Synthesis and Evaluation of the Ability of Poly(Methacrylic Acid-co-acrylamide)/nanoclay Composite Hydrogel in the Adsorption of Methylene Blue Dye

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Synthesis and evaluation of the ability of poly(methacrylic acid-co-acrylamide)/nanoclay composite hydrogel in the adsorption of methylene blue dye

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Abstract

The performance of poly(methacrylic acid-co-acrylamide)/nanoclay composite (poly(MAA-co-AAm)/NCC) hydrogel to adsorb methylene blue (MB) dye from aqueous solutions was investigated and the adsorption efficiency was improved by incorporating Cloisite 30B nanoclays in the adsorbent structure. The hydrogels were analyzed using FTIR, XRD, TGA, and SEM analysis. The effect of adsorbent dose, temperature, initial dye concentration, contact time, and pH on the efficiency of the adsorption process was investigated. Adsorption efficiencies of 98.57 and 97.65% were obtained for poly(MAA-co-AAm)/NCC and poly(MAA-co-AAm) hydrogels, respectively. Kinetic study revealed that the adsorption process followed pseudo-first-order kinetic model and α -parameter values of 6.558 and 1.113 mg/g.min were obtained for poly(MAA-co-AAm)/NCC and poly(MAA-co-AAm) hydrogels, respectively indicating a higher ability of nanocomposite hydrogel in adsorbing MB-dye. In addition, the results of the intra-particle diffusion model showed that various mechanisms such as intra-particle diffusion and liquid film penetration are important in the adsorption. The Gibbs free energy parameter of adsorption process showed negative values of -256.52 and -84.071 J/mol.K for poly(MAA-co-AAm)/NCC and poly(MAA-co-AAm) hydrogels indicating spontaneous nature of the adsorption. The results of enthalpy and entropy showed that the adsorption process was exothermic and random collisions were reduced during the adsorption. The equilibrium data for the adsorption process using poly(MAA-co-AAm)/NCC and poly(MAA-co-AAm) hydrogels followed Freundlich and Langmuir isotherm models, respectively. The maximum adsorption capacity values of 32.83 and 21.92 mg/g were obtained for poly(MAA-co-AAm)/NCC and poly(MAA-co-AAm) hydrogels, respectively. Higher adsorption capacity of nanocomposite hydrogel was attributed to the

presence of Cloisite 30B clay nanoparticles in its structure. In addition, results of R_L , n , and E parameters showed that the adsorption process was performed optimally and physically.

Keywords: Methacrylic acid-co-acrylamide copolymer, Hydrogel, Nanocomposite, Adsorption capacity, Aqueous solutions.

1. Introduction

Dyes are used as an important industrial raw material in many applications such as paper, textile and plastic industries [1]. The improper discharge of dye containing wastewater streams into the environment that can lead to many environmental problems [2]. In general, dyes can be classified into cationic, anionic, and nonionic categories [3]. Various studies have shown that among the various dyes used in industry, cationic dyes are more harmful because they easily bind to the cell cytoplasm [4, 5]. Methylene blue (MB) is one of the synthetic cationic dyes that is extensively used in industries such as textile, paper, pesticides, cosmetics, and printing due to its high solubility and stability in water [6]. Prolonged exposure to MB dye can cause various diseases such as vomiting, nausea, anemia, hypertension, respiratory failure, eye damage, local burns, increased transpiration, and mental disorders [7]. Therefore, it is important to eliminate contaminants such as dyes from industrial wastewater streams.

However, the refining of industrial effluents containing dyes is very difficult due to the presence of complex compounds with poor biodegradation, high pH and turbidity [8]. Various methods have been proposed to eliminate contaminants from wastewaters, however, most of them possess disadvantages such as high operating and maintenance costs, low performance, and production of toxic sludge [9]. Surface adsorption method has received much attention by many researchers due to the advantages of easy performance, high efficiency, no secondary sludge production, and environmental friendliness [10]. Various adsorbents such as different types of clay soils, natural fibers, carbon nanotubes, polymeric materials, zeolites, active carbon, and magnetic composites have been used for dye removal from aqueous solutions [11]. Clay soils show a high potential to adsorb heavy metals and organic compounds due to their suitable photochemical properties such as multilayer structure, high surface area, and high cation exchange capacity. Among the clay soils used, expandable layer silicates such as montmorillonite (MMT) have been recognized and used as adsorbents [12]. MMT clay is one of the low-cost adsorbents with a high cation exchange

capacity, which has the ability to absorb cationic pollutants due to high negative charges. Cloisite 30B is a natural MMT clay whose surface is modified by quaternary ammonium salts [13].

