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RESEARCH PAPER

Eco-Friendly Preparation of Moringa Oleifera Hydrogel Nanocomposites as Effective Adsorbent for Removal Drug: Adsorption Isotherm

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ABSTRACT

In this study, the preparation of low-cost, eco-friendly adsorbent Poly (Acrylic acid -acryl amide)/Moringa plant, (AAc-AM)/MO hydrogel composite, the composite preparation via free radical polymerization by using Specific ratios between (AM/AAc) as a monomer and moringa plant. The innovator adsorbent was estimated to be characterized by TGA and FT.IR, TEM, and FE-SEM. A suite of adsorption tests was studied using the optimal conditions like contact time, pH solution, the concentration of the drug, and weight of the hydrogel composite. The adsorption capacity decreased from (8.11 – 4.123 mg/g) when the importance of the hydrogel composite increased from (0.025-0.15 g), demonstrating the number of adsorption increases with increased pH, that increased adsorption capacity with continuous in a base medium. The adsorption isotherms of hydrogel composite could be illustrated well by the Freundlich Langmuir and Timken equations. The process of Drug adsorption on hydrogel composite depended on Freundlich isotherms more than Langmuir and Timken equations.

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INTRODICTION

Industry advancements in technology and resources have created more compounds and complexes, increasing the number of complexes with powerful properties. The environment affects living things. An increase in hidden substances indicates the potential for environmental hazards to organisms [1, 2]. Furthermore, medicines and personal care products (P.P.C.P.s), dyes, surfactants, some industrial additives, and many chemicals that have not been metabolized and discharged into sewers as well as wastewater treatment plants are imaginary to be endocrine disruptors (W.W.T.P.s). As a result, a challenge to other designers of treatment plants is posed, as well as an associated methodology to eradicate them. As a result, problems related to such expanding complexities have been debated to highlight the challenge in addressing these challenges [3, 4]. Medications significantly affect disease treatment and prevention in humans and animals. Yet, due to the nature of medicines, they may have unforeseen consequences for animals and microbes in the environment. Although the adverse effects on human and animal health are normally thoroughly explored in safety and toxicology studies, the potential environmental repercussions of pharmaceutical manufacturing

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and usage are less well recognized and have only lately become a research focus of interest [5, 6]. Low hormone medication concentrations in the water environment might interfere with the aquatic animal's normal hormone levels and affect physiological function Moringa plant. A 12 m-long tree found in South America, the Caribbean, the Pacific, Southeast Asia, the Arabian Peninsula, and Africa grows quickly in arid tropical climates [7, 8]. They are grown for their therapeutic properties, and the leaves, seeds, and other parts of them are edible. The origins of the Moringa plant have antibacterial characteristics, eliminate turbidity, don't change water pH, produce biodegradable sludge and have minimal sludge volume. Due to these factors, the Moringa plant can be successfully utilized in water treatment to remove pollutants from industrial or murky river or marine water. Tartrazine, Naphthol blue-black, and industrial hazardous dyes Ni (II) are all treated using Moringa plant seed powder [9, 10].

MATERIALS AND METHODS

Obtained Moringa plant from farms of Iraq – Diwaniyah. Acrylamide (AAm) (C.D.H. Himedia and purity 99.000%). Acrylic acid (A.A.) (C.D.H. Himedia and purity 99.000). N,N-Methylene-bis –acrylamide(M.B.A.)(C.D.H. Sigma Aldrich and purit (99.900). Potassium persulfate (K.P.S.), (C.D.H. Fluka and purity 99.900).

Synthesis of Poly (Acrylic acid -acryl amide)

Step 1- Cross-linked hydrogels were prepared by the free radical polymerization method in the presence of nitrogen gas, including dissolving 1g of acrylamide (A.A.M.) and dissolving it in (5)ml of D.W. Then (10) ml of acrylic acid was added to it, and mixing done until the two components are completely dissolved. A magnetic stirrer is used for this purpose. A solution of the cross-linking agent M.B.A. (methyl di acrylamide) was added to the mixture prepared by dissolving (0.05) g in (2) ml of D W. Then the potassium sulfate initiator solution (K.P.s), which was organized by taking 0.05 and dissolving it in (2)ml of distilled water, was gradually added to the reaction mixture.

