RESEARCH ARTICLE

Rhodamine B dye Adsorption on Graphene Oxide/Poly (acrylic acid-co-malic acid): Characteristics, Kinetics, and Isotherms Modeling

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Received: 03rd January, 2022; Revised: 14th January, 2022; Accepted: 19th March, 2022; Available Online: 25th January, 2022

ABSTRACT

In this work, graphene oxide/poly (acrylic acid-co-malic acid) (GO/P(AA-co-MA)) composite as adsorbents for Rhodamine B dye in aqueous solutions were studied with kinetic adsorptions. The adsorption method was used to remove dye from aqueous solutions using a high-efficiency surface that can swell and retain its pollutant inside, where the polymer was prepared poly (AA-co-MA). Then graphene oxide was loaded (GO/P(AA-co-MA)) to increase the surface efficiency and swelling process. Several important techniques were measured for the prepared polymer (p(AA-co-MA) and surface (GO/P(AA-co-MA)) for the x-Ray diffraction analysis (XRD), atomic force microscopy (AFM), and thermal gravimetric analysis (TGA). Several experiments were conducted to estimate the optimum conditions of adsorption, the most important of which is the equilibrium time, where the best equilibrium time was (60 min) and the effect of surface weight the best (0.05 g) that give the maximum adsorption efficiency (35.5 mg/g). Study three isotherm, Langmuir, Freundlich and Timken isotherms, was found to conform to the Freundlich isotherm depending on the value of ($R^2 = 0.9494$). Also, study adsorption kinetics. First order and the second order was found to obey the second-order kinetics depending on the value of ($R^2 = 1$) compared to the first-order kinetics the value of ($R^2 = 0.6821$).

Keyword: Adsorption, Cross-linking, Dye, Hydrogel, Isotherm, Kinetic, Rhodamine B, Swelling.

International Journal of Pharmaceutical Quality Assurance (2022); DOI: 10.25258/ijpqa.13.2.5

How to cite this article: Sadoon N, Abd G, Mahdi AB, Ghafel ST, Adhab AH, Aljeboree AM, Jasim LS. Rhodamine B dye adsorption on Graphene Oxide/Poly (acrylic acid-co-malic acid): Characteristics, Kinetics, and Isotherms Modeling. International Journal of Pharmaceutical Quality Assurance. 2022;13(2):123-127.

Source of support: Nil.

Conflict of interest: None

INTRODUCTION

Pollution is the utmost widespread difficulty problem that has caused a defect in the ecosystem and a dangerous problem that threatens human life. Therefore, it is found that the ratio of water contamination that affects the human system is increased in all industrial countries.[1-3] Dyes are one of the utmost significant contaminants in water that cause many dangers to humans, plants, and animals. They have a very toxic effect on living organisms in the water. Most of the dyes contain aromatic substances and are classified as one of the most dangerous dyes characterized by their toxicity and used in many industries, including the textile industry, paper dyeing, fabrics, and leather.[4-6] Many modern technologies have been used to get rid of these pollutants, including photolysis, ion exchange, photocatalyst, and adsorption. The adsorption process is one of the most important techniques used to remove dyes because it is cheap and highly efficient in removing pollutants.[7-9] This study depends on the preparation of a surface that can be swelling, keep its pollutant inside, and remove the pollutant easily. It is very efficient, cheap and easy to prepare. Several factors that affect the adsorption method have been studied, including the effect of equilibrium time and weight. The adsorption isotherms and adsorption kinetics of the first and second order were also studied.

EXPERIMENTAL PART

Adsorption Isotherm

A 0.05 g of P(AA-co-MA) was introduced to stoppered flasks holding known dye concentrations (10–500 mg/L) in distilled

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water. The flasks were shaken at 60 cycles per minute in a thermostatically controlled water bath until equilibrium was achieved. It was then decided whether to centrifuge the suspensions for 20 minutes. or wait for the equilibrium time to run its course. The calibration curve was used to compare the experimental data to the equilibrium concentrations. In order to determine the amount of medication adsorbed, the following equation was used:

$$Q \text{ or } x/m = (V(C_o-C_e))/m \quad (1)$$

Where: x is the quantity adsorbed, m is the weight of adsorbent (g), C_o is the initial concentration (mg/L), C_e is equilibrium concentration (mg/L), and V is a volume of solution (L).