Polymeric hydrogels have received much attention due to their advantages such as ease of preparation, high tendency to absorb water, high porosity, ease of operation, and diverse morphology [14]. Hydrophilic cross-linked polymers that form a three-dimensional network with the ability to absorb large amounts of water and aqueous fluids form hydrogels [15]. These hydrogel adsorbents respond to process conditions such as pH, redox, ionic strength, light, electric field, etc. [16, 17]. In the adsorption process, the hydrogels absorb contaminants to their surface until they are saturated. After the complete saturation of hydrogels, they can be disposed of as agricultural fertilizer or compost due to their biodegradability [18]. Among the hydrogels used in the adsorption process, those produced based on poly(methacrylic acid) show good absorption properties due to inclusion of many functional groups in their structure. These functional groups provide active centers for the adsorption of dye molecules upon swelling of the hydrogel system [19].

In the present study, it was hypothesized that fabricating nanocomposite hydrogels using Cloisite 30B clay nanoparticles could increase the efficiency of the adsorbent to remove MB-dye. Thus, poly(methacrylic acid-co-acrylamide/nanoclay composite (PMAc-co-Ac/NCC) hydrogels were synthesized and characterized. Moreover, the effect of clay concentration, pH, temperature, contact time, adsorbent dose, and initial MB dye concentration on the efficiency of the adsorption process was investigated. After determining the optimal value of the desired parameters, thermodynamic, equilibrium, and kinetic studies of the process were examined.

2. Materials and Methods

2.1. Materials

Methacrylic acid (MAA) with a MW of 86.06 g/mol, acrylamide (AAM) with a MW of 71.08 g/mol, and N,N' methylene bis-acrylamide with a MW of 154.17 g/mol, potassium persulfate were obtained from Merck (Darmstadt, Germany). Cloisite 30B nanoclay powder was obtained from Southern Clay Co. (Austin, TX, USA). All chemicals prepared from the suppliers were pure and analytical grade.

2.2. Synthesis of poly(MAA-co-AAM) and poly(MAA-co-AAM)/NCC hydrogels

Firstly, 2 g of acrylamide (AAm) monomer was dissolved in 10 mL of distilled to get a homogenous solution. Then, 0.02 g of methylene bis-acrylamide as a cross-linker was poured to the above solution with magnetic stirring and the obtained mixture was added to the three-neck flask followed by addition of 4.8 mL of methacrylic acid (MAA) monomer under nitrogen atmosphere to remove oxygen from the reaction medium. Finally, 0.1 g of potassium persulfate was added as an initiator for free radical copolymerization reaction at a temperature of 70 °C under vigorous stirring (1200 rpm). The copolymerization reaction was completed in 2-5 h depending on the monomer concentration. After the reaction was completed, the poly(MAA-co-AAm) hydrogel was dried and pulverized. The method of preparation of poly(MAA-co-AAm)/NCC hydrogel followed the same procedure as explained for poly(MAA-co-AAm) hydrogel except that after the preparation MAA monomer solution, a suitable amount of Cloisite 30B nanoclay was added and the solution was sonicated for 40-60 min to form a homogenous mixture.

2.3. Swelling of hydrogels

Swelling is an important characteristic of a hydrogel system affecting its adsorption performance [20]. In the present study, the effect of Cloisite 30B nanoclay concentration on the swelling value of the nanocomposite hydrogels was investigated. To measure swelling per cent, 0.2 g of hydrogel with different nanoclay concentrations was dispersed in distilled water (50 mL) at room temperature and kept stirred overnight. Then, the hydrogels were separated from the aqueous medium and the swelling per cent was calculated using Eq 1.

$$\text{Swelling (\%)} = \frac{(W_s - W_i)}{W_i} \times 100 \quad (1)$$

where W_s and W_i are the weights of swollen and initial hydrogels, respectively.