Step 2-The Poly (Acrylic acid -acryl amide) mixture then was added to the Moringa plant which is brought to the variety prepared by dissolving it(0.1)g in(20) ml of D.W. and left on the magnetic stirrer for half an hour; then, it was put it in the ultrasonic device for dissolution. Finally, the plant was added as drops,

Step 3-The mixture was transferred to the water bath for an hour to complete the polymerization;

Stepn4- Then, the polymer was extracted

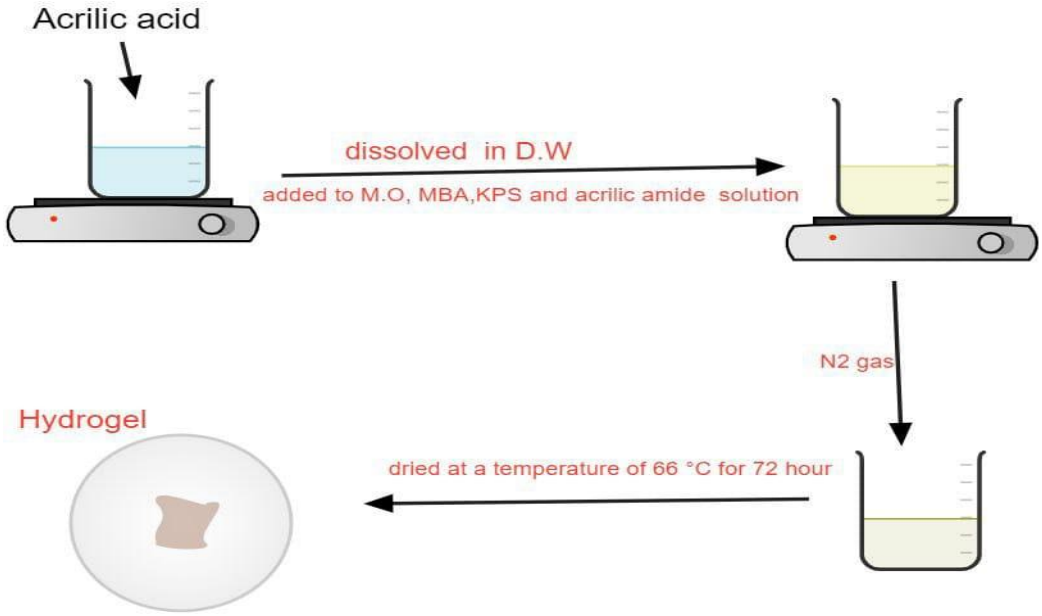

Fig. 1. Methods synthesized of hydrogel P(AAC- -AM)/MO.

