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Synthesis and Characterization of Poly (Acryl Amide - Maleic Acid) Hydrogel: Adsorption Kinetics of a Malachite Green from Aqueous Solutions

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ABSTRACT
Poly (acrylamide-maleic acid) hydrogel synthesized via free radical polymerization of acrylic acid and maleic acid as monomers, using N,N-methylene bis acryl amide as cross-linker and potassium persulfate as initiator. The synthesized hydrogel was described by Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), Thermogravimetric analysis (TGA) and UV-visible spectroscopy. The synthesis hydrogel was used as adsorbents for removal of a cationic dye, malachite green (MG) from aqueous solution. The synthesized adsorbents showed high efficiency in removal of malachite green and a very high adsorption capacity. The results showed the adsorption equilibrium time was reached in 60 min and the adsorption method is found the direct pseudo second order kinetics.

Keywords: graphene oxide, hydrogel composites, adsorption, crystal violet

INTRODUCTION

Hydrogels are water swell able, three networks dimensional polymeric. The capability of hydrogels soak up water is large and might be the maximum amount as one thousand times the weight of the polymer. Hydrogels get it significant applications and extensively studied as a result of the mix of glassy behaviors with elastic. Hydrogels are employed in the domain of pharmacy, biotechnology medicine, agriculture, biotechnology, food manufacturing, etc. Hydrogels are most generally employed in the controlling it release of drugs [1, 2]. The chemical and physical characteristics of hydrogels can depend on the polymers, monomers and crosslinked from that they are made. They will composed of varied chemical material [3-6]. The removal colour from textile wastewaters may be main environmental problems due to the difficulty of treatment such waters in traditional methods. Coloured waters are distasteful on beauty the basis for drinker and agricultural functions. Some groups have been used several adsorbents materials for the abstraction of ionic and cationic dyes from aqueous solutions [7]. About all dye, types are poisonous, carcinogenic, and mutations therefore they can source human health problems. Abstraction of dyes before to discharge wastewater in our natural bodies of water is very important. The low cost of clean methods and biodegradable adsorbents can be perfect tools to reduce the environmental influence caused by fabrication and textile waste [8-11]. Among the applied to the waste water treatment operations in the textile industry, adsorption has the usefulness to be effective and lower cost possible [12]. Hydrogels are like to ion exchange resins in sundry respects; for example, they are polymeric substance and removal aqueous contaminated via electrostatic interfaces. However, but unlike the resins, rigid structures, water structures and flexible and can be absorb a lot of water compared to the resins [13]. The existence of exact functional groups (-COOH, -CONH$_2$, -OH,-SO$_3$H , -NH$_2$) in hydrogel three dimensional networks allows the Removal of absorbers and recovery of aquatic pollutants .The pollutants are often adsorbed above the external surface in addition to the swelled hydrogels [14]. The free radical polymerisation is the common method widely used for the production of hydrogel [15, 16]. In a model hydrogel production, a monomer reacts with a crosslinking agent to formulation a three dimensional crosslinking polymer network [17]. Because of the importance of poly (acrylamide-maleic acid) crosslinking hydrogels in several areas, it is required to dealing with the physical and chemical properties of hydrogels. The

present research includes the preparation of chemical crosslinking poly (acrylamide-maleic acid) hydrogels via free radical polymerisation of acryl amide with the maleic acid in the found of a crosslinked agent N, N'-methylene bis acryl amide (MBA) and potassium persulfate (KPS), N, N, N',N'-tetra methyl ethylene diamine (TMEDA) as coinitiating systems , and to determine its efficiency in removing dye such as malachite green (MG) from aqueous solutions.