2.4. Adsorption study of hydrogels

The adsorption of MB dye using two types of hydrogels was studied. The effect of various parameters such as monomers (AAm to MAA) ratio, nanoclay concentration, temperature, adsorbent dose, initial pH, contact time, and initial MB dye concentration on the adsorption process efficiency was evaluated. To investigate the effect of initial pH on the efficiency of the adsorption process, the initial pH in the range of 3-10 was evaluated at constant experimental conditions such as temperature of 25°C, contact time of 60 min, adsorbent dose of 1.5 g/L, MB dye concentration

of 10 mg/L and mixing speed of 500 rpm. When the optimal pH was determined, other parameters such as temperature (25-50°C), contact time (10-250 min), adsorbent dose (0.5-4 g/L) and the initial concentration of dye (10-100 mg/L) at the specified optimum pH were examined. The adsorbent was then separated from the aqueous solution and the percentage of MB-dye adsorption (R) and adsorbent adsorption capacity (q_e) were determined using the following Eqs:

$$R(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

$$q_t = \frac{(C_i - C_e)V}{m} \quad (3)$$

where C_i and C_e are the initial and final concentration of MB dye (g/L), V is the volume of the solution used (L), and m is amount of dry adsorbent used (g).

3. Results and discussion

3.1 Properties of hydrogel adsorbents

3.1.1 FTIR analysis

Fourier-transform infrared (FTIR) is a useful technique to specify chemical structures and possible interactions between the functional groups of constituents of a material [21]. FTIR spectra of Cloisite 30B nanoclay and both hydrogel adsorbents before and after the adsorption of MB dye are shown in Figure 1. Cloistite 30B nanoclay (Fig. 1a) exhibited characteristic peak at wavenumbers of 1045 cm^{-1} and 462-725 cm^{-1} attributed to the vibrations of Si-O-Si bonds [22] and Si-O-Al functional groups [23]. Both hydrogel adsorbents before adsorption process (Fig. 1 b,c) showed characteristics peaks at 3400-3445 cm^{-1} attributing to vibrations of -OH and -NH bonds, 2853-2928 cm^{-1} assigning to vibrations of the C-H bonds, 1545 cm^{-1} indicating ester groups, 1640-1645 cm^{-1} ascribing to -OH bond vibrations or the interaction between carbonyl and vinyl groups, 450-965 cm^{-1} demonstrating low-intensity vibrations of C=O, C-C, C-O bonds [24]. Hydrogel adsorbents after the adsorption process (Fig. 1 d,e) did not show large differences in their FTIR spectra, only minor changes in the range and intensity of peaks in their structure was observed, which could indicate that the bond between the MB dye molecule and the adsorbents' surface is physical due to weak Van der Waals forces [25].

Fig. 1. FTIR spectra of (a) Cloisite 30B nanoclay, (b) poly(MAA-co-AAm) hydrogel before adsorption, (c) poly(MAA-co-AAm)/NCC hydrogel before adsorption, (d) poly(MAA-co-AAm) hydrogel after adsorption, (e) poly(MAA-co-AAm)/NCC hydrogel after adsorption.

3.1.2 XRD analysis

X-ray diffraction (XRD) analysis can determine spacing distance or height in clay nanoparticles [26]. In this work, the XRD patterns of Cloisite 30B nanoclay and two types of adsorbents measured at θ range of $0.5-10^\circ$ are shown in Figure 2a. As the results show, a peak is observed in the structure of Cloisite 30B at 2θ of 4.25° indicating the crystalline phase (001) in its structure. The distance between the crystalline phases and clay galleries in the Cloisite 30B (d_{001}) determined using Bragg's law ($n\lambda = 2d_{001}\sin\theta$) was 1.94 nm. After the placement of Cloisite 30B in the structure of poly(MAA-co-AAm)/NCC hydrogel the peak of the 001-crystalline phase was completely disappeared, indicating that the silicate layers in the structure of the nanocomposite hydrogel had no accumulation. This also indicated that the polymer chains have been successfully placed between the Cloisite 30B composite silicate layers and exfoliated structure of nanocomposite has been performed successfully [27].