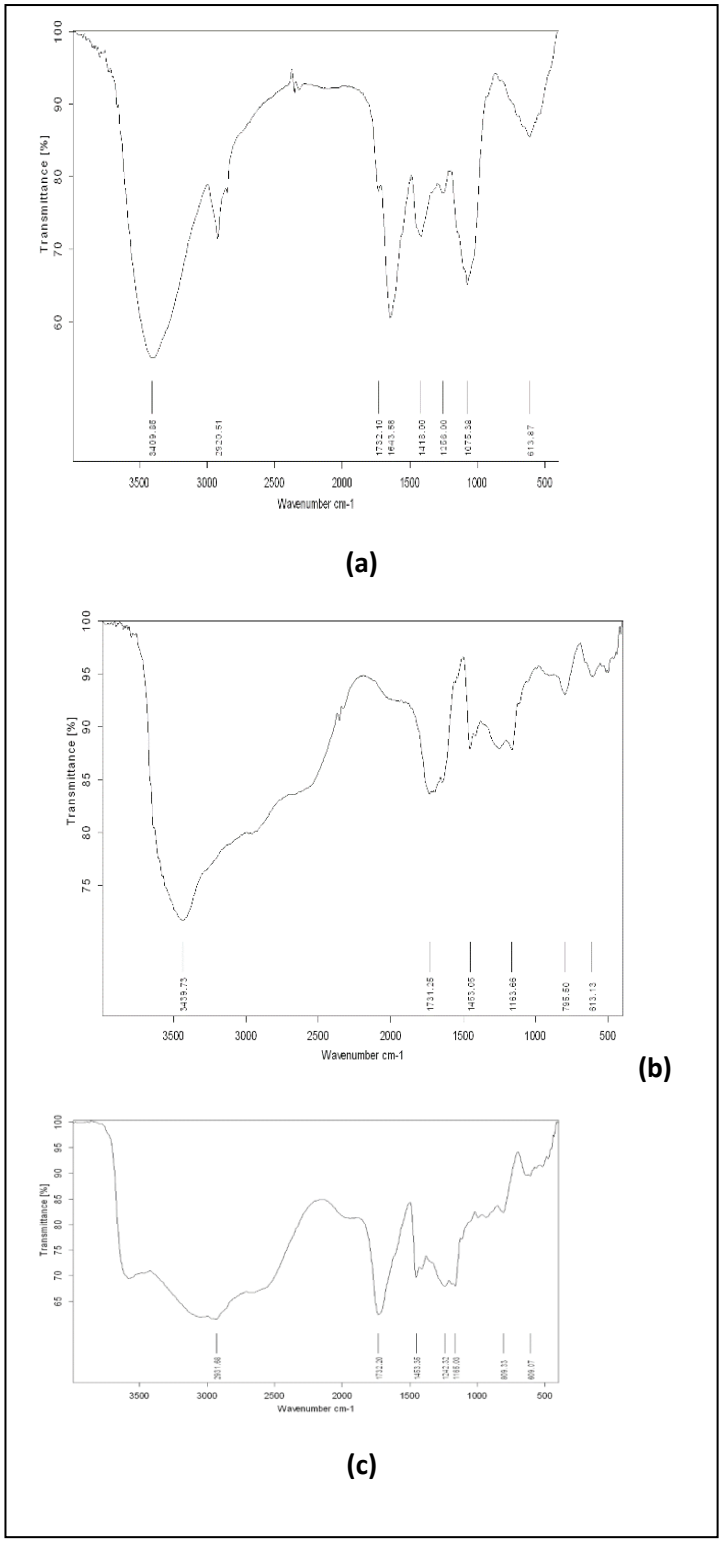

Fig. 2. FT-IR spectrum of a) Moringo plant, b) hydrogel composite, c) Hydrogel composite after adsorption.

and washed several times with distilled water to eliminate the unreacted substances. It was dried at a temperature of 66 °C for 72 hours with the ground to be ready for experiments .added in the form of drops, As in Fig. 1.

RESULT AND DISCUSSION

Characterization

To detect and characterize the locations of the functional groups in the compounds, to describe the nature of the interaction, and to demonstrate the impact of resonance, induction, and hydrogel bonding on the displacement of positive numbers, infrared spectroscopy (FT-IR), one of the most practical and efficient techniques, was used. (FT-IR) spectroscopy was used to measure the different functional groups in hydrogel and drug-loaded composite materials. In line with Fig. 2. It was noticed the following: Wide absorption bands in the hydrogel spectrum's (3550-2650) cm^{-1} area cause asymmetric aliphatic vibrations of the N-H, O-H, methylene group, aliphatic, and aromatic stretches to interfere. Both the stretching vibration carbonyl C=O and the crosslink (MBA) caused by the carbonyl groups from the carboxylic acid, extra intensity vibration in range (2460-1000)cm^{-1} is