Equilibrium Adsorption of Rhodamine B

One of the most significant factors affecting the adsorption method that has been studied is the effects of adsorption time, where the equilibrium time range was from 1 to 360 minutes, and the effect of mass surface, where weight was taken from 0.01 to 0.06 gm to get the best adsorption efficiency, as the experiment depends on preparing a series of solutions with concentration (10–500 mg/L), A volume of 10 mL of dye solution and put in Shaker water bath for one hour at a speed of 150 rpm. The residual concentration is then separated in a bulk centrifuge at 5000 rpm for 10 minutes. The equilibrium concentration was measured via UV-vis spectrophotometer at a wavelength of λ_{max} = 553 nm, and the adsorption efficiency was calculated through the equation (1).

RESULT AND DISCUSSION

TGA Analysis

Through the results, a technical measurement (TGA) of the prepared hydrogel surface, the hydrogel thermal behavior is observed, which is characterized by its relative stability, where the percentage of loss is 8.7% in the range (39.9–210°C).[10,11] Temperatures (212.87–441.27°C), and loss of weight of hydrogel from 98.28 to 44.43 where the second step for weight loss is the loss of -CONH2 and –COOH as shown in Figure 1.

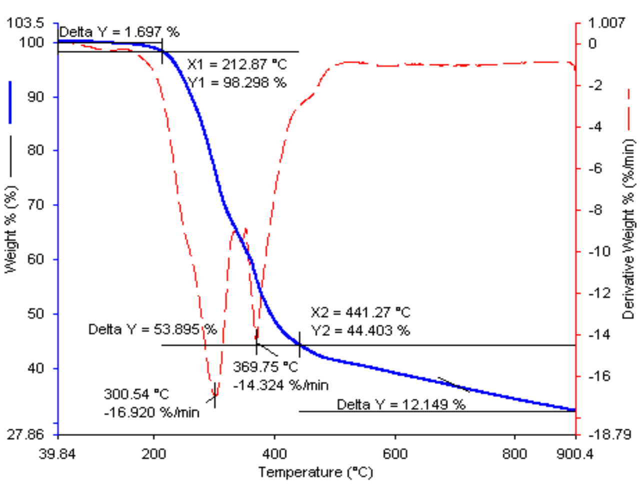

Figure 1: TGA analyses of (GO/ P(AA-co-MA) hydrogel

XRD Analysis

XRD technique was used for pure graphite and graphite oxide, and after loading graphite oxide onto hydrogel, the measured (XRD) technique for pure graphite, and it was noted that one sharp peak was 2θ 25.6 degrees. It depends on the formation of the Epoxide group, OH, C=O, which depends on increasing the distance between the layers. Also, the XRD technique was measured for the hydrogel surface after the graphite oxide loading process,[12,13] where it was noted that the shape is amadelphous with broad, blunt peaks, i.e. non-crystalline, meaning that the surface has a non-crystalline nature as appearing in Figure 2.

AFM Analysis

Atomic force microscopy (AFM) was utilized to estimate the surface hydrogel's topography, as shown in Figure 3. Image 2D and 3D dimensional of the hydrogel, The image shows that the prepared surface has a bumpy nature by clear roughness.

