

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

Layth S. Jasim ^{1*}, Nadher D. Radhy ², Hayder O. Jamel ²

¹ Department of Chemistry, College of Education, University of Al-Qadisiyah, IRAQ

² Department of Chemistry Pharmaceutical, College of Pharmacy, University of Al-Qadisiyah, IRAQ

Received 23 August 2018 • Revised 1 November 2018 • Accepted 24 November 2018

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 absorb a lot of water compared to the resins [13]. The existence of exact functional groups (-COOH, -CONH₂, -OH, -SO₃H, -NH₂) in hydrogel three dimensional networks allows the Removal of adsorbents 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 °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 °C/min from 40 oC to 900 °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 λ_{max} MG = 617.0 nm in **Figure 1**.

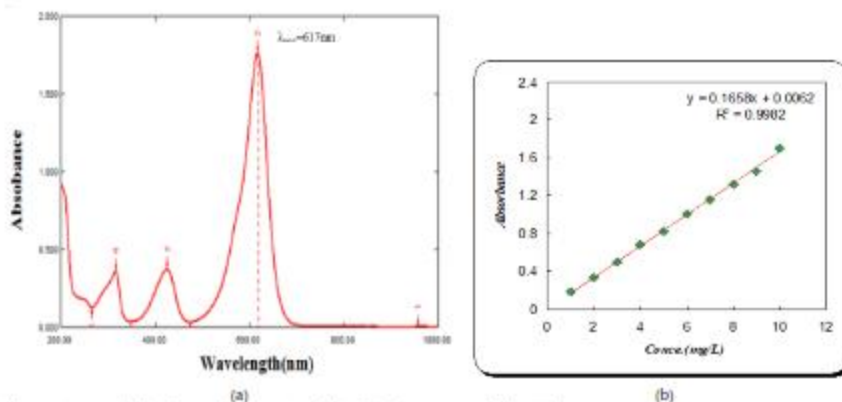


Figure 1. a. UV-Visible absorption spectra and b. Calibration curves of the MG dye a

Solutions of several concentrations of MG dye prepared by serial dilutions. Absorbance values of these solutions were measured at the selected λ_{max} (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].

$$Q_e \text{ or } \frac{x}{m} = \frac{V(C_0 - C_e)}{m} \quad (1)$$

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} due 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} due 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 due 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} due to a characteristic are carbonyl groups in the carboxylic acids. The weak peaks at 1020 and 1200 cm^{-1} due to C-N bands and the weak peaks at 2800 and 1410 cm^{-1} are attributed to $-\text{CH}_2-$ groups on the polymer chains [21].

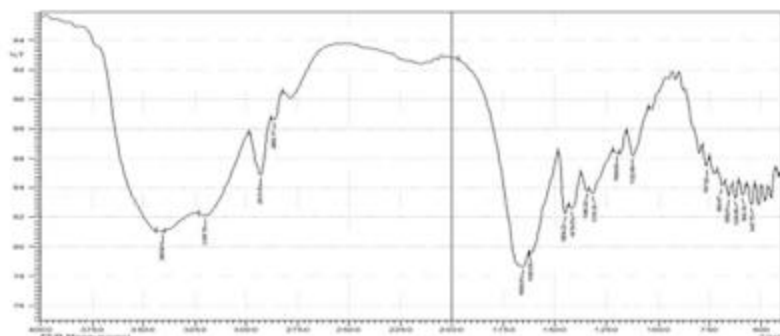


Figure 2. FTIR spectra of poly (AAM-MA) hydrogel

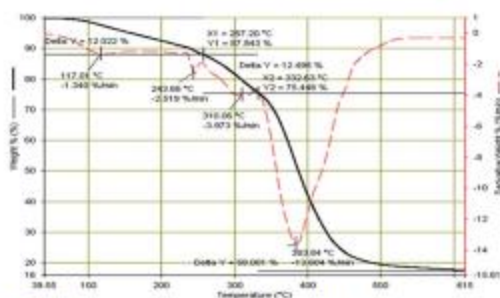


Figure 3. Thermogram of the poly (AAM-MA) hydrogel

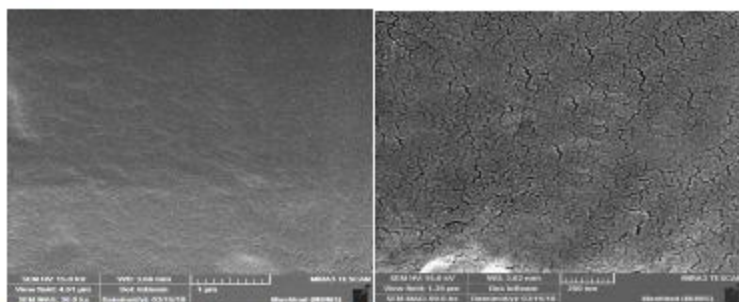


Figure 4. FE-SEM images of Poly (AAM-MA) hydrogel

Thermal performance of the poly (AAM-MA) hydrogel 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 CO₂ 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.