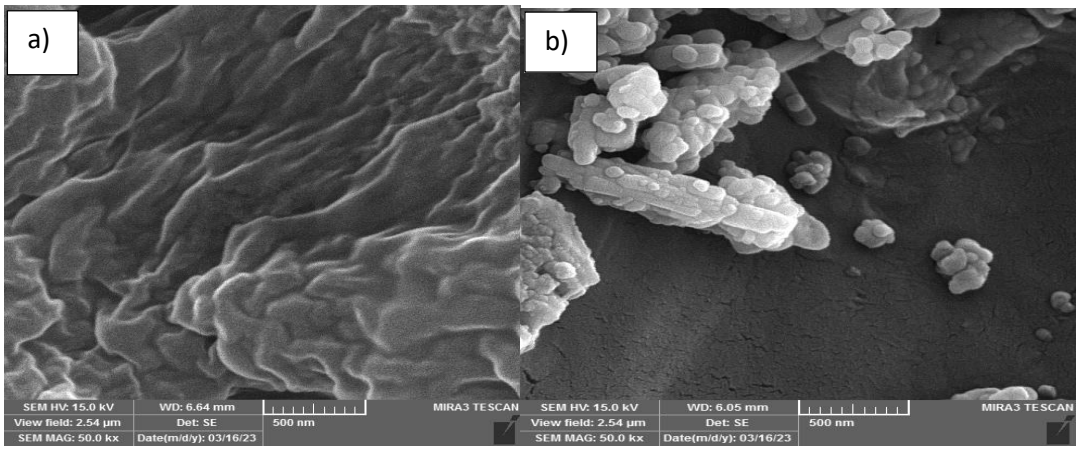

Fig. 3. FE-SEM picture from a) hydrogel composites in(500) nm and b) hydroel composites after dasorpton in (500) nm .

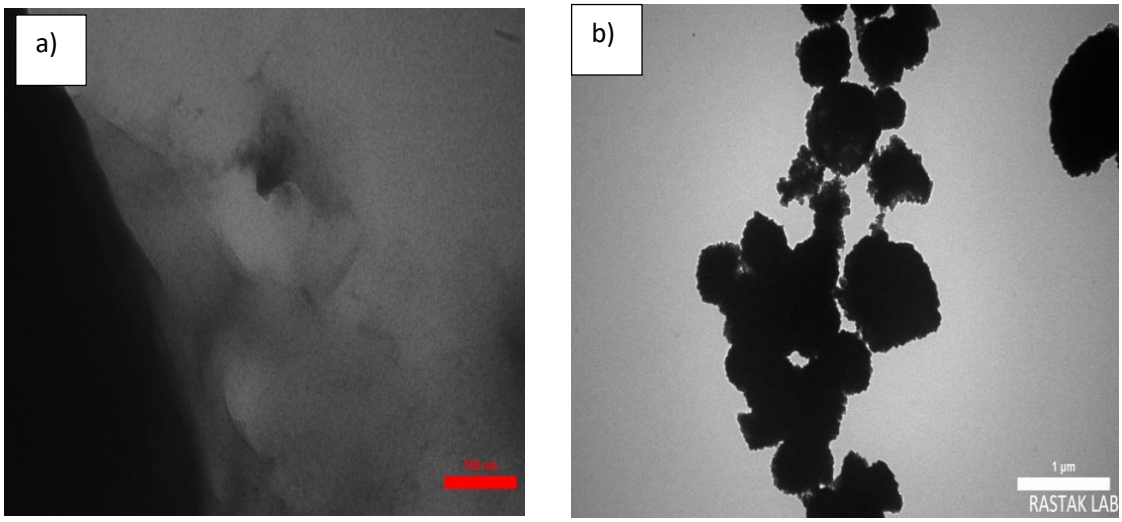

Fig. 4. TEM picture for (a) moringo plant , (b)hydrogel(AAC-AM) composite .

connected to N-H, OH bending and, C-N, C-O, C-C turning [11]. It was observed that the absorption peak migrated towards certain functional groups in the case of composite spectra, particularly in the carbonyl area. Because of hydrogen bonding, the stretching vibrations of carboxyl and amide groups are moved to lower vibrations.[10-13]. The drug-loaded composites' FTIR spectra are more upward-looking and exhibit enhanced band intensity. The absorption peaks show new bands with high wave numbers (3500-2600) cm^{-1} in foreign countries, which are related to the modern interaction between the functional groups of the drug, and the vibration of the carbonyl group is diminished