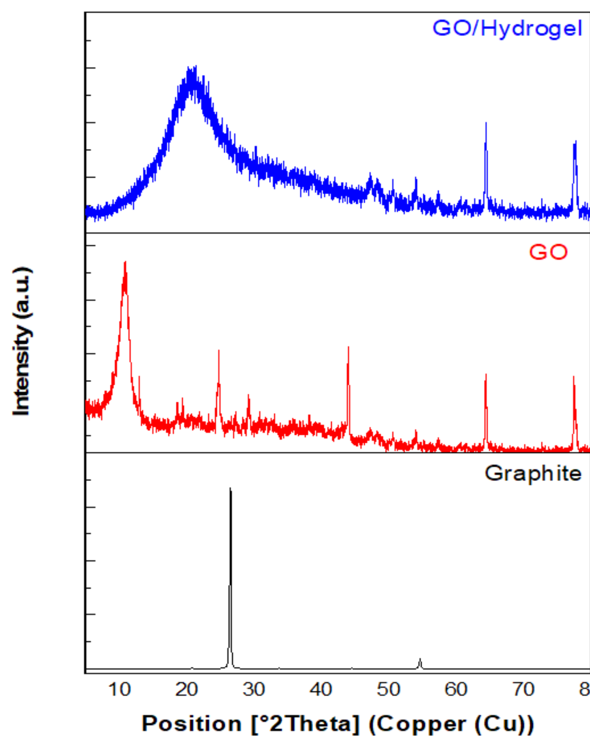

Figure 2: XRD of Graphite, Graphene oxide, and GO/hydrogel

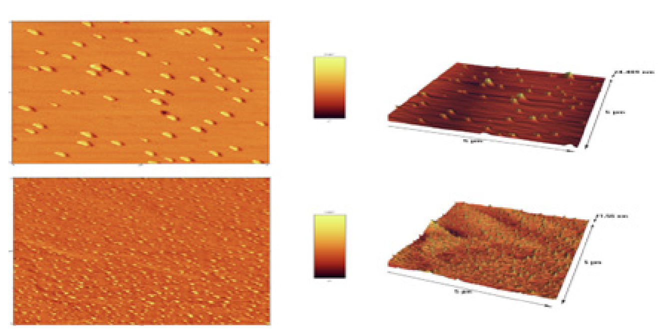

Figure 3: 2D and 3D-AFM images of hydrogel

Transmission Electron Microscopy (TEM) Analysis

TEM technique was used for the surface of the prepared after the process of loading graphite oxide on the polymer (GO/Poly (AA-co-MA), where it was observed that some small cavities and protrusions appeared as evidence of loading (GO) on the polymer[14] as appear in Figure 4.

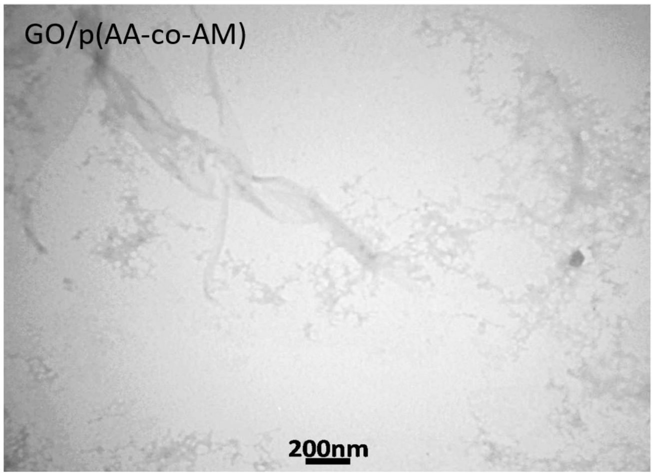

Figure 4: TEM image of GO/P(AA-co-MA) hydrogel

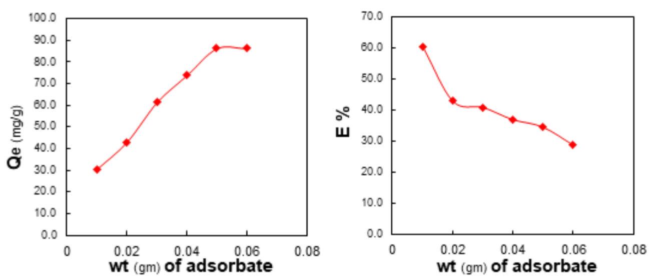

Figure 5: Effect of weight hydrogel on adsorption

Effect of Adsorbent Dosage

Adsorbent amount variation appears that the rising mass hydrogel in an aqueous medium leads to dye removal. The plot of adsorption capacity and percentage E% of dye against the weight of the hydrogel. As appear in Figure 5, it is observed that the E% removal is increased by rising in the weight adsorbent. This might be reflected in the surface area increase of the hydrogel, which increases the binding sites.[1,5,15,16]