EXPERIMENTAL

Chemicals and Materials

Acryl amide (AAm, 98%; Merck) and maleic acid (MA, 98%; Fluka) were use as monomers. N, N'-methylene-bisacrylamide (MBA 99%; Sigma Aldrich) was used as a crosslinking agent. Potassium persulphate (KPS, 99%; Merck) was used as an initiator. N, N, N', N'-tetra methyl ethylene diamine (TMEDA, 98%; Sigma Aldrich) was used as an accelerator. All these substances were used to the preparation of hydrogel. Malachite green (MG, 98%; Merck) was use a model of dye in adsorption. Hydrochloric acid (HCl, 35%; Sigma-Aldrich) and Sodium hydroxide (NaOH, 98%; Sigma-Aldrich). Sodium chloride (NaCl 99%; Fluka) and Deionized water (DI) was use through all the complete experimental in this research.

Preparation of Poly (AAm-MA) Chemically Crosslinked Hydrogels

The poly (AAm-MA) chemically crosslinked hydrogels were synthesized by free radical copolymerisation method in aqueous medium, included 1.0 g of (AAm) and 0.04 g of (MA) were dissolved in 2.0 mL double distilled water (DI) and blended by a magnetic bar, 0.02 mmol of crosslinked (MBA), 0.015g of initiator (APS) and 1mL of (TMEDA) were added sequentially, dissolved in double distilled water to total volume of 10 mL. The product solution was carried in to PVC straw, diameter 0.30 cm, and put in an electrical oven at 60°C for time of 2 h. The hydrogels were taken out from the straw, turn over little cylindrical items, and place in double distilled water (DI) for 4–5 h to removal the unreacted salts. The water was replaced each 30 minutes. Then the hydrogel was dried at 35 ^{0}C until they achieved the constant weight. The hydrogels produced were very transparent, very soft, flexible, and cylindrical in shape.

Characterization of Chemically Crosslinked Hydrogels

Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectrometric (Shimadzu 8400S, Japan) study was used to describe the chemical structure of poly (AAm-MA) hydrogel. In addition, spectra within the frequency range (4000-400) cm^{-1}.

Field Emission scanning electron microscopy (FE-SEM)

The surface morphology of the hydrogel was examined using Field Emission scanning electron microscopy (FE-SEM) (Tescan MIRA3, Germany). Analysis of the poly (AAm-MA) hydrogel. The hydrogel was coated with a thin layer of gold under reduced pressure and their FE-SEM images were taken.

Thermogravimetric analysis (TGA)

Poly (AAm-MA) hydrogel was initial dried in a vacuum oven to a fixed weight and then thermogravimetric diagram was determine by TGA (TGA4000, Perkin Elmer, USA) at a heating rate of 10 ^{0}C/min from 40 oC to 900 ^{0}C.

Preparation Surface of Hydrogel

The surface of the poly (AAm-MA) crosslinked hydrogel in powder forms was ground and sieved by using different mesh sieve (100-400) µm. The particle size of 100 µm was used for the surface in all experiments of this work.

Determination of Maximum Absorption (λ_{max})

To determine the maximum wavelength of the MG dye, the ultraviolet-visible absorption spectra of the dye solution (10 mg/L) was recorded by wavelengths of 200-800 nm. The maximum wavelength of the MG dye solution was found at the wavelength λmax MG = 617.0 nm in **Figure 1**.

