



Methylene Blue Cationic Dye Removal using AA-Am Hydrogel As An Efficient Adsorbent

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Abstract

Hydrogel of acrylic acid-acrylamide (AA/Am) has been prepared to investigate its efficiency in the adsorption of a toxic cationic methyl blue (MB) dye from synthetic aqueous solutions. Batch conditions of various pH, initial dye concentrations, adsorbent doses, ionic strength and temperatures have been studied. The optimum conditions of MB dye adsorption were at a contact time of four hours, 1.5 g/l of hydrogel, in an aqueous solution of pH 10, at 40 °C, and the % removal of the dye under these conditions reached about 95%, and the dye adsorption kinetic process has been analysed using pseudo first and second-order kinetic models. The results presented that the adsorption kinetics of MB dye followed a pseudo second-order model very well. FTIR, SEM and XRD tests have been also conducted to illustrate the properties and characterizations of the prepared hydrogel.

Key words: Acrylamide, Acrylic Acid, Hydrogel, Dye Removal, Methylene Blue, Wastewater treatment.

1. Introduction

Wastewater is one of the most important environmental barriers to the growth of the different industries specially the textile industry. Many types of synthetic dyes are used and thus large amounts of highly pigmented wastewater are discharged into the textile industry as the absorption of these dyes by fabrics is very poor [1].

Dyes are colored compounds that give materials their various hues and make them resistant to washing, light, air, acids, and bases [2-3]. Due to their high solubility in water, industrial dyes are one of the most frequent forms of water pollutants, and industrial wastewater requires chemical treatment to remove dangerous chemicals and fulfil legal limits before being released to public sewage systems or surface waters [4].

Removing dyes from wastewater and making them usable, while continuing to develop new technological systems to remove organic pollutants present in water, such as dyes and heavy metals, from

their aqueous solutions, using methods such as adsorption, filtration, sedimentation, ion exchange, and others [5-7]. Adsorption research has shown two forms of adsorption: physical adsorption and chemical adsorption, with physical adsorption bonding occurring similarly to chemical bonding. This adsorption is particular, in the sense that it must occur owing to the presence of a certain surface, under specified circumstances, and with activation energy [8].

Hydrogel polymers are now frequently employed in wastewater treatment due to their apparent ability to efficiently flocculate at low concentrations [9]. Hydrogels are three-dimensional, cross-linked aqueous polymers that may expand in water or an aqueous solution several hundred times their dry volume without melting.

Hydrogels have hydrophilic groups including OH, CONH₂, COOH, and SO₃H, which may adsorb and trap ionic dyes via ion exchange, electrostatic

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attraction, hydrogen bonding, van der Waals force, and catastrophic water interaction [10].

The major components used in the creation and processing of hydrogels are acrylic acid and acrylamide (AA/Am). Because acrylic acid reacts well with electrophilic agents and free radicals, free radical polymerization is widely utilized to make acrylic acid hydrogels [11].

Acrylic acid is a crosslinked monomer used to make high-water-swelling hydrogels as strength and pH sensitivity. Additionally, acrylic acid monomers are combined with other polymers to create a variety single or multicomponent system [12]. It has a carboxylic acid group connected to a phenyl group, as well as a carboxylic end. The inclusion of ionized carboxylic acid groups improves the hydrogel's ionic of hydrogel morphologies [13].

The most prevalent form of hydrogel is acrylamide-based hydrogels, which are tiny molecular weight monomers that exhibit a substantial size mutation in response to physical and chemical stimuli. Water stability is lacking in this hydrogel, which can be improved by using acrylamide with groups like alkyl and alkyl hydroxyl. Furthermore, the amide group reaction converts acrylamide and polyacrylamide polymers into a variety of components [14-15].

The aim of this research was to prepare grafted chitosan hydrogel with (acrylamide-acrylic acid), and then study its swelling kinetics after investigation of a suitable mathematical model which may be used to describe it.

2. Materials and Methods

2.1 Materials

Acrylic acid (AA) with molecular weight 72.06 g/gmol (Research Lab) and acrylamide (Am) (Baker Chemical Co., USA) were used as starting monomers for the preparation of the super-adsorbent hydrogel. Potassium persulfate (KPS) were supplied from Merck, Germany as an initiator. Methylene bis-acrylamide (MBA) as a cross linker was supplied from Fluka-Germany. Methylene Blue (MB) dye was produced from Oxford lab Fine Chem LLP. (Mwt 319.86). Hydrochloric acid, sodium hydroxide and ethanol were used for washing and pH adjustment. All experiments were performed using RO water.

2.2. Methodology

2.2.1 Preparation of AA/Am Hydrogel

Acrylic acid has been neutralized using 5M NaOH. Acrylamide crystals were made by dissolving

acrylamide monomer in a large volume of cold acetone, then cooling the solution to 10°C and drying the crystals. 30 ml neutralized acrylic acid and 400 ml DW were mixed with 6 g acrylamide crystals. As a cross-linker and initiator, 0.005 g/ml MBA and 0.1 g/l KPS were added, and the reaction mixture was heated at 70°C for 1 hour [15].

The produced hydrogel was washed with 70% ethanol. The produced hydrogel was filtered and dried at 70°C using convection oven, (113 Litters, 30-250°C Model 1350 GM, WWR Scientific) until constant weight was achieved, Figure (1) shows the synthesis scheme of poly (acrylic acid-co-acrylamide) copolymer.