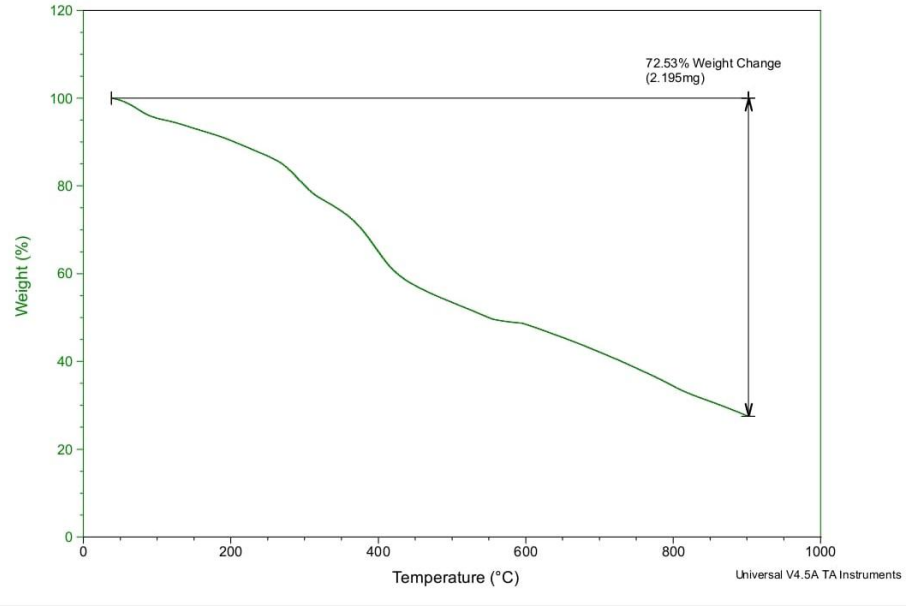

Fig. 5. TGA picture of hydrogel composite (AAC- -AM).

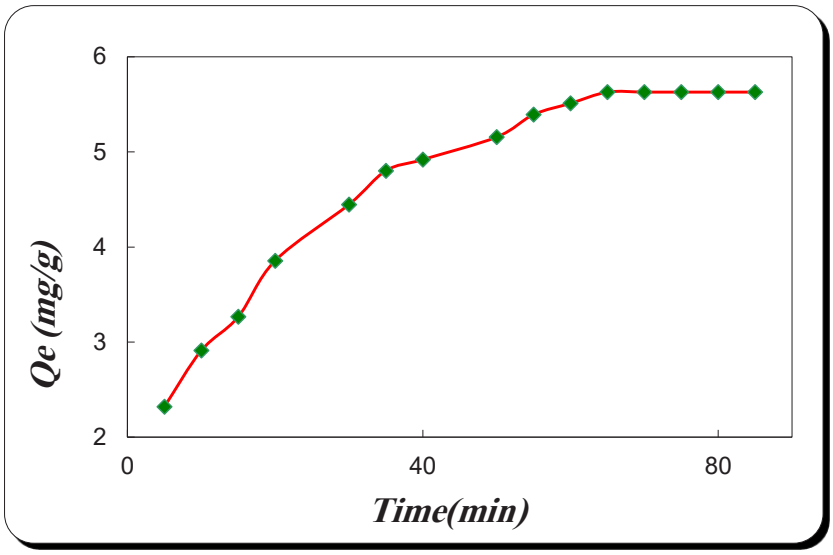

Fig. 6. Effect of contact time.

to a lower level due to the hydrogen bond wave number in more than one region indicating drug adsorption on the surface complex. Furthermore, new intensity vibrations (1300-1110) cm^{-1} are connected to (C=C) [12].