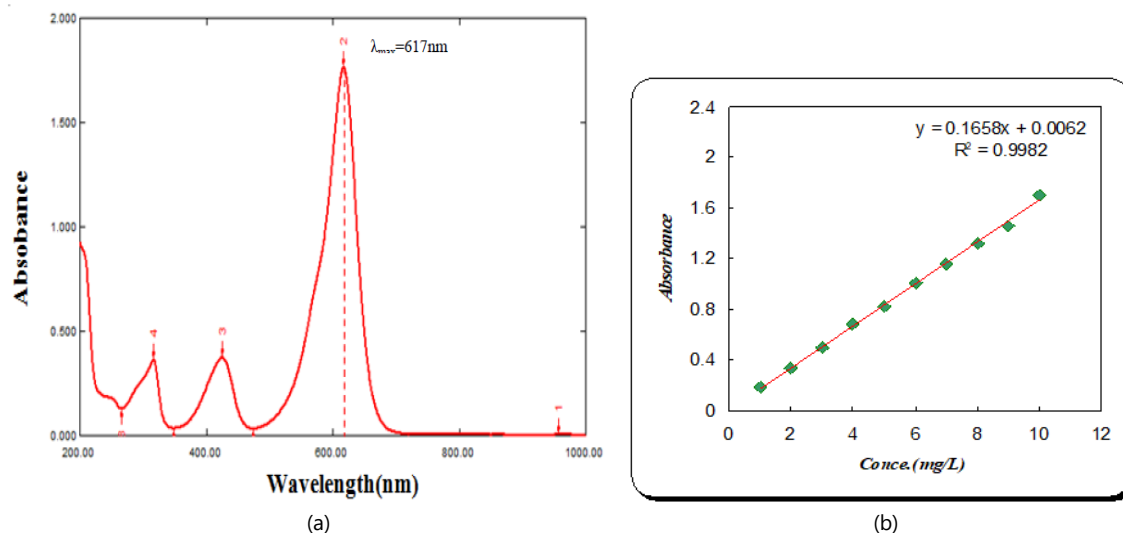(a)   (b)

Figure 1. a. UV-Visible absorption spectra and b. Calibration curves of the MG dye a

Solutions of several concentrations of MG dye prepared by serial dilutions. Absorbance values of these solutions were measured at the selected λmax (617.0 nm) value for MG dye and draw against the concentration values MG in **Figure 1 b**.

Calculate the Quantity Adsorbed

The amount of MG dye adsorbent on the surface of poly (AAm-MA) hydrogel is determine by the following equation [18].

$$Q_e \ or \ \frac{x}{m} = \frac{V(C_o - C_e)}{m} \tag{1}$$

Kinetic Studies

The effect of equilibrium time has been calculated by addition 0.05 g of poly (AAm-co-MA) hydrogel into 10 mL MG dye solution, initial concentration (100mg/L) under shaking. Fixed solution temperature at 25°C with thermostatic controls and shaker. After Difference time periods, the samples were centrifuged and taken for spectrophotometrically determination of MG dye content.

RESULTS AND DISCUSSION

Characterization of Poly (AAm-MA) Hydrogel

The FTIR spectrum in **Figure 2** The bands range at about 1700 cm^{-1} due to the shift in the stretching vibration connected with the hydrogen directly overtone for bonded labor absorption strong C=O group. The sharp peak at 1650 cm^{-1} duo to the C=O group and associated to amide group. On a much wider absorption peaks in the areas of 3100 and 3450 cm^{-1} duo to the N-H and O-H bands and are associated to the polymer chains [19, 20]. The wide peak at 3450 cm^{-1} is duo to a representative peak of the primary amine. The weak peak at 1550 cm^{-1} is attribute to O-H band in the –COOH group. The bands at 1720 -1700 cm^{-1} duo to a characteristic are carbonyl groups in the carboxylic acids. The weak peaks at 1020 and 1200 cm^{-1} duo to C-N bands and the weak peaks at 2800 and 1410 cm^{-1} are attributed to -CH$_2$- groups on the polymer chains [21].
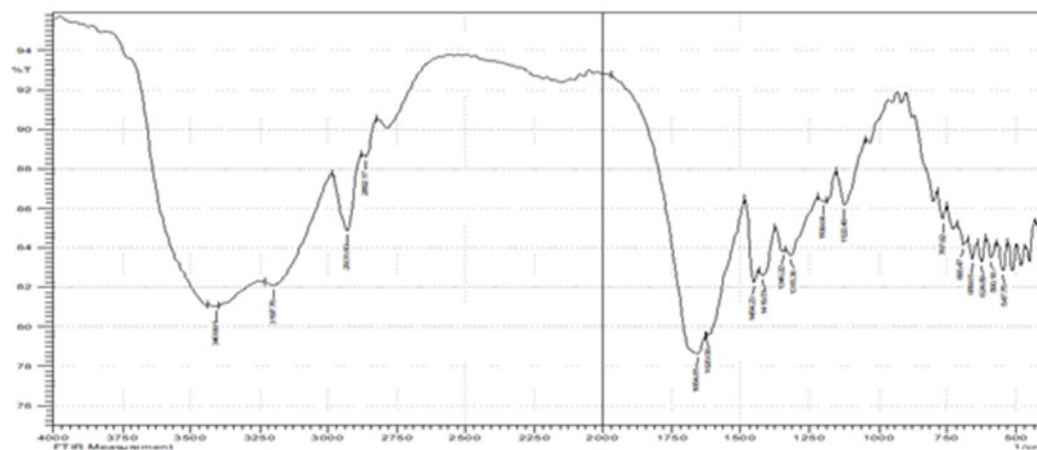
Figure 2. FTIR spectra of poly (AAm-MA) hydrogel
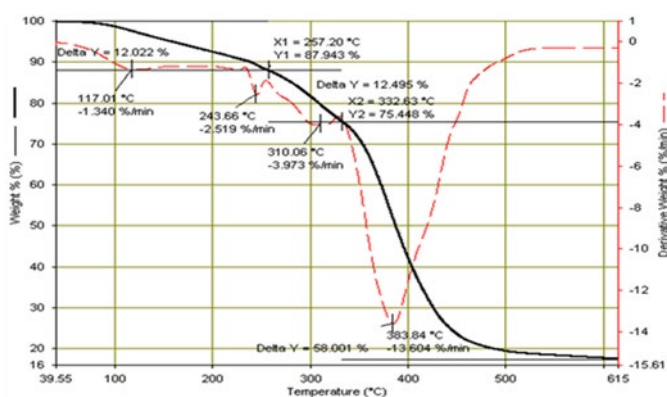

