear Langmuir curve's equations:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Q_b \times b} + \frac{C_{eq}}{Q_0} \quad (2)$$

$C_{eq}$  is the concentration of dye solution (mg/L) at equilibrium,  $Q_{eq}$  is the amount of dye adsorbed per unit weight of copolymer (mg/g).  $Q_0$  gives the theoretical monolayer adsorption capacity (mol/g) and  $b$  is the Langmuir constant which is related with the energy of adsorption (L/mol). A plot of  $C_{eq}/Q_{eq}$  versus  $C_{eq}$  yields a straight line with slope  $1/Q_0$  and intercept  $b$ .

To identify the favour ability of the adsorption, dimensionless constant separation factor  $R$  is expressed as:

$$R_L = \frac{1}{1 + (b \times C_0)} \quad (3)$$

$R_L$  value indicates the state of adsorption as follows;  $R_L > 1$ , unfavourable;  $R_L = 1$ , linear;  $0 < R_L < 1$ , favourable;  $R_L = 0$ , irreversible<sup>[21]</sup>.

In the present study, the theoretical monolayer adsorption capacity was found 7 mg/g and Langmuir constant was found 0.006 L/mg.  $R_L$  value was 1 which means the adsorption of dye is linear. However Langmuir isotherm model is not sufficient to explain adsorption of equilibrium.

The changes in the standard Gibb's free energy were calculated using Langmuir isotherm constant  $b$ . The equation was shown below<sup>[21]</sup>:

$$\Delta G = -RT \ln b \quad (4)$$

The negative standard Gibb's free energy values indicate the feasibility of the process and its spontaneous nature. The standard Gibb's free energy determined as -12.7 kJ/mol. This value represents the adsorption occurred spontaneously and process is feasible.

The Freundlich isotherm is an empirical equation based on a heterogenous surface. A linear form of the Freundlich expression will yield the constant  $K_F$  and  $n$ .

$$\ln q_{eq} = \ln K_F + \left(\frac{1}{n}\right) \times \ln C_{eq} \quad (5)$$

Therefore, a plot of  $\ln q_{eq}$  versus  $\ln C_e$  enables the constant  $K_F$  and exponent  $n$  can be determined.  $K_F$  can be defined as adsorption of distribution coefficient and represents the quantity of dye adsorbed with copolymer for an equilibrium concentration. The slope  $1/n$ , ranging between 0 and 1 is a measure of adsorption intensity of surface heterogeneity, becoming more heterogeneous as its value gets closer to the zero. If the adsorption intensity,  $n$  is less than 1, it indicates that adsorption intensity is good over the entire range of concentration studied, but if the  $n$  value is more than 1, it means that adsorption intensity is favourable at high concentration but much less at lower concentration<sup>[22]</sup>.

In our work,  $K_F$ ,  $n$  and  $1/n$  values determined as  $0.013 \text{ mol}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$ , 1.7 and 0.6, respectively. If the value  $n$  is more than 1 it means that the adsorption intensity is good at high concentrations and the value  $1/n$  indicates that the surface of copolymer is more likely to be heterogenous. As can be seen from the results,  $n$  value is more than 1 which means adsorption intensity is favourable at high concentrations for Direct Brown 2.  $1/n$  value is between 1 and 0. This value also indicates that the surface of adsorbant is heterogenous. Both constants correlates with adsorption nature. Moreover, based on this data we can assume that synthesized copolymer can be used to remove azo dyes from equilibrium even at high concentrations.

The Dubinin-Raduskevich isotherm does not assume a homogenous surface or constant sorption potential. The linear Dubinin-Raduskevich equation is,

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (6)$$

Where  $q_e$  is the amount of dye adsorbed at equilibrium,  $\beta$  is a constant related to the adsorption energy,  $q_m$  is the theoretical saturation capacity,  $\epsilon$  is the Polanyi potential, that is equal to  $RT(1 + 1/C_e)$ . The slope of the plot of  $\ln q_e$  versus  $\epsilon^2$  gives  $\beta$  ( $\text{mol}^2/\text{kJ}^2$ ) and the intercept yields the sorption capacity,  $q_m$  ( $\text{mol/g}$ )<sup>[23]</sup>. The sorption free energy could be further calculated as follows;

$$E = -(2\beta)^{-1/2} \quad (7)$$

The  $E$  value can be used for estimating the type of adsorption process. Two main types of adsorption may occur: physical and chemical adsorption. In physical adsorption equilibrium is usually rapidly attained and easily reversible, because the energy requirements are small (usually no more than 4.2 kJ/mol). The chemical adsorption is specific and involves forces which are much stronger than those in physical adsorption. So the sorption energy for chemical adsorption

should be between 8 and 16 kJ/mol which is also indicates that the adsorption follows ion-exchange mechanism<sup>[24]</sup>.