3.1.3 TGA analysis

Thermogravimetric analysis (TGA) is a technique to assess thermal stability of compounds by recording their weight loss as function of increasing temperature [28]. In this study, TGA was performed at a temperature range of 20-900°C. Fig. 2b shows TGA thermograms of both types of adsorbents. An initial weight loss as function of moisture evaporation occurred at 100-150 °C. The second weight of about 20% was seen at 150-300°C probably relating to degradation of acrylamide as well as hydrogel bonds [29]. The main characteristic peaks at this temperature range appeared at 196°C for poly(MAA-co-AAm) hydrogel and 201°C for poly(MAA-co-AAm)/NCC hydrogels. The degradation at 350-450°C was possibly related to the destruction of C-H bonds in methacrylic acid [30] structure, in which the hydrogels lost about 50 % of their initial weight. The major characteristic peaks at this temperature range appeared at a 388 °C for poly(MAA-co-AAm) hydrogel and 399 °C for poly(MAA-co-AAm)/NCC hydrogel. The final degradation stage occurred at 600-700 °C indicating the successful formation of a hydrogel. A total weight loss of 85-89% was observed from temperature of 20 to 900 °C. TGA results also indicated that the degradation of poly(MAA-co-AAm) hydrogel had a sharp slope compared to the poly(MAA-co-AAm)/NCC hydrogel which implies that the thermal stability of nanocomposite hydrogel was improved.

Fig. 2. a) X-ray diffraction (XRD) and b) thermo-gravimetric analysis (TGA) results of Cloisite 30B, poly(MAA-co-AAm), and poly(MAA-co-AAm)/NCC hydrogels

3.1.4 SEM results

SEM analysis was used to evaluate the surface morphology hydrogel samples before and after MB dye adsorption [31]. According to SEM results, Cloisite 30B nanoclay (Fig. 3a) showed a layered

structure that was in parallel with XRD results (Fig. 2a). Poly(MAA-co-AAm) hydrogel (Fig 3b) exhibited smooth surface while poly(MAA-co-AAm)/NCC hydrogel (Fig. 3c) showed rather rough surface with small grooves and pores that might be due to inclusion clay nanoparticles in the structure of the nanocomposite hydrogel. After the adsorption process of MB dye using the adsorbents, extensive changes were observed in the surface of the adsorbents indicating that the pores and grooves on the surface were covered, which could be due to the adsorption and placement of MB dye molecules on the surface of the adsorbents (Fig. 3d, e).

Figure 3. SEM images of a) Cloisite 30B nanoclay, b) poly(MAA-co-AAm) hydrogel before dye adsorption, c) poly(MAA-co-AAm)/NCC hydrogel before dye adsorption, (d) poly(MAA-co-AAm)/NCC hydrogel after dye adsorption and (e) poly(MAA-co-AAm) hydrogel after dye adsorption

3.2. Adsorption efficiency

3.2.1. Effect of MMA to AAm ratio in the copolymer structure

Reaction coefficients of monomers (r_1 and r_2) is a suitable criterion to evaluate the active presence of monomers in the copolymerization process. When the reaction coefficient of one monomer is higher than that of another monomer, the placement of the monomers in the copolymer structure will be random [32]. In the present study, the activity coefficients for MMA and AAm monomers were found to be 1.94 and 0.30, respectively, indicating a higher activity of MMA compared to AAm, and therefore, indicating its stronger contribution in the structure of the synthesized copolymer. To optimize the effect of MMA and AAm monomers on the efficiency of MB-dye adsorption, copolymers with MMA: AAm ratios of 1:2, 1:1 and 2:1 were synthesized and their effect on adsorption maximum efficiency was evaluated in experimental conditions (pH = 8, temperature = 25°C, adsorbent dose = 1.5 g/L, contact time = 60 min, initial dye concentration = 10 mg/L, and mixing speed = 500 rpm). Result showed that copolymers with MMA: AAm ratios of 1:2, 1:1 and 2:1 gave maximum efficiencies of 43.7, 83.4 and 93.5%, respectively. Thus, synthesized nanocomposite hydrogel adsorbent with MMA: AAm ratio of 2:1 provided the highest adsorption efficiency.