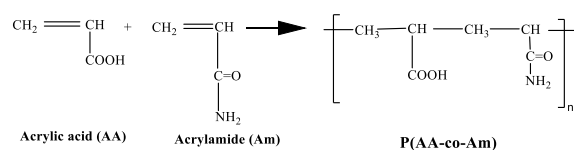


Figure 1: Chemical Reaction of preparing Poly(Acrylic Acid- Acrylamide) Copolymer

2.2.2. Characterization

The structure of the produced hydrogel was determined using Fourier transform infrared spectroscopy (FTIR) on an FT/IR-6100 type A Jasco Japan TGS detector with an absorbance range of 500 to 4000 cm^{-1} and a scanning speed of 2 mm/s . A scanning electron microscope (SEM) model QUANTA FEG 250 was used to examine the surface morphology of the produced hydrogel samples.

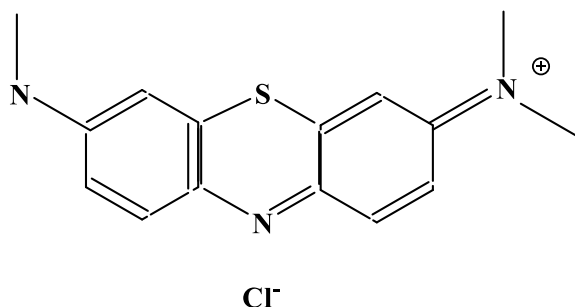
The temperature of the powdered material was elevated 10 degrees Celsius per minute up to 500 degrees Celsius for the thermal analysis using a Shimadzu TGA-50H. Philips X-Ray Diffraction apparatus PW/1710 with Monochrom TOR, Cu-radiation at 40 K.V., 35 mA, and scanning speed of 0.02 degree /sec was used for XRD analysis.

2.2.3. Dye Solution Preparation

The properties and the structure of methylene blue dye are illustrated in Table (1) and Figure (2). MB dye was accurately weighed and then dissolved in RO water to prepare a concentrated stock solution of 1 g/l from which dilute solutions were prepared for experiments according to the required dye concentrations. The absorbance values of the prepared solutions were measured to confirm their concentrations with a spectrophotometer at 660 nm.

Table (1) Properties of Methylene Blue [1]

Chemical formula	C ₁₆ H ₁₈ ClN ₃ S
Molecular weight	319.85 g/mol
Melting point	100–110 °C
Density	1.0 g/ml at 20 °C
Water Solubility	40 g/l at 20 °C
λ _{max}	660 nm

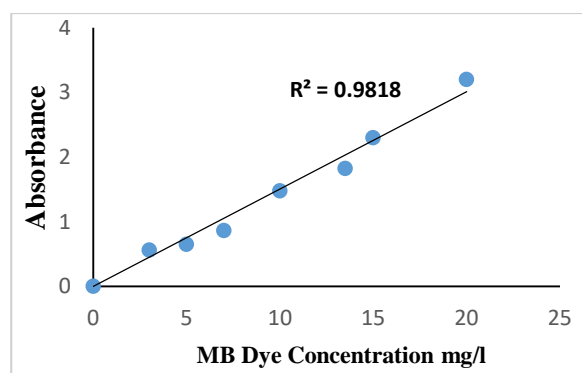
**Figure 2: Structure of Methylene Blue Dye**

2.2.4 Spectroscopic Measurements

Electron absorption spectra of the dye solution samples were recorded by JENWAY 6310 Spectrophotometer at maximum wavelength of 660 nm.

2.2.5 Calibration of MB in Aqueous Solution

The calibration curve is illustrated in Figure (3), was plotted using a spectrophotometric measurement of the colour absorption at different known dye concentrations, and the measurements were confirmed by repeating it three times. The calibrated results are very effective in determining the relevant adsorption capabilities of the various adsorbents where the R² value was > 98%. Figure (3) shows the graphical representation of the methylene blue dye calibration.

**Figure 3: Calibration Curve**

2.2.6 Swelling Measurements

The dried hydrogel samples were immersed in RO water with different pH value (3, 5, 7, 9 and 11) and with different ionic strength (0.1%, 2% and 3%). Samples were taken then weighed after indicated time intervals where the excess water on their surface was gently removed by filter paper.

Swelling ratio (SR) is calculated by the following Equation (1) [14]:

$$SR (\%) = \left[\frac{W_s - W_d}{W_d} \right] \times 100 \quad (1)$$

Where, W_s and W_d are the weight of the swollen and dry samples, respectively. SWR was calculated as grams of absorbed water per grams of dry hydrogel (g/g).

2.2.7 Adsorption Studies

In the MB solutions, a specific amount of the produced (AA/Am) hydrogel was introduced in accurate volumes and concentrations. The combination was filtered after a given amount of contact time, and the filter liquor was obtained.

Absorbance of MB solutions before and after adsorption was measured at 660 nm on a JENWAY 6310 spectrophotometer using RO water as a blank solution. After the adsorption process, the calibration curve was used to define the concentration of MB solutions and subsequently, the adsorption capacity and the removal rate have been calculated according to Equations. (2) and (3) [16], respectively:

$$q_t = \frac{C_0 - C_t}{m} V \quad (2)$$

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

Where: q_t is the amount of adsorbed dye per unit mass of a hydrogel (mg/g); V is the volume of aqueous solution (l), and m is the amount of adsorbent (g), C₀ and C_t are the initial and residual concentrations of dye (mg/ml) at a given time t, respectively.