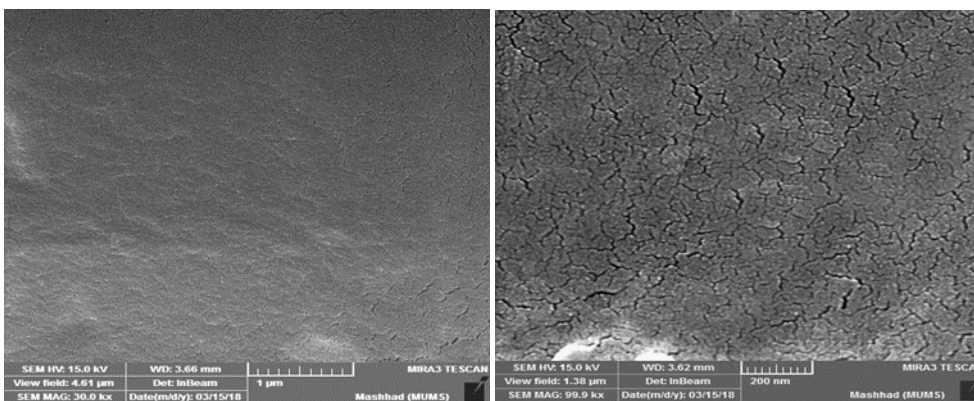**Figure 3.** Thermogram of the poly (AAm-MA) hydrogel

Figure 4. FE-SEM images of Poly (AAm-MA) hydrogel

Thermal performance of the poly (AAm-MA) hyd0rogel was studied by thermal in **Figure 3** which shows that degradation of the hydrogel in a three stage weight loss, initial stage in 117°C due to loss moisture water molecules in the hydrogel, second stage is temperature between range (257-332 °C) attribute to loss CO_2 and amide group respectively, Three stage in above 383.84 °C was represented the dissociation polymer chains in the polymer backbone. Obviously that the hydrogel is highly stable up to 250 °C [22]. Meanwhile the proposed hydrogel is to be used for the removal of MG dye at this range of temperature.