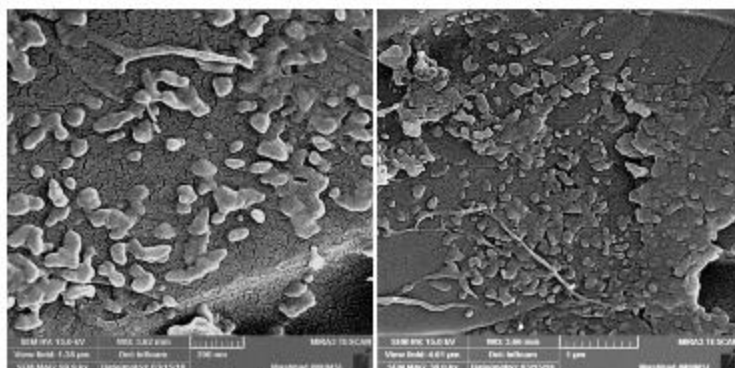


Figure 5. FE-SEM images of adsorption MG dye on of Poly (AAM-MA) hydrogel

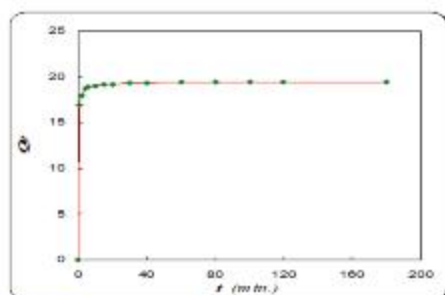


Figure 6. The effect of equilibrium time on adsorption capacity

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]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

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:

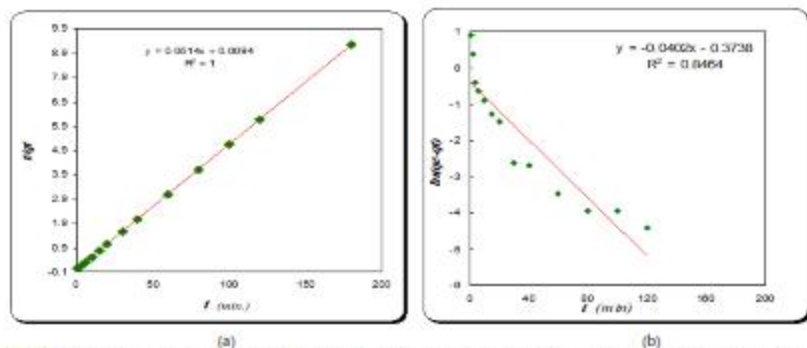


Figure 7. a. Pseudo first order kinetics for adsorption MG b. Pseudo second order kinetics for adsorption of MG

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 ($\text{g. mg}^{-1}.\text{min}^{-1}$)	q_e (mg/g)	R^2	h ($\text{mg. g}^{-1}.\text{min}^{-1}$)
Malachite green	0.0402	0.066115	0.8464	106.303	19.45525	1	161.616

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

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:

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

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

REFERENCES

- Dubrovskii S, Afanas'eva M, Lagutina M, Kazanskii K. Comprehensive characterization of superabsorbent polymer hydrogels. *Polymer bulletin* 1990;24(1):107-113. <https://doi.org/10.1007/BF00298329>
- Peppas NA. *Hydrogels in medicine and pharmacy*. Vol. 1, Fundamentals; Crc Press, 1986.
- Maruthamuthu M, Subramanian E. Binding of Evans Blue onto Poly (N-vinyl-2-pyrrolidone). *Polymer Bulletin* 1985;14(3-4):207-212.
- Sheth G, Bhattacharya N. Interaction of Polyvinyl Pyrrolidone with Disazo Dyes. *Textile Research Journal* 1987;57(2):92-97. <https://doi.org/10.1177/004051758705700206>
- Kozuka H, Takagishi T, Yoshikawa K, Kuroki N, Mitsuishi M. Binding of anthraquinone dyes by crosslinked polyvinylpyrrolidone. *Journal of Polymer Science Part A: Polymer Chemistry* 1986;24(10):2695-2700. <https://doi.org/10.1002/pola.1986.080241023>