3. Results and Discussion

Figure (4) demonstrates the produced poly AA/Am hydrogel.



Figure 4: Produced Poly (Acrylic Acid-Acrylamide) Copolymer Hydrogel.

3.1 SEM

Scanning Electron Microscopy was used to investigate the surface appearance and structure of copolymers. The raw AA seems to be spherical in form with a smooth surface as shown in Figure (5). Due to the absence of a spherical form and the existence of a large network structure and more pores, the generated hydrogel has a noticeably different surface morphology [17].

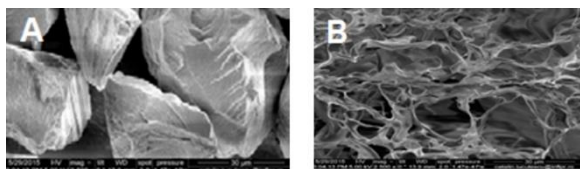


Figure 5: SEM for (A) Am and (B) (AA-Am) hydrogel.

3.2 Thermogravimetric Analysis (TGA)

TGA curves up to 500 °C for raw monomers and the prepared hydrogel are depicted in Figure (6). For AA, Am and the prepared hydrogel, 3 stages have been noticed: the 1st stage represents a continuous weight loss starting from the beginning of heating up to 100°C getting 22%, 16%, 15% & 12% weight decrease, respectively.

Which may be attributed to the loss of adsorbed water? The 2nd & 3rd of the decompositions process happens at nearly 235°C and 400°C, respectively, weight loss of 83%, 74%.71% and 65% for the four samples were due to the degradation of AA and the hydrogel chains and formation of methane, water and carbon monoxide [18-19]. Thus, it can be concluded that, the prepared hydrogel has lower degradation

temperature can lead to formation of compounds with more thermal stability [20].

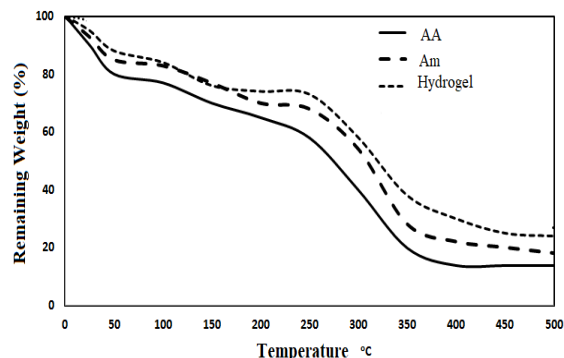


Figure 6: TGA of Acrylic Acid, Acrylamide, and the Synthesized Hydrogel.

3.3 FTIR

In comparison to the raw monomers, FTIR was utilized to characterize the structure of the synthesized hydrogel. The FTIR spectra of Poly (Am-AA) hydrogel, acrylamide, and acrylic acid monomers are shown in Figure (7). It's worth noting that several peaks in the manufactured hydrogel have vanished. The peak assigned to the vibration of H in C=C-H at 990 cm⁻¹ is almost visible in the band of acrylic acid and acrylamide, but it becomes weaker in the spectrum of the prepared hydrogel; where, the peak indicated by C-C (1166 cm⁻¹) becomes obvious in the band of synthesized hydrogel, which may be attributed to polymerization reaction has occurred the hydrogel has been obtained [13].

Due to the steric effect generated by the creation of the network structure, N-H and O-H vibrations have a blue shift, and the adsorption peak of C-H in the methylene group is evident at 2950 cm⁻¹, but the peak ascribed to the vibration of H in CH₂=CH-COOR at 3030 cm⁻¹ has vanished. Furthermore, the hydrogen bond stretching vibration of methylene in saturated compounds is greater, and the distinctive peak has moved due to the reduction of conjugate effect when the carbon-carbon double bond reaches saturation state following the polymerization process [21].

There were two primary peaks seen in the spectra of both acrylic acid and acrylamide, as well as in the synthesized hydrogel, in the band range between 1600 and 1800 cm⁻¹, although in different places. The peaks occurred in acrylamide, and the C=C and C-O vibration-induced peaks were relocated to 1612 and 1673 cm⁻¹, respectively.

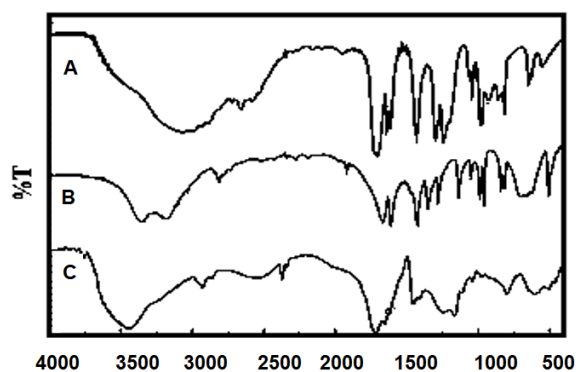


Figure 7: FTIR Spectra of (A) Acrylic Acid, (B) Acrylamide, and (C) AA-Am Hydrogel

The C=C and C-O vibrations are ascribed to the 1630 and 1700 cm^{-1} bands of acrylic acid, respectively. The peaks induced by C=O (1730 cm^{-1}), C-O (1670 cm^{-1}), (1655 cm^{-1}), C-C (1615 cm^{-1}), O=C-O (1560 cm^{-1}) are overlapped to a tune spectrum, leaving only two small peaks (1715, 1665 cm^{-1}) indicative of C=O vibration remarkable, indicating that the targeted hydrogel had been successfully synthesized [22].