Obtained results revealed that theoretical saturation capacity is 13.4 mg/g and  $\beta$  is  $-0.0023$ . The value  $E$  calculated as 14.7 kJ/mol which is between 8 and 16 kJ/mol. The result shows the adsorption was chemically occurred with ion-exchange mechanism. Our copolymer has  $-\text{NH}_2$  residue which is positively charged at pH 3 and carboxyl and sulfonyl groups of Direct Brown 2 is negatively charged. As a result, it is inevitable that the adsorption occurred in a chemical nature. This type of adsorption for dye removal studies is feasible because dye removal can be performed in a more controlled manner. Also, the calculated Gibbs free energy from Langmuir constant supports the result of Dubinin-Raduskevich isotherm model. Both results showed that synthesized copolymer is efficient to remove Direct Brown 2.

Each isotherm model can not be used to explain the related adsorption nature due to the properties of adsorbant material. Therefore, according to the correlation constants ( $R$ ), the best isotherm model fits to the dye adsorption by using copolymer is both Freundlich and Dubinin-Raduskevich isotherm models with 0.964 and 0.961 correlation constants, respectively. Both models can be used to explain dye adsorption process. All the adsorption isotherm curves can be seen in Figures 9a, b and c and constants can be seen in Table 2.

### 3.9 Adsorption kinetics

In order to investigate the mechanism of adsorption, several kinetic models are available to describe sorption kinetics. The pseudo-second order kinetic and intra-particle diffusion models were applied to test experimental data.

The pseudo-second order kinetic model is expressed as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where  $k_2$  (kg/g.min) is the pseudo-second order rate constant. The linear plot of  $1/q$  versus  $t$  gives the second-order rate constant and  $q_e$  (g/kg). This model is used to predict behavior over the whole range of adsorption and is in agreement with the chemisorption mechanism being rate-controlling step<sup>[25,26]</sup>.

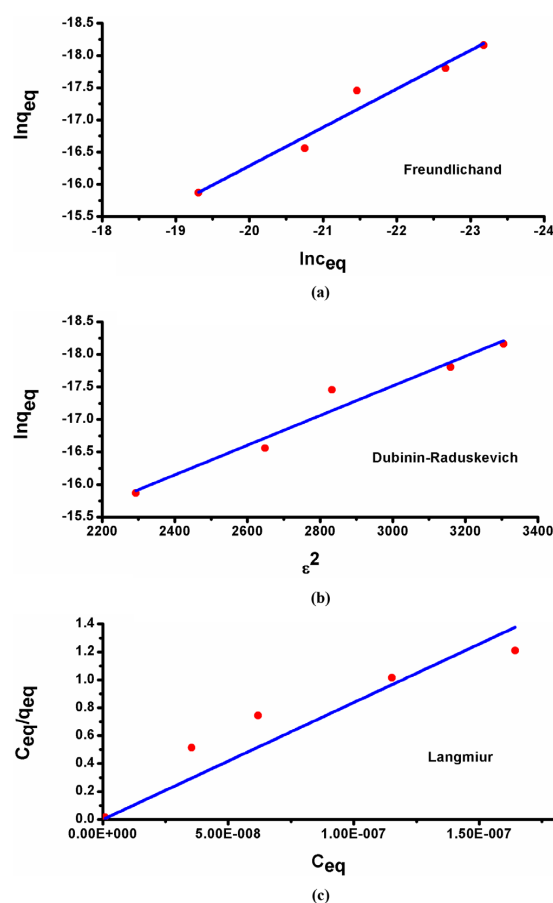
In order to identify the diffusion mechanism, the intra-particle diffusion model is expressed as:

$$q = k_p t^{1/2} + c \quad (9)$$

Where  $k_p$  (mg/g.min<sup>1/2</sup>) is the intra-particle diffusion rate constant and  $c$  (mg/g) is a constant which gives information about the thickness of the boundary layer. The plot of  $q$  versus  $t^{1/2}$  could yield a straight line passing through the origin if the adsorption process obeys the sole intra-particle diffusion model. The line does not pass through the origin; therefore,

intra-particle diffusion is not the only rate-limiting step. It could be stated that this process is complex and involves more than one mechanism<sup>[14]</sup>.