6. Kim WS, Seo KH, Hwang YY, Lee JK. Effect of temperature on the binding of methyl orange by crosslinked poly (4-vinylpyridine). *Journal of Polymer Science Part C: Polymer Letters* 1988;26(8):347-350. <https://doi.org/10.1002/pol.1988.140260803>
7. Khare SK, Panday KK, Srivastava RM, Singh VN. Removal of victoria blue from aqueous solution by fly ash. *Journal of Chemical Technology & Biotechnology* 1987;38(2):99-104. <https://doi.org/10.1002/jctb.280380206>
8. Crini G. Non-conventional low-cost adsorbents for dye removal: a review. *Bioresource technology* 2006;97(9):1061-1085. <https://doi.org/10.1016/j.biortech.2005.05.001>
9. Aksu Z. Application of biosorption for the removal of organic pollutants: a review. *Process biochemistry* 2005;40(3-4):997-1026. <https://doi.org/10.1016/j.procbio.2004.04.008>
10. Li S, Liu X, Huang W, Li W, Xia X, Yan S, Yu J. Magnetically assisted removal and separation of cationic dyes from aqueous solution by magnetic nanocomposite hydrogels. *Polymers for Advanced Technologies* 2011;22(12):2439-2447. <https://doi.org/10.1002/pat.1782>
11. Zhu H-Y, Fu Y-Q, Jiang R, Yao J, Xiao L, Zeng G-M. Novel magnetic chitosan/poly (vinyl alcohol) hydrogel beads: preparation, characterization and application for adsorption of dye from aqueous solution. *Bioresource technology* 2012;105:24-30. <https://doi.org/10.1016/j.biortech.2011.11.057>
12. Aberkane-Mechebbek L, Larbi-Youcef S, Mahlous M. Adsorption of dyes and metal ions by acrylamide-co-acrylic acid hydrogels synthesized by gamma radiation. In *Materials Science Forum*, Trans Tech Publ, 2009;609:255-259. <https://doi.org/10.4028/www.scientific.net/MSF.609.255>
13. Tang SC, Wang P, Yin K, Lo IM. Synthesis and application of magnetic hydrogel for Cr (VI) removal from contaminated water. *Environmental Engineering Science* 2010;27(11):947-954. <https://doi.org/10.1089/ees.2010.0112>
14. Ozay O, Ekici S, Baran Y, Aktas N, Sahiner N. Removal of toxic metal ions with magnetic hydrogels. *Water Research* 2009;43(17):4403-4411. <https://doi.org/10.1016/j.watres.2009.06.058>
15. Shinde UP, Yeon B, Jeong B. Recent progress of in situ formed gels for biomedical applications. *Progress in polymer science* 2013;38(3-4):672-701. <https://doi.org/10.1016/j.progpolymsci.2012.08.002>
16. Thakur VK, Thakur MK. Recent trends in hydrogels based on psyllium polysaccharide: a review. *Journal of Cleaner Production* 2014;82:1-15. <https://doi.org/10.1016/j.jclepro.2014.06.066>
17. Hasirci V, Yilgor P, Endogan T, Eke G, Hasirci N. 1.121. *Polymer Fundamentals: Polymer Synthesis*. 2011.
18. Atkins P, De Paula J, Keeler J. *Atkins' physical chemistry*; Oxford university press. 2018.
19. Abdel-Aziz H, Hanafi H, Abozaha S, Siyam T. Preparation of poly (acrylamide-maleic Acid) resin by template polymerization and its use for adsorption of Co (II) and Ni (II). *International Journal of Polymeric Materials* 2010;60(1):89-101. <https://doi.org/10.1080/00914037.2010.504166>
20. Mutar MA, Radia ND. Controlled release from crosslinked polyacrylic acid as drug delivery theophylline. *Iraqi National Journal of Chemistry* 2012;(45):67-85.
21. Jaism L, Radhy N, Kmal R. A study of Adsorption of Azure B and C from Aqueous Solutions on Poly (Acryl amide-co-Crotonic acid) Hydro gels Surface. *Chem. and Pro. Eng. Research* 2015;32:62-69.
22. Tang Y, Wang X, Zhu L. Removal of methyl orange from aqueous solutions with poly (acrylic acid-co-acrylamide) superabsorbent resin. *Polymer bulletin* 2013;70(3):905-918. <https://doi.org/10.1007/s00289-013-0910-7>
23. Zheng Y, Cosgrove DJ, Ning G. High-resolution field emission scanning electron microscopy (FESEM) imaging of cellulose microfibril organization in plant primary cell walls. *Microscopy and Microanalysis* 2017;23(5):1048-1054. <https://doi.org/10.1017/S143192781701251X>
24. Radhy ND. Naproxen Sodium Release from Poly (acrylic acid-co-N-vinyl-2-pyrrolidone) Hydrogels. *Al-Qadisiyah Journal of Pure Science* 2018;21(1):64-76.
25. Al-Taweel SSJ, Jassim LS, Khlwy FS. A study of Adsorption of Crystal Violet from Aqueous Solution on Polyester. *Journal of al-qadisiyah for pure science (quarterly)* 2007;12(4):120-129.
26. Trade HA, Jassim LS, Al-Taweel SSJ. A study of adsorption of crystal violet from aqueous solution on kaolin. *Iraqi National Journal of Chemistry* 2007;(28):642-654.
27. Al-Hayder L, AL-Juboory M. Removal study of imidacloprid from aqueous solution by adsorption onto polyacrylamide cross-linked. *J. Chem. Pharm. Res.* 2015;7:1138-1144.
28. Alwan SH, Alshamsi HAH, Jasim LS. Rhodamine B removal on A-rGO/cobalt oxide nanoparticles composite by adsorption from contaminated water. *Journal of Molecular Structure* 2018;1161:356-365. <https://doi.org/10.1016/j.molstruc.2017.11.127>