3.4 Effect of pH on Hydrogel Swelling

Figure (8) shows the effect of pH on the swelling ratio of poly-AA/Am hydrogel at 20°C in different solutions with pH 3 to 11, and the equilibrium swelling ratio was affected by changing pH of the swelling solution where swelling ratios are improved with increasing value of pH from 3 to 9 where, hydrogel shows a maximum swelling ratio (95%) at pH 9 and minimum (63%) at an acidic medium pH 3, but the trend is changed at pH 11 where it exhibits the least swelling ratio (50%).

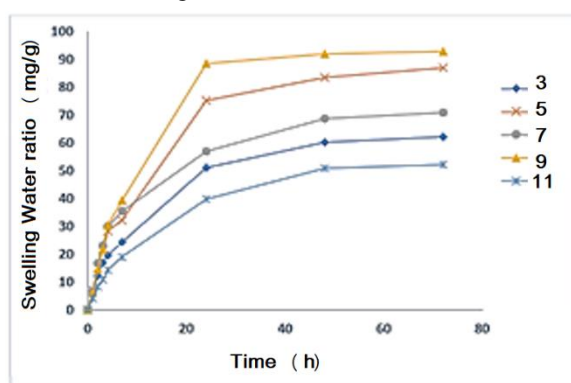


Figure 8: Effect of pH on poly Hydrogel Swelling.

This impact might be due to the creation of a hydrogen bond between the -COOH of AA and the -CONH₂ of the Am units in the hydrogel at lower pH levels, resulting in polymer-polymer interactions

prevailing over polymer-water interactions, lowering the water swelling ratio.

But with increasing the pH, it can be noticed that, the swelling of the hydrogels increases significantly. This may be attributed to the carboxyl group of AA in the hydrogel because the electrostatic repulsion force acting between the charged carboxyl groups of AA increases the wetting of the hydrogels, causing swelling. Conversely, the hydration of hydrogels decreases with decreasing pH value because the electrostatic repulsion force disappears between the uncharged carboxylic groups.

As a result, this causes the hydrogels to expand due to the higher electrostatic repulsion, and thus the swelling capabilities of the hydrogels are increased. on the other hand, the swelling loss for the highly basic solutions (pH 11) may be due to the effect of charge screening of overabundant Na⁺ ions in the swelling medium, where the carboxylate anions were shielded and the anion-anion repulsion effective was banned [12,22].

3.5 Effect of Ionic Strength on Swelling

Different concentrations of a saline solution have been used. The results showed that when the concentration of cations is increased, a stronger “charge sifting effect” is achieved, which causes insufficient electrostatic and anion repulsion and a decrease in the osmotic pressure between the polymer network and the external solution.

Therefore, the swelling ratio of the AA/Am hydrogel was reduced. In most cases, the swelling capacity of ionic hydrogels in saline solutions is much lower than in pure water. Because the ions linked to the polymer network are stationary and are regarded isolated from the outside solution by a semi-permeable barrier, it is generated by the unequal osmotic pressure of the ions in the medium and the polymer network [2]. Because the external solution contains Na⁺ and Cl⁻, the build-up of osmotic pressure is significantly slower.

Furthermore, when the swelled hydrogel is placed in solutions containing various concentrations of NaCl, the presence of sodium ions in the external solution causes a decrease in the osmotic swelling pressure, which is caused by the difference in counter ions between the gel phase and the solution phase.

The difference between the concentrations of counter ions in the gel phase and the solution phase diminishes as the concentration of sodium ions in the swelling medium rises, lowering the equilibrium water absorption of the hydrogel sample as shown in Figure (9). When the hydrogels are placed in pure

water, the maximum osmotic pressure increases, resulting in maximal swelling [4,18].

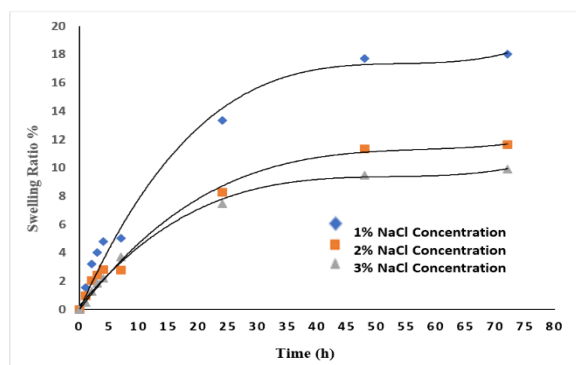


Figure 9: Effect of Ionic Strength Concentration on AA/Am Hydrogel Swelling

3.6. Investigation of Adsorption Parameters

The effect of different factors on MB dye adsorption capacity has been characterized for the prepared hydrogel.

3.6.1. Effect of Initial Concentration of MB Dye

Figure (10) showed the consequence of the different initial concentrations of MB (5,10,15,18 & 20 mg/l) on the AA/Am hydrogel decolourization efficiency. As shown, by increasing the initial MB concentration the dye removal percentage reduced from 90 to 50%. This might be due to the increased number of surface-active sites in relation to the total number of dye molecules in the aqueous solution, allowing all dye molecules to interact with the hydrogel.