3.2.2. The effect of Cloisite 30B clay weight percent, adsorbent dose and pH

Effect of Cloisite 30B weight percent on swelling and adsorption efficiency of the poly(MAA-co-AAm)/NCC hydrogel adsorbent was investigated. As can be seen from Fig. 4a increasing weight percent of clay nanoparticles up to 10 %wt. increased swelling and adsorption efficiency of adsorbent. This might be related to involvement of more hydrophilic groups in the structure of nanoclay composite (NCC) adsorbent due to the presence of clay nanoparticles. Moreover, SEM analysis (Fig. 3c) of NCC adsorbent exhibited rough surface with small grooves and pores, which could imply for its increased swelling and adsorption. Weight concentration of 10% was found to be an optimum amount of nanoclay incorporation and concentrations more than 10 %wt. decreased swelling and adsorption efficiency again. This can be probably explained by the fact that at higher concentration clay nanoparticles becomes accumulated among copolymer chains in the formed hydrogel system, which reduces the penetration of MB-dyes molecules in NCC adsorbent structure [5].

Fig. 4b demonstrates the effect of adsorbent dose at concentration of 0.5 - 4 g/L on adsorption efficiency of NCC adsorbent. Increasing adsorbent dose from 0.5 to 4 g/L increased adsorption efficiency from 79 to 96% for poly(MAA-co-AAm) hydrogel and 87 to 99 % for poly(MAA-co-

AAm)/NCC hydrogel. This can be explained by possible increased number of unsaturated active sites providing sufficient surface area for MB-dye adsorption as a result of increased adsorbent does [3]. In addition, adsorbent dose of 1.5 - 2 g/L was found to be an optimum dose to improved adsorption efficiency, since no further increase was seen beyond this concentration.

Initial pH is regarded as an important factor of adsorption that can influence surface load and thereby, functional groups' ionization degree on adsorbent surface [33, 34]. The effect of initial pH on the efficiency of MB-dye adsorption process using two types of hydrogel adsorbents is shown in Fig. 4c. Increasing the initial pH from 3 to 8, significantly increased adsorption efficiency of both adsorbents. A maximum efficiency was obtained at pH = 8. Alkaline pHs (pH > 8) did not significantly increase adsorption efficiency. At acidic conditions (pH < 5), the adsorption process efficiency was low, which could be due to various factors such as 1) the competition among H⁺ ions and MB-dye molecules to be located on the adsorbent surfaces, 2) high density positive charges of adsorbent surface produce electrostatic repulsion forces between the surface and MB-dye molecule [35]. Higher adsorption efficiency of adsorbents at pHs > 5 can be explained by reduction of the density of H⁺ charges on the adsorbent surface, which leads to initiation of negative charge and increase in the number of deprotonated COOH groups at the adsorbent surface [36], which can increase adsorption performnace.

Figure 4. a) effect of Cloisite 30B clay concentration on swelling and adsorption efficiency of poly(MAA-co-AAm)/NCC hydrogel (at adsorbent dose of 1.5 g/L, pH of 8, temperature of 25 °C, contact time of 60 min, dye concentration of 10 mg/L, and mixing speed of 500 rpm, b) effect of adsorbent dose on adsorption efficiency of both types of hydrogels, and c) effect of pH on adsorption efficiency of both types of hydrogels.

3.2.3. Thermodynamic study and effect of temperature

Fig. 5a shows temperature effect on the adsorption efficiency of both types of adsorbents. Heating from 25 to 40 °C significantly decreased the efficiency of MB-dye adsorption. Thus, a temperature of 25 °C was found as an optimum temperature for the adsorption process. This could be related to exothermic nature of process that heating adversely affects the adsorption. To investigate thermodynamic parameters such as enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°) were calculated using Eqs. 4 and 5.

$$\Delta G^{\circ} = - R T \ln K_D \quad (4)$$

$$\ln K_D = \frac{-\Delta H^{\circ}}{R T} + \frac{\Delta S^{\circ}}{R} \quad (5)$$

Where R is the universal gas constant, T is the absolute temperature (K), K_D is the equilibrium constant ($K_D = C_A / C_e$), C_A and C_e are the concentration of MB-dye adsorbed and the concentration of dye remained after adsorption.

The linear relationship of $\ln K_D$ vs. $1/T$ for the determination of thermodynamic parameters is shown in Fig. 5b and the thermodynamic parameters determined for the MB-dye adsorption process is presented in Table 1. The negative values were obtained for ΔG° using both types of adsorbents indicating that the adsorption process is considered as spontaneous and desirable. ΔH° values of poly(MAA-co-AAm) hydrogel and poly(MAA-co-AAm)/NCC hydrogel were -84.071 kJ/mo and -106.153 kJ/mol, respectively, indicating that the adsorption is exothermic [37] emphasizing on role of temperature in the process. In addition, negative values were obtained for ΔS° parameter, which indicates that the collisions between the MB-dye molecules with the adsorbent surface are not random and the random collisions were decreased during the adsorption process.