The field emission scanning electron images were captured at 500 nm. With the help of this investigation, it was possible to determine the particles' shape, the clusters' makeup, and the adsorbent surfaces' porosity before and after adsorption. The figure shows just a slight modification; the surface of the composite is

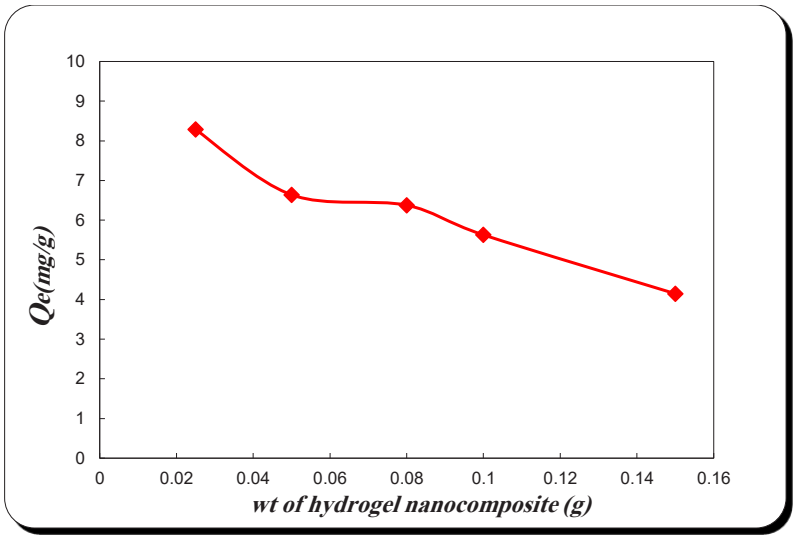

Fig. 7. Effect of weighthydrogel composite on Glyphage drug(drug conc:100 mg/L,Temp. :25 °C).

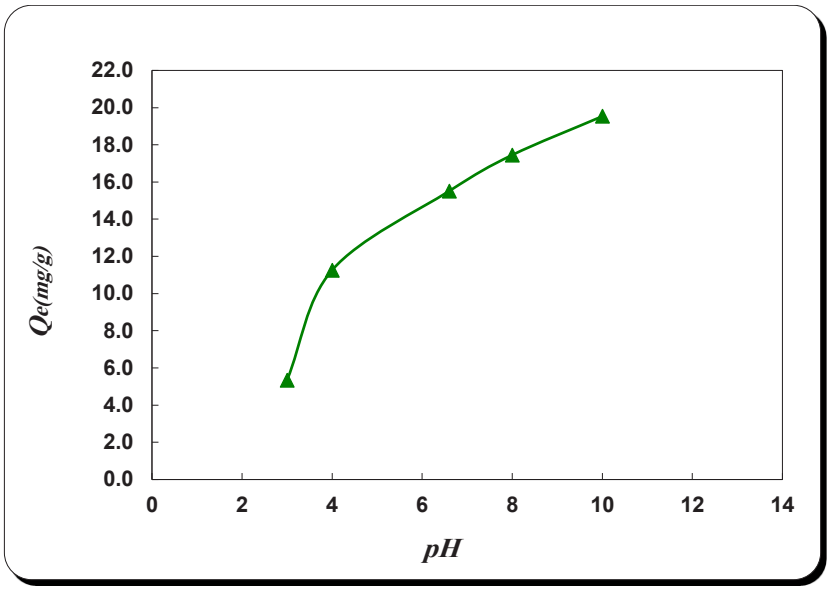

Fig. 8. Effect of solution pH of hydrogel composite 0.1g, Glycophage concentration (100) mg/L, Temp 25 °C.

rather rough. Fig. 3b shows characters following drug adsorption due to its rich functional groups, which include carbonyl, carboxyl, and hydroxyl, and sponge-like structure from the cross-linked hydrogel network. The porous network provides additional adsorption sites, making it a tiny ball-shaped agglomeration [13].

Morphological properties of the synthesized moringa plant, as shown in Fig. 4a. A clear view of images as the material was formed as a powder; it was found that the samples had many layers[14, 15]. The semitransparency of the moringa plant indicates that the material is unstable. The morphology of the moringa plant showed that it was made up of thick layers of flat flakes, had a rough surface that wasn't crumpled, and had particles of different sizes. And a high level of exfoliation. This made the structure disordered and free of wrinkles. Images of TEM micrographs for composite drug-adsorbent are represented in Fig. 4b. This means that the hydrogel mixed form elastic forces between moringa plant layers and assist in exfoliating plant layers [16-18].