Adsorption Isotherm

Three types of adsorption isotherms, Freundlich, Langmuir and Temkin, were studied. As shown in Figure 6(a), the Langmuir isotherm model is based on the active sites of the surface of the preparation. These active sites can adsorb to the monomolecular layer, and there is no interaction between the adsorbed molecules. The Freundlich isotherm is shown in Figure 6(b). Adsorption depends on heterogeneous surfaces. This isotherm depends on the quantities of adsorbents concentrated on the surface. The Temkin isotherm is shown in Figure 6(c) comprises an element that considers the adsorbent-adsorbent interactions. By ignoring the minuscule and significant value of the concentrations, the model assumes that the heat of adsorption for all molecules in the layer will decrease linearly rather than logarithmically with coverage. AM hydrogel system using Langmuir, Freundlich and Timken isotherms. Table 1, Figure 6 shows the highest correlation coefficients (R^2 =0.9494) related to the Freundlich model.[8,13,14]

Kinetics Adsorption

Adsorption Kinetic of the data were analyzed using the first and second order. The Lagergren –first-order calculate in eq.:

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

kinetic linear of the c second-order can be calculated in the equation:

$$q_t = (K_2 q_e t)/(1+K_2 q_e t) \quad (3)$$

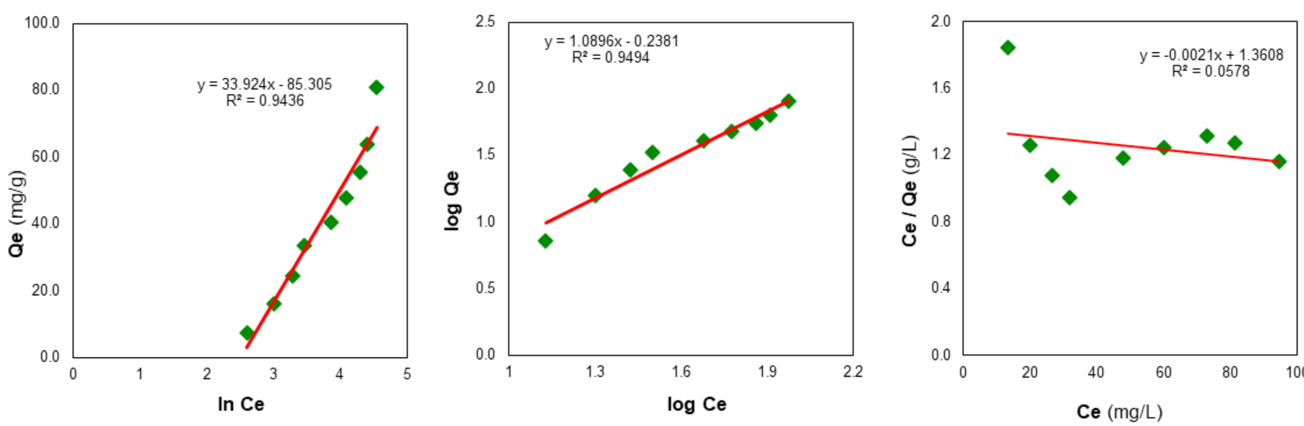

Figure 6: isotherm Langmuir (A), isotherm Freundlich (B), and isotherm Temkin (C) of dye adsorption on to hydrogel

Table 1: Adsorption isotherms of the adsorption dye onto the hydrogel

Langmuir equation			*Freundlich eq.*			*Temkin eq.*		
$K_{L\ (L/mg)}$	$q_{m\ (mg/g)}$	R^2	K_F	n	R^2	$K_{T\ (L/g)}$	$B_{\ (J/mol)}$	R^2
-0.0015	-476.190	0.0578	0.578	0.918	0.9494	0.081	33.924	0.9436