Figure 5. a) the effect of temperature on the efficiency of the adsorption process (at optimal adsorbent dose, initial pH of 8, dye concentration of 10 mg/L, contact time of 60 min, and mixing speed of 500 rpm), and b) linear relationship of Van-t-Hoff for determination of thermodynamic parameters

Table 1. Thermodynamic parameters for MB-dye adsorption process using two types of adsorbents

Adsorbent	T (°C)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol.K)
Poly(MAA-co-AAm) Hydrogel	25	-7.504	- 84.071	- 256.52
	30	-6.353		
	35	-4.805		
	40	-4.425		
	45	-2.035		
Poly(MAA-co-AAm/NCC (10 %wt.) Hydrogel	25	-10.493	- 106.153	- 321.934
	30	-8.617		
	35	-6.038		
	40	-5.651		
	45	-3.969		

3.2.4. Kinetic study and the effect of time

Equilibrium contact time is an important factor in economic wastewater treatment systems [38]. Rapid absorption of contaminants (such as heavy metals) and equilibrium in a short period of time indicates the effectiveness of the adsorbent used in the wastewater treatment process [39]. Fig. 6a demonstrates the effect of contact time (10 - 250 min) on the efficiency of the adsorption process. Increasing contact up to 80 min increased the adsorption efficiency followed by a reduction after 80 min. The increase in the efficiency of the adsorption process by increasing contact time can be due to the presence of sufficient surface and empty active sites for the placement of MB-dye molecules. After 80 min, the adsorption process reached an equilibrium.

Kinetic behavior is an important parameter that controls the amount of contaminant adsorption and the time of adsorption process. Kinetic behavior of MB-dye adsorption using two types of adsorbents was studied in time range of 10 - 250 min. Pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich and intra-particle diffusion kinetic models were used according to Eqs. 6 - 8 [40]:

$$\text{Pseudo - First - Order : } q_t = q_e (1 - e^{-k_1 t}) \quad (6)$$

$$\text{Pseudo - First - Order : } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (7)$$

$$\text{Elovich : } q_t = \frac{1}{\beta} \ln(\alpha \beta t) \quad (8)$$

Where q_t and q_e are dye adsorption capacity per grams of dry adsorbent determined from experimental results and kinetic models (mg/g), k_1 is the constant rate of adsorption (min^{-1}), k_2 is the constant rate of pseudo-second-order kinetic model (g/mg.min), α is the initial absorbance (mg/g.min), and β is the desorption constant (g/mg).

Nonlinear relationship of PFO, PSO and Elovich kinetic models for MB-dye adsorption process using both types of adsorbents (at 10 %wt. of clay nanoparticles) are shown in Fig. 6b, c and the variables determined using these models are reported in Table 2. Results showed that the kinetic behavior of the adsorption process followed the PFO model, since this model provides a higher correlation coefficient compared to other models and its root-mean-square error (RMSE) is lower. The PFO kinetic model showed that chemical reactions do not play an effective role in the MB-dye adsorption process. In addition, α parameters for poly(MAA-co-AAm) hydrogel and poly(MAA-co-AAm/NCC hydrogel were determined to be 1.113 and 6.558 mg/g.min, respectively indicating the higher performance of NCC adsorbent to adsorb MB-dye [41].

The intra-particle diffusion model assumes that the capacity of dye adsorption changes with the expression $t^{1/2}$, which has been used in previous research to study the kinetics of the adsorption [42]. The linear relationship of the intra-particle diffusion model is shown in Eq. 9:

$$\text{Intra-particle Diffusion : } q_t = K_{\text{int}}\sqrt{t} + I \quad (9)$$

Where K_{int} ($\text{mg/g.min}^{1/2}$) is the parameter of intra-particle diffusion rate, which is determined from the slope of the q_t diagram vs. $t^{1/2}$ (Fig. 6d). According to this model, if the q_t plot vs. $t^{1/2}$ is a straight line, the intra-particle diffusion is the limiting step in the adsorption process, and if the plot is not a straight line, the liquid film diffusion is the limiting adsorption process [43]. The constants and correlation coefficient (R^2) of the intra-particle diffusion model are reported in Table 2. According to Fig. 6d, the q_t versus $t^{1/2}$ diagram for the MB-dye adsorption process is not a straight line, indicating that the adsorption process using these adsorbents is complicated process and includes adsorption and intra-particle diffusion [48].