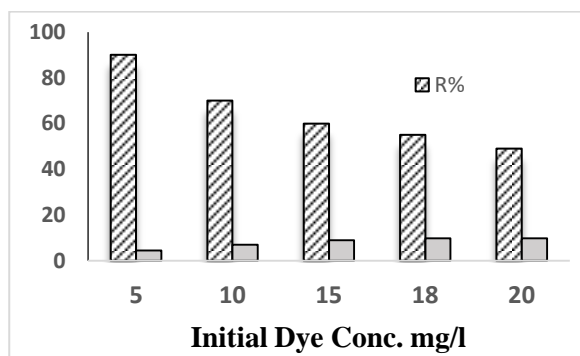


Figure 10: Effect of MB Initial Concentration on % Removal of Dye & Adsorption Capacity
(25°C, 0.1 g Hydrogel, 10 mg/l Initial Dye Conc., pH 7 and 3 hr)

It was found that when the MB concentration was greater than 18 mg/l, the adsorption sites on the adsorbent were completely adsorbed, and thus the adsorption amount of a hydrogel at a MB

concentration of 18 mg/l was similar to that at MB concentration of 20 mg/l.

3.6.2 Effect of Initial pH

MB dye adsorption on AA /Am hydrogel depends closely on the initial pH of the aqueous solution. Figure (11) shows the effect of pH value on the adsorption capacity of a hydrogel. It is noticeable that the removal % of adsorbed dye increased significantly from 35 to 76 when the initial pH ranged from 3 to 5 respectively, while the rate of increase was less with the pH range 5-11 to reach about 93% dye removal.

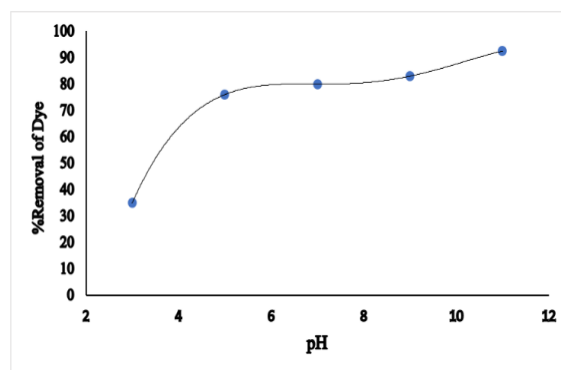


Figure 11: Effect of pH on MB dye Adsorption
(25°C, 0.1 g Hydrogel, 10 mg/l Initial MB Solution, 100 ml Dye Solution & 3 hr)

The carboxylic acid groups of AA could be ionized by increasing the pH resulting in further interactions between the cationic dye (MB) and the negative charge of the AA groups. As a result, electrostatic repulsion forces are generated between the polymer networks and the ionized groups.

Which led to the production of a network-like ultra-fine structure of the hydrogels, thus increasing the degree of absorption (MB)? Because the carboxylic acid groups in the hydrogels are made up of protons at low pH, there is more competition between MB cations and H for binding sites in the adsorbents, and dye adsorption drops to lower levels.

3.6.3 Effect of Temperature

When studying the dependence of MB adsorption capacity on temperature at 25, 40, 60 and 80 °C, it is shown in Figure (12). The percentage of removing MB dye from the aqueous solution increased from 80 % to 91% with the increase in temperature from 25 to 40°C respectively. This is due to two different factors; Firstly, the diffusion rate of adsorbent particles increases through the outer boundary layer and the inner pores of the adsorbent particle, and secondly, decreasing of that diffusion in the case of sol. viscosity for highly concentrated suspensions. In

addition, the temperature change will change balance ability of adsorbents for a specific characteristic adsorbate [23].

One possible reaction mechanism is the interaction between the hydrogel and the cationic group in the dye molecule; such a reaction can be favoured at moderate temperatures. Electrostatic forces of attraction between the cationic dye ions and the hydrogel surface; a hydrogen bond can form between the hydroxyl groups of the AA/Am hydrogel and a nitrogen atom of the dye. Due to volume breakdown during heating, increasing the temperature over 40°C lowered the absorption. It has been demonstrated that hydrogels undergo a continuous volume shift from low temperature to high temperature, with a highly inflated gel network collapsing. This behaviour shows that this is an exothermic sorption mechanism.

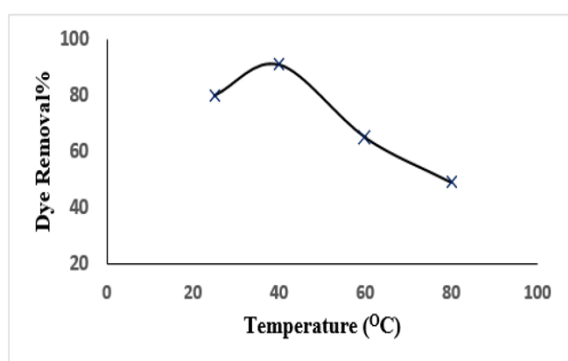


Figure 12: Effect of Solution Temperature on The MB Dye Removal onto AA/Am Hydrogel.

(25 °C, 0.1 g Hydrogel, 10 mg/l Initial MB Solution, pH 7.0 & 3 hr)

3.6.4. Effect of Adsorbent Dose

The adsorbent dose was also an important parameter to improve the adsorption behaviour of dye removal, and this effect was studied by adding different doses of adsorbents to 100 ml of MB solution (10 mg/l) at room temperature (25°C) and at solution pH of 7.0. Then determine the final concentration of the methyl bromide solution after a contact time of 3 hours.