Table 2: Parameters of the kinetic adsorption of Rhodamine B dye

Pseudo- first-order					
R^2	QE (mg/g)	k_1(min^{-1})	Intercept	Slope	
0.6882	4.128	0.017	1.418	-0.017	
Pseudo- second-order					
h (mg. g^{-1}. min^{-1})	R^2	q_e (mg/g)	k_2 (g. mg^{-1}.min^{-1})	Intercept	Slope
21.008	1.0000	34.722	0.017	0.048	0.029

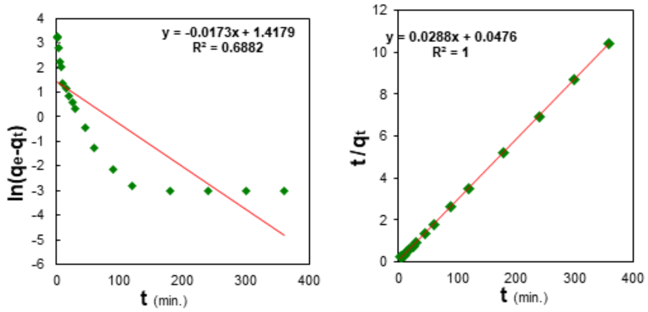

Figure 7: effect of kinetic adsorption of the first-order (a). second-order (b) Equilibrium time

The adsorption kinetics process defines the investigational data elected for dye adsorption onto hydrogel as shown in Figure 7. An investigational data study was done using the first order and second order Table 2 results display adsorption of dye by use of hydrogel is a viable method because the value ($R^2 = 1$) is top of the second-order compared to the first order.[16-20]

CONCLUSION

This research is based on studying the adsorption isotherm (Freundlich, Langmuir, and Temkin). The results found that it obeys the Freundlich isotherm depending on the value of ($R^2 = 0.9494$). Also, the adsorption kinetics were studied (first-order and second-order), and it was found that they obey the second model depending on the value of ($R^2 = 1$). The best hydrogel weight (0.05g) gave the highest adsorption efficiency at one hr equilibrium time.