Figure 6. a) effect of contact time on the efficiency of the adsorption process (at optimal adsorbent dose, initial pH of 8, temperature of 25 °C, dye concentration of 10 mg/L, mixing speed of 500 rpm), b, c) nonlinear relationship of kinetic models for MV-dye adsorption process using two types of adsorbents (containing 10 % wt. of clay nanoparticles), and d) linear relationship for intra-particle diffusion model

Table 2. Kinetics constants and variables determined for adsorption process using both adsorbents

Kinetic model	Poly(MAA-co-AAm) hydrogel	Poly(MAA-co-AAm)/NCC hydrogel
Pseudo-first order Model		
$q_{e,cal}$	4.981	6.635
K_1	0.041	0.06
R^2	0.9812	0.9875
RMSE	0.1524	0.132
Pseudo-second order Model		
$q_{e,cal}$	5.598	7.255
K_2	0.01	0.013
R^2	0.9391	0.9362
RMSE	0.2742	0.2983

Elovich equation		
α (mg/g.min)	1.113	6.558
β (g/mg)	1.025	1.015
R^2	0.8277	0.7588
RMSE	0.4612	0.58
Intraparticle diffusion Model		
$K_{i,1}$ (mg/g.min ^{1/2})	0.6332	0.8222
I_1 (mg/g)	0.0929	0.7474
R^2	0.9955	0.9928
$K_{i,2}$ (mg/g.min ^{1/2})	0.0072	0.0082
I_2 (mg/g)	4.8261	6.5079
R^2	0.915	0.9749

3.2.5. Isotherm study and the effect of initial concentration of MB-dye

Fig. 7a shows the effect of the initial concentration of MB-dye in the range of 10-100 mg/L on adsorption efficiency. A maximum adsorption efficiency (98.6%) was obtained at dye concentration of 10 mg/L. Our results indicated that initial dye concentration is regarded as a negative factor reducing the efficiency of the adsorption process. Increasing the dye concentration led to decrease in adsorption efficiency. This is due to the fact that higher concentrations of dye molecules either limit existing active sites on adsorbent molecules or increase electrostatic repulsion forces between the adsorbent surface and MB-dye molecules [44].

In the adsorption process, the study of equilibrium concentration is an important and effective parameter, because it shows the relationship between the adsorbed phase (contaminant) in the aqueous solution and the adsorbent surface. To study the equilibrium behavior, different isotherm models can be used. In the present study, the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models have been used. The nonlinear relationship of the isotherm models is shown in Eqs. 10 - 12, respectively:

$$\text{Langmuir : } q_e = \frac{q_m k_L C_e}{1 + k_L C_e}, \quad R_L = \frac{1}{1 + K_L + C_o} \quad (10)$$

$$\text{Freundlich : } q_e = k_f C_e^{\frac{1}{n}} \quad (11)$$

$$\text{Dubinin - Radushkevich : } q_e = q_m \exp (-\beta \varepsilon^2), \quad \varepsilon = R T \ln \left(1 + \frac{1}{C_e}\right) \quad (12)$$

Where q_e and q_m are equilibrium and maximum adsorption capacities (mg/g), respectively, K_L is the Langmuir model constant, k_f and n are the Freundlich model constants, R is the universal gas constant, T (K) is the absolute temperature, ε is the Polanyi coefficient, and β is the activity coefficient (mol^2/J^2).

Fig. 7c and d show the nonlinear relationship of the isotherm models for the MB-dye adsorption both types of adsorbents and the constants and variables determined for the adsorption process are reported in Table 3. Based on results, the equilibrium data of the MB-dye adsorption using poly(MAA-co-AAm) and poly(MAA-co-AAm/NCC followed the Langmuir and Freundlich models, respectively (with higher R^2 and lower RMSE). Therefore, homogeneous and heterogeneous surfaces have an effective role in the adsorption process. In addition, the value of K_L parameter showed that the ability of poly(MAA-co-AAm/NCC hydrogel was higher than that of poly(MAA-co-AAm) hydrogel in MB-dye adsorption. The values of the R_L and n parameters showed that the adsorption process is desirable. The value of parameter ε for MB-dye adsorption using poly(MAA-co-AAm) hydrogel and poly(MAA-co-AAm/ gave values of 1.634 and 2.179 kJ/mol, respectively concluding that the adsorption process is physical ($\varepsilon < 8$ kJ/mol) [10].