Thermal Gravimetric Analysis

Its curved (TGA) is for the adsorbent hydrogel composite shown in Fig. 5. It shows that the sample goes through multiple stages during the pyrolysis process; if the initial weight loss of the polymer is observed at the temperature (90°C), it is due to the loss of water molecules from the adsorbent polymer; the loss was also noted 46.16.% of the polymer weight in the thermal range (241-385°C)which indicates the dissociation of the carboxyl and amide groups in the cross-linked polymer. In contrast, the sharp decrease in the weight of the polymer, which reaches 69.90% at the temperature range of 385-550 °C, refers to the breaking of polymer chains [19-21].

Effect of contact time

One of the significant effects of the agent on the adsorption capacity is the removal of the drug at a concentration of (100) mg / L studied at different time intervals at the pH of (6) weight of composite (0.1) g, as shown in Fig. 6, shows how the adsorption shows the composition of the drug on the surface since the drug's adsorption increases with time until it reaches (60) min. After this time, it stops because all active sites of the composite is saturated because it's loaded with adsorbates [22-24].

Effect of weight composite

When using different weight ranges of composites (0.15-0.025) g with (100) mg/L of the

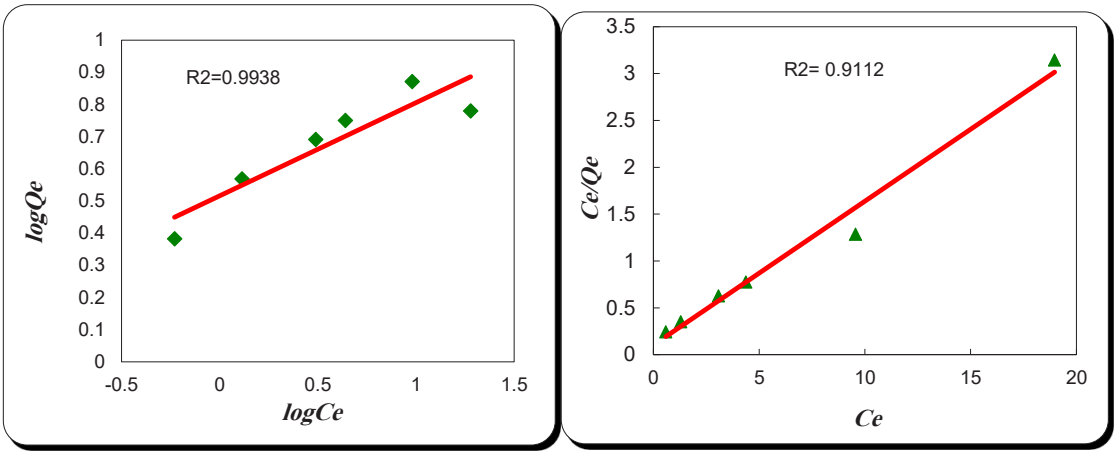

Fig. 9. Isotherm Langmuir (a), isotherm Freundlish (b), of Gly drug.

Table 1. Two Adsorption isotherm factors for adsorption of drug onto hydrogel composite.

Adsorption Isotherm	Freundlich			Langmuir		
	N	K_f	R^2	q_m	K_L	R^2
Gly,drug	3.4602	3.283	0.9938	6.510	1.28	0.9112

drug, the adsorption of the drug from solution was observed to increase with increasing surface weight until reaching (0.1) g [25], which shows that it is possible to fill all active sites in the surface composite, also due to the saturation state and adsorbent that adsorption capacity decrease from (8.11-4.123)mg/g when the weight of hydrogel composite increase from (0.025-0.15)g [26] as shown in Fig. 7.