REFERENCE

1. Jan SU, Ahmad A, Khan AA, Melhi S, Ahmad I, Sun G, Chen CM, Ahmad R. Removal of azo dye from aqueous solution by a low-cost activated carbon prepared from coal: adsorption kinetics, isotherms study, and DFT simulation. Environmental Science and Pollution Research. 2021 Feb;28(8):10234-10247. https://doi.org/10.1007/s11356-020-11344-4.
2. MJ Alshamri A, M Aljeboree A, B Alqaragully M, F Alkaim A. Removal of toxic textile dyes from aqueous solution through adsorption onto coconut husk waste: Thermodynamic and isotherm studies. Caspian Journal of Environmental Sciences. 2021 Jul 1;19(3):513-522.
3. Hassan H, Salama A, El-Ziaty AK, El-Sakhawy M. New chitosan/silica/zinc oxide nanocomposite as adsorbent for dye removal. International journal of biological macromolecules. 2019 Jun 15;131:520-526.
4. Ganduh SH, RQK MA, Aljeboree AM, Jasim LS. Selective Spectrophotometric Determination of 4-amino Antipyrine Antibiotics in Pure Forms and their Pharmaceutical Formulations. International Journal of Drug Delivery Technology. 2021;11(2): 371-375.
5. Zhao B, Jiang H, Lin Z, Xu S, Xie J, Zhang A. Preparation of acrylamide/acrylic acid cellulose hydrogels for the adsorption of heavy metal ions. Carbohydrate polymers. 2019 Nov 15;224:115022.
6. Divyapriya G, Srinivasan R, Nambi IM, Senthilnathan J. Highly active and stable ferrocene functionalized graphene encapsulated carbon felt array-A novel rotating disc electrode for electro-Fenton oxidation of pharmaceutical compounds. Electrochimica Acta. 2018 Sep 1;283:858-870.
7. Yasin AS, hyun Kim D, Lee K. One-pot synthesis of activated carbon decorated with ZnO nanoparticles for capacitive deionization application. Journal of Alloys and Compounds. 2021 Jul 25;870:159422.
8. Jasim LS, Aljeboree AM. Removal of Heavy Metals by Using Chitosan/Poly (Acryl Amide-Acrylic Acid) Hydrogels: Characterization and Kinetic Study. NeuroQuantology. 2021 Feb 1;19(2):31-38.
9. Faleh YA, Radhy ND. Removal of Metformin hydrochloride from Aqueous Solutions by using Carboxymethyl cellulose-g-poly (acrylic acid-co-acrylamide) Hydrogel: Adsorption and Thermodynamic Studies. InIOP Conference Series: Earth and Environmental Science 2021 Jun 1 (Vol. 790, No. 1, p. 012062). IOP Publishing.
10. Aljeboree AM, Mohammed RA, Mahdi MA, Jasim LS, Alkaim AF. Synthesis, characterization of p (Ch/aa-co-am) and adsorptive removal of pb (ii) ions from aqueous solution: Thermodynamic study. NeuroQuantology. 2021 Jul 1;19(7):137-143.
11. Jawad MA, AJK ND, Radia ND. Role of Sodium Alginate-g-poly (Acrylic acid-fumaric acid) Hydrogel for Removal of Pharmaceutical Paracetamol from Aqueous Solutions by Adsorption. International Journal of Pharmaceutical Quality Assurance. 2021;12(3):202-205.
12. Yazidi A, Atrous M, Soetaredjo FE, Sellaoui L, Ismadji S, Erto A, Bonilla-Petriciolet A, Dotto GL, Lamine AB. Adsorption of amoxicillin and tetracycline on activated carbon prepared from durian shell in single and binary systems: Experimental study and modeling analysis. Chemical Engineering Journal. 2020 Jan 1;379:122320.
13. Aljeboree AM, Abbas AS. Removal of pharmaceutical (paracetamol) by using CNT/TiO2 Nanoparticles. Journal of Global Pharma Technology. 2019;11(01):199-205.
14. Kamil AM, Mohammed HT, Alkaim AF, Hussein FH. Adsorption of Congo red on multiwall carbon nanotubes: Effect of operational parameters. Journal of Chemical and Pharmaceutical Sciences. 2016;9(3):1128-1133.
15. Zaheer Z, Aisha AA, Aazam ES. Adsorption of methyl red on biogenic Ag@ Fe nanocomposite adsorbent: Isotherms, kinetics and mechanisms. Journal of Molecular Liquids. 2019 Jun 1;283:287-298.

16. Dhiman J, Prasher SO, ElSayed E, Patel RM, Nzediegwu C, Mawof A. Heavy metal uptake by wastewater irrigated potato plants grown on contaminated soil treated with hydrogel based amendments. Environmental Technology & Innovation. 2020 Aug 1;19:100952.
17. Kim YS, Kim JH. Isotherm, kinetic and thermodynamic studies on the adsorption of paclitaxel onto Sylopute. The Journal of Chemical Thermodynamics. 2019 Jan 1;130:104-113.
18. Alkaim AF, Aljobree AM. White marble as an alternative surface for removal of toxic dyes (Methylene Blue) from aqueous solutions. Internat J Adv Sci Technol. 2020;29(5):5470-5479.
19. Ghaedi M, Sadeghian B, Pebdani AA, Sahraei R, Daneshfar A, Duran CE. Kinetics, thermodynamics and equilibrium evaluation of direct yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon. Chemical Engineering Journal. 2012 Apr 1;187:133-141.
20. Yao Y, Bing H, Feifei X, Xiaofeng C. Equilibrium and kinetic studies of methyl orange adsorption on multiwalled carbon nanotubes. Chemical Engineering Journal. 2011 May 15;170(1):82-89..