FE-SEM common technique used to determine the surface morphology of poly (AAm-MA) hydrogel was shown in **Figure 4** the surface of the hydrogel is smooth, homogenous, clear, neat morphology, and has a sponge-like structure and impact network due to the strong bonding of the crosslinked agent in the polymer chains [23]. After adsorption MG dye on the surface of hydrogel was shown in **Figure 5** observe fill the pores on the surface completely in the form of a layer by the molecules of the dye and then the surface became completely covered with particles of dye and this confirms that the process of adsorption.
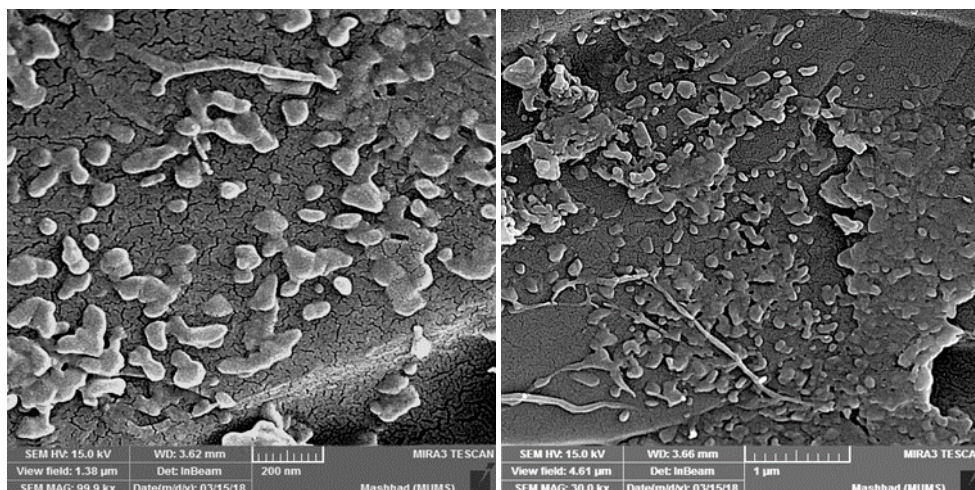
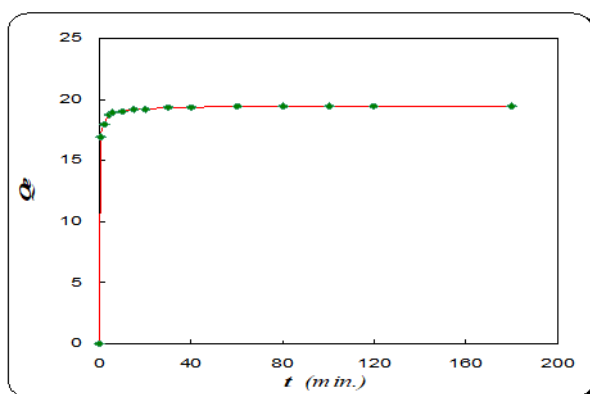**Figure 5.** FE-SEM images of adsorption MG dye on of Poly (AAm-MA) hydrogel

Figure 6. The effect of equilibrium time on adsorption capacity

Adsorption Kinetic Models

The time required to reach the equilibrium state of adsorption MG dye on surface of hydrogel was calculated as a function of equilibrium time with a constant concentration of dye at different time intervals (1-180 min) at 25 °C, a constant weight of hydrogel 0.05g and pH 7.0 the results are shown in **Figure 6**, The time needed to reach equilibrium is 60 min. The adsorption process increases over time so that the adsorption is high rapid in the first 5 min and gradually increases to reach the contact time at 60 min. This is due to the high number of available adsorption active sites in the surface of the adsorbents then adsorption is slower and more difficulty because all the active sites of the surface are occupied by dye molecules [24].

The kinetic models of the adsorption process that describe the experimental data were used well for adsorption of the dye on the surface. The kinetic reaction models were used to analyze the experimental data. The reaction rate constants of the dye removal from the solution by poly (AAm-co-MA) hydrogel calculated using pseudo first order and pseudo second order equations.