3.6.5 Effect of Ionic Strength

Many studies on dye adsorption revealed that the concentration and type of the electrolyte ionic species introduced to the dye-bath had a significant impact on the amount of dye removal [19]. Figure (14) depicts the effect of Na on the % elimination of MB (13). Several sorption studies were conducted to investigate the effect of ionic strength on MB dye adsorption on AA/Am hydrogel. This was determined by adjusting the initial NaCl content in the solution from 0% to 3%. Figure 14 shows that when the ionic

strength concentration is increased from 0 to 3 percent, the percent removal of dye adsorbed decreases from 76 to 18. The following is how these findings can be explained: When the amount of NaCl salt in the solution rises, the surface of the sorbent material becomes less accessible for methylene blue absorption. The quantity of methylene blue adsorbed decreases as a result.

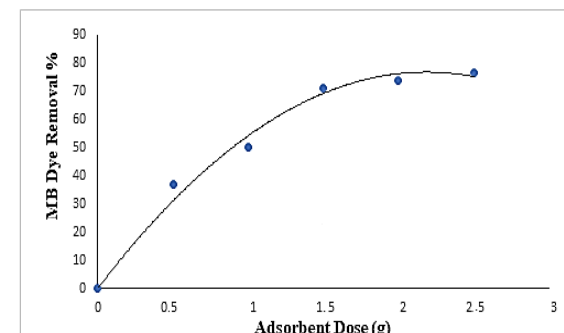


Figure 13: Effect of Adsorbent Hydrogel Dose on % Removal of MB Dye.

(25°C, 10 mg/l Initial MB Dye Solution, pH 7.0 & 3 hr)

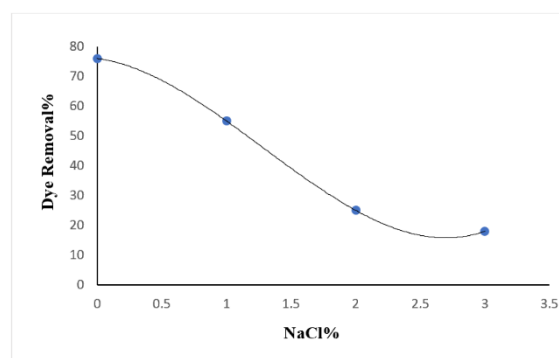


Figure 14: Effect of Ionic Strength on The Adsorption of MB Dye onto AA/Am Hydrogel.

(25°C, 0.1 g Hydrogel, 10 mg/l Initial MB Dye Solution, pH 7.0 & 3 hr)

strength concentration is increased from 0 to 3 percent, the percent removal of dye adsorbed decreases from 76 to 18. The following is how these findings can be explained: When the amount of NaCl salt in the solution rises, the surface of the sorbent material becomes less accessible for methylene blue absorption. The quantity of methylene blue adsorbed decreases as a result.

When a sorbent comes into contact with a species of sorbate in solution, they are guaranteed to be

surrounded by a double electric diffuse layer, according to one of the earlier investigations. The thickness of this layer is far more essential than whether or not there is salt present. The absorption of methylene blue on surface sorbent is inhibited by the presence of salts in solutions. Furthermore, when the electrostatic attraction between the adsorbent surface and the adsorbate ions is attractive, as it is in this system, an increase in ionic strength reduces adsorption capacity [25].

From the previous results, the MB dye adsorption experiment was carried out under the obtained optimum conditions with a contact time of 4 hours, 1.5 g/l of hydrogel, in an aqueous solution of pH 9, at 40 °C, and the % removal of the dye under these conditions reached about 95%, Figure (15) illustrates the gradation of colors from left to right till reach the best removal of color at the optimum condition.



Figure 15: Adsorption Experiment of The Optimum Conditions.

(40°C, 1.5 g/l Hydrogel, 10 mg/l Initial MB Dye Solution, pH 9 & 4 hr)

3.7 Adsorption Kinetic Modelling

Adsorption kinetics is an essential factor to consider when assessing adsorption effectiveness. The rate of MB uptake is described by the dynamics of sorption. The rate of dye adsorption is affected by the adsorbent's contact time with the adsorbent as well as diffusion mechanisms [26-27].

The adsorption process is a multi-step process that begins with dye molecules being transferred from the aqueous solution to the adsorbent's boundary layer (first step), followed by diffusion at the sorbent's surface (second step), and finally dye molecules being diffused into porous sites via diffusion of pores [1].

Figure (16) shows the usual kinetic curve for the time-dependent adsorption of MB on poly AA/Am hydrogel. The hydrogel's MB adsorption was fast in the first three hours, and a pseudo-static condition was established after around five hours. The use of dynamic models to characterise the evolution and efficiency of adsorption has piqued researchers'

curiosity. The pseudo-first-order and pseudo-second-order models were employed to examine the kinetic data of methylene blue adsorption by the poly AA/Am hydrogel under the tested experimental circumstances since they were deemed the most common models in practical usage for kinetic calculations [25].

Equation (4) stated the model of pseudo first-order adsorption kinetics.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \text{Where,} \quad (4)$$

k_1 (l/min) is the pseudo first-order adsorption rate constant estimated from the slope of a plot $\log(q_e - q_t)$ versus t , Figure (16)

The pseudo second-order kinetic model is expressed as in Equation (5)

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

Where k_2 (g/g*min) is pseudo second-order adsorption rate constant calculated from a linearized from this equation represented by Equation (6).