Figure 7. a) effect of MB-dye initial concentration on the adsorption efficiency (at optimal adsorbent dose, pH of 8, temperature of 25 °C, optimum contact time, mixing speed of 500 rpm), nonlinear relationship of isotherm models for MB-dye adsorption process using b) poly(MAA-co-AAm) hydrogel and c) poly(MAA-co-AAm)/NCC (10 %wt Cloisite B)

Table 3. Constants and variables determined using isotherm models for MB dye adsorption process using the desired adsorbents

Models	Parameters	Poly(MAA-co-AAm) hydrogel	Poly(MAA-co-AAm)/NCC (10 %wt Cloisite B) hydrogel
Langmuir	q_m (mg/g)	21.92	32.83
	K_L (L/mg)	0.7443	0.9407
	R^2	0.9752	0.9302
	R_L	0.013-0.118	0.0105-0.096
	RMSE	1.11	2.986
Freundlich	n	4.462	4.216
	K_f (mg/g (L/mg) ^{1/n})	9.96	15.13
	R^2	0.9352	0.9687
	RMSE	1.792	2
Dubinin–Radushkevich (D-R)	E (KJ/mol)	1.634	2.179
	q_m (mg/g)	19.51	28.86
	$\beta \times 10^{-7}$ (mol ² /J ²)	1.872	1.053
	R^2	0.8365	0.7759
	RMSE	2.847	5.351

Table 4. Comparison of adsorption capacity of poly(MAA-co-AAm) and poly(MAA-co-AAm)/NCC (10 %wt Cloisite B) hydrogels with other adsorbents used in MB-dye adsorption process

Adsorbent	MB dye	Reference
MIL-101(Cr)	22	[45]
Wheat shells	21.50	[46, 47]
CMC/kC/AMMT composite beads	10.75	[48]
Starch-based high-performance adsorptive hydrogel	296.766	[49]
N-isopropylacrylamide/itaconic acid/pumice composite hydrogel	22.18	[50]
Poly(AMPS-co-IA)	24.10	[51]
P(NIPAAm/IA)	17.67	[51]
Activated lignin-chitosan composite extrudates	36.25	[52]
CMC/graphene oxide hydrogel	58.24	[53]
Poly(MAA-co-AAm)	21.92	Present study
Poly(MAA-co-AAm)/Cloisite 30B (10 % wt.)	32.83	Present study

4. Conclusions

In the present study, synthesized poly(MAA-co-AAm) and poly(MAA-co-AAm)/NCC hydrogels by radical polymerization method was used to adsorb MB-dye. FTIR, TGA, XRD and SEM analysis showed that the synthesized adsorbents were successfully developed and the silicate layers of Cloisite 30B nanoclay were successfully placed between nanocomposite copolymeric chains. Poly(MAA-co-AAm)/NCC hydrogels adsorbent exhibited superior adsorption efficiency compared to poly(MAA-co-AAm) hydrogel. Meanwhile such adsorbent had an advantage of application at lower concentration dose using low contact time. Thermodynamic study revealed exothermic and spontaneous nature of adsorption process using both types of adsorbents. Also, the equilibrium behavior of poly(MAA-co-AAm) and poly(MAA-co-AAm)/NCC followed the Langmuir and Freundlich models, respectively. The values of R_L , n and ϵ parameters showed that the adsorption process is desirable and physical. The kinetic behavior of the adsorption process followed the pseudo-first-order kinetic model, which shows the low effect of chemical events in the adsorption process. In addition, the intra-particle diffusion model showed that various mechanisms such as intra-particle diffusion and liquid film penetration are effective in the adsorption process. Therefore, based on the mentioned results, it can be stated that the use of poly(MAA-co-AAm) and poly(MAA-co-AAm)/NCC hydrogels can be a promising method in removing MB-dye from aqueous solutions and can be used to purifying dye containing aqueous solutions.

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