The Lagergren equation was used for the first order rate to describe the experimental results. The linear form of the Lagergren equation is [25]:

$$ln\ (q_e - q_t)\ =\ ln\ q_e - k_1 t \tag{2}$$

Where q_e (mg/g) represented the equilibrium adsorption, capacity and q_t (mg/g) refer to the quantity of dye adsorbed at time. Values of k_1 for MG-poly (AAm-co-MA) hydrogel system can be calculate from the slope of the draw of ln (q_e-q_t) against t, **Figure 7 a**. The adsorption kinetic parameters from **Figure 7 b** are indicated in **Table 1**. The adsorption data also counterfeit analysis a pseudo second order mechanism [26]. The linear form of the equation is:
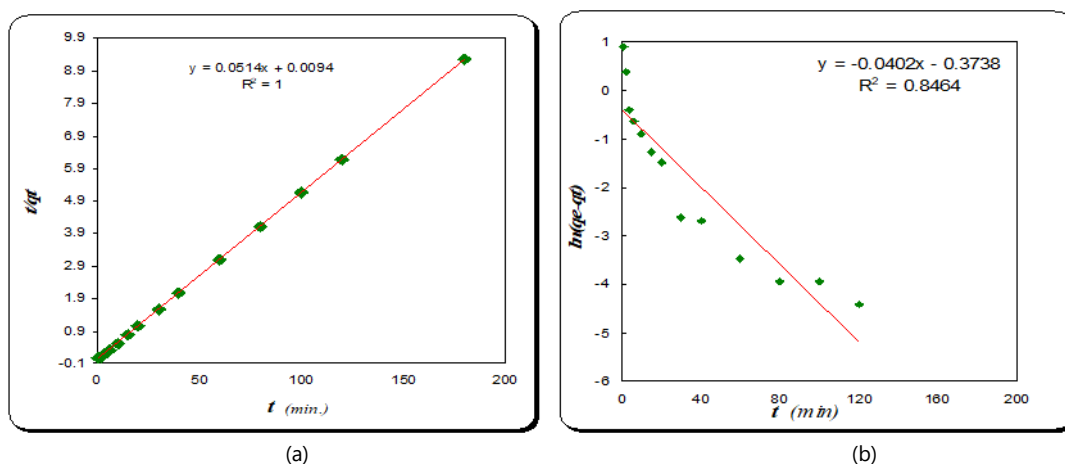
(a)   (b)

Figure 7. a. Pseudo first order kinetics for adsorption MG b. Pseudo second order kinetics for adsorption of MG

Table 1. Adsorption kinetic parameters of MG on poly (AAm-MA) hydrogel

Dye	Pseudo- first order			Pseudo- second order			
	k_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g. mg^{-1}.min^{-1})	q_e (mg/g)	R^2	h (mg. g^{-1} .min^{-1})
Malachite green	0.0402	0.688115	0.8464	106.383	19.45525	1	181.818

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \qquad (3)$$

Where k_2 is the refer to rate of constant to the pseudo second order adsorption. When the initial adsorption rate is $h = k_2 q_e^2$ Then equation (3) is:

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \qquad (4)$$

By drawing t/q_t against t, **Figure 7**, a straight line can be gotten and q_e, k_2 and h can be determined [27].

The adsorption kinetic parameters from **Figure 7** are listed in **Table 1**, the kinetic coefficients and correlation coefficients (R^2) were calculated for both models as shown in **Table 1**. The results showed that the value of the correlation coefficient (R^2) was high for the false pseudo-second order equation model compared to the pseudo-first order equation. The amount of dye absorbed calculated in this model pseudo-second order is very close to the value calculated in the experiments compared to the amount of the absorbed substance calculated in the pseudo-first order equation model [28].

CONCLUSIONS

Poly (AAm-MA) hydrogel was synthesized via a free radical polymerization by acryl amide and maleic acid as a monomers and MBA as crosslinked agent. The results obtain from the experimental refer to that the adsorption equilibrium time was reached within 60 min and the adsorption process is found to fit pseudo second order kinetics. The poly (AAm-MA) hydrogel could be used as adsorbents in wastewater treatment for the removal of MG dye. The hydrogel is highly stable untiled to 250 °C. Meanwhile the proposed hydrogel can be used for the removal of MG dye from aqueous solutions

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