The plot of t/q_t versus t would exhibit a straight line if pseudo second-order kinetics is applicable, Figure (16), where t was the adsorption time (min), q_t and q_e were the adsorption capacity at time t and at equilibrium, respectively (mg/g).

Figures (17) and (18) show data that was fitted using the Laguerre pseudo first-order equation and pseudo second-order equation, respectively. As demonstrated in Figures, the adsorption of MB on poly AA/Am hydrogel suited the pseudo second-order equation rather well. The kinetic equation was $t/q_t = 0.1707 t + 0.1882$, with $k_2 = 9.16 \times 10^{-5}$ g/mg*min and $R^2 = 0.9979$ as the correlation coefficient.

It should be noted that the calculated values of q_e for the pseudo-first-order kinetic equation less agreed with the experimental values as shown in Figure (17), where the R^2 was 0.9688. These results demonstrate that a pseudo-first-order model cannot be used to predict the MB adsorption kinetics on the prepared poly AA/Am hydrogel.

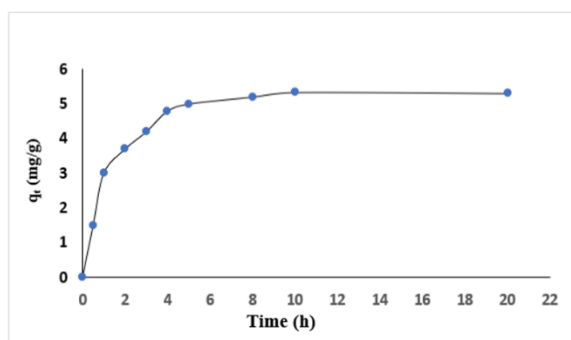


Figure 16: Effect of Contact Time on A Hydrogel Adsorption capacity
(40°C, Adsorbent Dose 1.5 g/l, Initial MB Dye Concentration 10 mg/l)

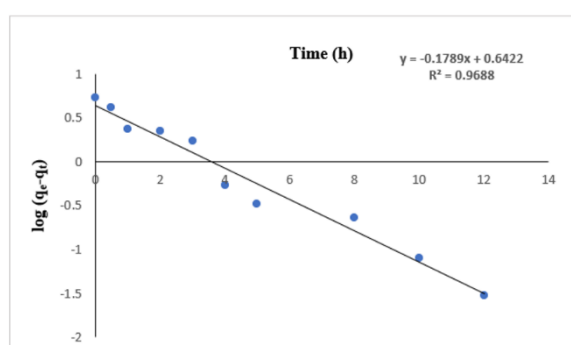


Figure 17: Pseudo First Order Kinetic Equation Describing the MB Dye Adsorption onto AA/Am Hydrogel
(25°C, pH 7, Adsorbent Dose 1.5 g/l, Initial MB Dye Concentration 10 mg/l)

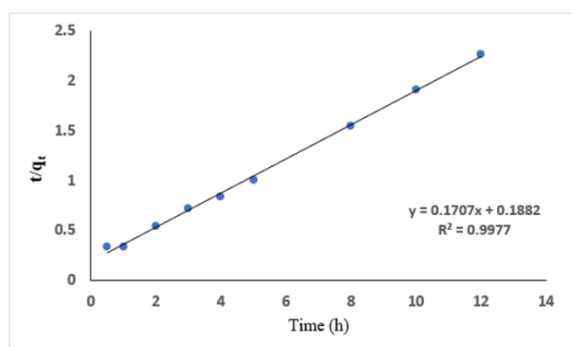


Figure 18: Pseudo Second Order Kinetic Equation Describing the MB Dye Adsorption onto AA/Am Hydrogel.
(25°C, pH 7, Adsorbent Dose 1.5 g/l, Initial MB Dye Concentration 10 mg/l)

4. Conclusions

In this work, a biodegradable hydrogel was prepared from poly acrylic acid-acrylamide (AA/Am) copolymer, its properties were tested and then the effects of temperature, pH, hydrogel quantity and ionic strength on the degree of dye removal in

aqueous solutions on its capacity to adsorb a cationic methylene blue dye were studied, the results showed the viability of the prepared hydrogel and its ability to reduce dye concentration up to 95%. The adsorption kinetics were also studied, which came to agreement with a pseudo-second order very well

Abbreviations

RO Water: Water obtained by reverse osmosis process.