Effect of pH solution

Pharmaceuticals' considerable impact on adsorption capacity. Metformin dosage of (100) mg/g, a temperature of 25°C, a rotating speed of 150 rpm, the adsorbent mass of the composite material of (0.1) g, and a contact duration of (60) min were used to determine the impact of pH on the drug absorption. It was discovered that when using pH values between (3 and 11), the quantity of adsorbent rises with acid function until it reaches pH=11, representing the ideal acid function. Fig. 8, therefore, shows that when the acidity of the solution increases, the number of adsorption increases in the range (of 2-6), and this can be understood. The sort of active group in the medicine and the composite Fig. 8 should first be displayed for clarification [27]. The composites feature a variety of functional groups, including oxygenate functional groups and epoxy (C-O-C), carboxylic acid (COOH), carbonyl (C=O), and hydroxyl (OH) [28]. This group exhibits hydrophilic behavior and is sensitive to pH changes. It is susceptible to both protonation and deprotonation. To acquire the ability to ionize and to carry neutral, positive, and negative charges. The metformin medication also contains hydroxyl, amide, carbonyl, and secondary amine groups [21].

Adsorption isotherms

Adsorption Isotherm appears as adsorbate (Gly) drug adsorption at 25℃. The experimental adsorption was performed according to the arrangement of drug molecules on the surface of the hydrogel composite based on multilayer and monolayer adsorption [29]. The present research studied the equilibrium condition of a drug in hydrogel hybrid and liquid phase solution of a drug, three types of Adsorption isotherms like Freundlich isotherm, Langmuir isotherm, and Temkin.The Adsorption Freundlich isotherm was based on heterogeneous and multilayer adsorption. The linear equation is calculated:

$$\ln q_e = \ln K_f + \frac{1}{2} C_e \quad (1)$$

Where n and kf can be evaluated from the linear plot of (ln qe versus ln Ce), n was a deviation from the linearity of adsorption, and 1/n was a heterogeneous factor. kf (L/g) as the Adsorption constant was related to the bond energy. Freundlich Langmuir isotherm theory is based on two assumptions: adsorption energy was constant over the process, and the adsorption of adsorbates occurs on a homogeneous surface via monolayer adsorption. The linear equation is calculated [30].

$$\frac{C_e}{q_e} = \frac{1}{q_m . K_L} + \left(\frac{1}{q_m}\right) * C_e \quad (2)$$

Two kinds of isotherm, Freundlich and isotherm Langmuir, are useful. Data appeared in Fig. 9 and Table 1. Linear type of isotherm Langmuir was more compatible with the experimental adsorption data, which approves that monolayer adsorption of the drug, occurred onto hydrogel composite and acceptor groups of medicines are distributed homo-generously and uniformly on the hydrogel composite. From the data of Table 1, according to the values (R2) of all the Adsorption isotherms [31].

Qe: equilibrium adsorbed-amount (mg. g^{-1}), Ce: the equilibrium solution's adsorbate concentration (mg. L^{-1}),A_T Equilibrium binding constant of isotherm (L.g^{-1}). R is general gas constant (8.314J. mol^{-1} K^{-1}) ,T: Temperature in Kelvin and B:Constant connected to sorption heat (J.mol^{-1}).

The isotherm constants A_T and B_T are determined from a plot of q_e versus ln c_e and its slope and intercept. This isotherm model's applicability suggests that the adsorbate is evenly scattered throughout the adsorbent's surface. The experimental data was fitted to various isotherms as listed in Table 1 and Fig. 9.

CONCLUSION

This work created composite (AAC-AM)/MO using free radical polymerization techniques. This composite was recommended to be characterized by FE-SEM and FT-IR spectra of the composite before and after the adsorption was completed

to demonstrate the nature of the functional group. It has shown effective high efficiency from removing the metformin and reached 90.3%. Used field emission scanning electron to characterize the morphology, it offers a porous network and looks like a composite of spongy uneven layers. According to the experimental findings, the ideal state may have been fixed. The perfect pH for metformin adsorption is (pH=6), the ideal contact duration is (60) min, and the perfect dose form of the adsorbent is (0.1) g. Freundlich's isotherm model shows several methods for establishing the adsorption process. Multilayers represent Freundlich's isotherm model, Adsorption processes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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