In our study, as seen in Figures 10a and b, the pseudo-second order kinetic model fits to the adsorption process with 0.999 correlation coefficient. This supports that the rate-limiting step of dye adsorption may be chemisorption. Thus, intra-particle diffusion model ( $R^2=0.978$ ) also confirms that intra-particle diffusion is not the only rate-limiting step and involves more than one mechanism because the line does not pass through the origin. The rate limiting step in our study is chemisorption mechanism. As seen in section 3.8, our adsorption occurred with ion-exchange mechanism which is also called chemisorption. The isotherm data and kinetic data comply with each other. Pseudo-second order and intra-particle diffusion kinetic models' constants were calculated and are given in Table 3.

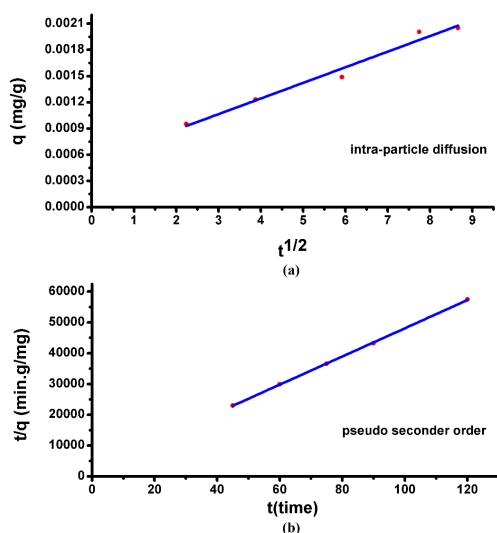


**Figure 9.** Freundlich isotherm (a), Dubinin-Raduskevich isotherm (b), and Langmuir isotherm (c), models.

**Table 2.** Langmuir, Freundlich and, Dubinin-Raduskevich isotherms constants for adsorption of Direct Brown 2.

Langmuir constants				Freundlich constants			Dubinin-Raduskevich constants			
Q <sub>0</sub> (mg/g)	b (L/mg)	R <sup>2</sup>	R <sub>L</sub>	K <sub>f</sub> (mol <sup>1-1/n</sup> L <sup>1/n</sup> g <sup>-1</sup> )	n	R <sup>2</sup>	q <sub>m</sub> (mg/g)	E (kJ/mol)	β	R <sup>2</sup>
7	0.006	0.943	1	0.013	1.7	0.964	13.4	14.7	-0.0023	0.961





**Figure 10.** Pseudo second-order kinetic model (a) and Intra-particle diffusion kinetic model (b).

**Table 3.** Pseudo-second order and intra-particle diffusion kinetic model constants for adsorption of Direct Brown 2.

	Pseudo-secondorder	Intra-particlediffusion
$k^2$ ( $\text{min}^{-1}$ )	89.5	-
$q_c$ (g/kg)	0.0022	-
$c$ (mg/g)	-	0.002
$K_p$ ( $\text{mg/g.min}^{1/2}$ )	-	0.005
$R^2$	0.999	0.978

## 4. Conclusions

In this study, we prepared Poly(AA-co-AMA) with different mole ratios by radicalic polymerization. The copolymers were used for removal of azo dye such as Direct Brown 2 from aqueous solution. The adsorption capacity was found to be highly dependent on the amount of the acrylamide, and pH of the solution. Adsorption capacity of poly(AA-co-AMA) copolymers was increased by increasing with amount of AA due to its positively charged  $-\text{NH}_2$  residue in given pH. The maximum adsorption capacity is found to be 100% at pH 3. The kinetic studies showed that the adsorption process was consistent with the pseudo second-order kinetic model, indicating the chemical adsorption was the rate-limiting step. The adsorption of Direct Brown 2 onto Poly(AA-co-AMA) copolymer correlated well with the Freundlich and Dubinin-Raduskevich equation compared to Langmuir equation. The copolymer which released 63% of the adsorbed dye in alkaline conditions has potential for re-usage. The novelty of this study is newly synthesized copolymer (PAMA) and its potential to remove azo dyes' from wastewater.

Consequently, the copolymer can be used as an effective adsorbent for the removal of Direct Brown 2, and has potential applications in related industrial and environmental areas.

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