DW: Distilled water

λ_{\max} : wavelength of the absorption spectrum

References

- Sivakumar, R., Lee, N.Y., (2021). Adsorptive removal of organic pollutant methylene blue using polysaccharide-based composite hydrogels, *Chemosphere*, 286(Pt 3), 131890.
- Sorour, M., Hani, H., Shaalan, H., El Sayed, M., El-Sayed, M.H. (2015). Softening of seawater and desalination brines using grafted polysaccharide hydrogels. *Desalination and Water Treatment*, 55, 2389–2397
- El Sayed, M., Alaraby, R., Amin, A., (2021). Swelling Kinetics Investigation of Polymer Hydrogel Composed of Chitosan-g-(AA-AM). *Egyptian Journal of Chemistry*, 64, No. 10 pp. 5999 – 6005.
- Benaïss, H., (2018). Influence of ionic strength on methylene blue removal by sorption from synthetic aqueous solution using almond peel as a sorbent material: experimental and modelling studies. *Journal of Taibah University for Science*, 4(1), 31-38.
- Li, S., (2010). Removal of Cationic Dye from Aqueous Solution by a Macroporous Hydrophobically Modified Poly(acrylic Acid-acrylamide) Hydrogel with Enhanced Swelling and Adsorption Properties, *CLEAN - Soil, Air, Water*, 38(4), 378-386.
- Lapwanit, S., Sooksimuang, T., Trakulsjaritchok, T., (2018). Adsorptive removal of cationic methylene blue dye by kappa-carrageenan/poly(glycidyl methacrylate) hydrogel beads: Preparation and characterization, *Journal of Environmental Chemical Engineering*, 6(5), 6221-6230.
- Abdel-Fatah, M.A., Hawash, S.I., Shaarawy, H.H., Cost-effective clean electrochemical preparation of ferric chloride and its applications, *Egyptian Journal of Chemistry*, 2021, 64(7), pp. 3841–3851
- Zhou, Y., (2011). Removal of methylene blue dyes from wastewater using cellulose-based super adsorbent hydrogels. *Polymer Engineering & Science*, 51(12), 2417-2424.
- Sricharoen, P., (2021). Ultrasound-irradiated synthesis of 3-mercaptopropyl trimethoxysilane-modified hydroxyapatite derived from fish-scale residues followed by ultrasound-assisted organic dyes removal. *Sci Rep*, 11(1), 5560.
- Giraldo, S., et al., (2021). Experimental and Theoretical Insights on Methylene Blue Removal from Wastewater Using an Adsorbent Obtained from the Residues of the Orange Industry, *Molecules*, 26(15).
- Turan, E., Çaykara, T., (2007). Swelling and network parameters of pH-sensitive poly(acrylamide-co-acrylic

- acid) hydrogels, *Journal of Applied Polymer Science*, 106(3): p. 2000-2007.
12. Hu, X.-S., Liang, R., Sun, G., (2018). Super-adsorbent hydrogel for removal of methylene blue dye from aqueous solution, *Journal of Materials Chemistry A*, 6(36), 17612-17624.
 13. Mohamed, R.R., et al., (2018). Synthesis of an efficient adsorbent hydrogel based on biodegradable polymers for removing crystal violet dye from aqueous solution, *Cellulose*, 25(11), 6513-6529.
 14. Sorour, M., et al., (2013). Free radical grafting kinetics of acrylamide onto a blend of starch/chitosan/alginate, *Carbohydr Polym*, 98(1), 460-4.
 15. Mohamed H. Sorour, Marwa M. Elsayed, Abdelghani M. G. Abulnour, Shadia R. Tewfik, and H.A.H. Hayam F. Shaalan, (2020). Functional Analysis of Selected Ion Electrically Conductive Hydrogel: Production and Applications in Seawater Treatment. *International Journal of Recent Technology and Engineering (IJRTE)*, 8(6).
 16. Abdel-Fatah, M.A., Khater, E.M.H., Hafez, A.I., Shaaban, A.F., (2020). Performance of fouled NF membrane as used for textile dyeing wastewater, *Membrane and Water Treatment*, 11(2), pp. 111–121
 17. Paulino, A.T., (2006). Removal of methylene blue dye from an aqueous media using superadsorbent hydrogel supported on modified polysaccharide, *J Colloid Interface Sci*, 301(1), 55-62.
 18. Mahmoud, G.A., Mohamed, S.F., Hassan, H.M. , (2014). Removal of methylene blue dye using biodegradable hydrogel and reusing in a secondary adsorption process. *Desalination and Water Treatment*, 54(10), 2765-2776.
 19. Kuang, Y., Zhang, X., Zhou, S., (2020). Adsorption of Methylene Blue in Water onto Activated Carbon by Surfactant Modification, *Water*, 12(2).
 20. Yilmaz, E., Guzel Kaya, G., Deveci, H., (2019). Removal of methylene blue dye from aqueous solution by semi-interpenetrating polymer network hybrid hydrogel: Optimization through Taguchi method. *Journal of Polymer Science Part A: Polymer Chemistry*, 57(10), 1070-1078.
 21. Heidari, S., et al., (2018). Synthesis of an efficient copolymer of acrylamide and acrylic acid and determination of its swelling behavior, *Journal of Petroleum Exploration and Production Technology*, 8(4),1331-1340.
 22. Abdel-Fatah, M.A., Hussein, N.H., Hawash, S.I., Shaarawy, H.H., Investigation of using sidr leave extracts in nano-silver preparation, *ARPJ Journal of Engineering and Applied Sciences*, 2016, 11(19), pp. 11649–11654
 23. Saber-Samandari, S., et al., (2014). Efficient removal of anionic and cationic dyes from an aqueous solution using pullulan-graft-polyacrylamide porous hydrogel, *Water, Air, and Soil Pollution*, 225(11).
 24. Hurairah, S.N., Lajis, N.M., Halim, A.A., (2020). Methylene Blue Removal from Aqueous Solution by Adsorption on Archidendron jiringa Seed Shells. *Journal of Geoscience and Environment Protection*, 08(02), 128-143.
 25. Karmaker, S., Sintaha, F., Saha, T.K., (2019). Kinetics, Isotherm and Thermodynamic Studies of the Adsorption of Reactive Red 239 Dye from Aqueous Solution by Chitosan 8B. *Advances in Biological Chemistry*, 09(01), 1-22.