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RESEARCH PAPER

Economic Removal of Paracetamol drug from Aqueous Solution Using Olive Leaf Plant Hydrogel Nanocomposite as an Effective Adsorbent

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ABSTRACT

Paracetamol is a pain reliever and fever reducer that is commonly used in Malaysia. Because paracetamol is a medicinal substance, it is not biodegradable and will not degrade quickly. This will cause an environmental and health hazard because the residue will seep into wastewater, groundwater supplies, and eventually drinking water. In this study, has been prepared of low cost eco-friendly adsorbent Poly (Acrylic acid -acryl amide)/ Olive leaf plant, (AAc-AM)/OL hydrogel composite, the composite was prepared by free -radical polymerization by using a Specific ratio between hydrogels composite as a monomer and olive leaf plant. The resulting hydrogels were characterized by Fourier transform infrared (FTIR), thermo gravimetric analysis (TGA), and Field emission scanning electron microscopy (FESEM). A series of adsorption experiments were carried out under the Optimal conditions such as contact time and solution , pH ,the concentration of the drug ,and weight of the hydrogel composite .The adsorption capacity decrease from (8.11 – 19.3($mg.g^{-1}$ when the weight of the hydrogel composite increase from (0.025-0.15(g, demonstrating the quantity of adsorption increased with increased pH ,that increased adsorption capacity with continuous in a base medium. Adsorption isotherms of hydrogel composite are well described by the Freundlich, Langmuir and Temkin isotherm. The maximum sorption capacities of paracetamol onto Hydrogel is 17.857 mg g^{-1}.

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INTRODICTION

Adsorption is a phenomenon in which gas or liquid substances another on the surface of another solid substance in the form of molecules, atoms or ions, and is a physical or chemical association of substance molecules acting on surface active sites through weak van der waals forces. Adsorption can also involve the removal of dissolved solids in a solution or recovery of dissolved solvents through solid surfaces, a process known as (Desorption) [1, 2],The adsorption process is usually accompanied by a decreased in energy (Surface Free Energy (ΔG), and by a lack of entropy (ΔS)since adsorbed molecules are confined due to binding to surface atoms Olea europaea L., an evergreen tree in the Oleaceae family [3, 4]. Olive leaf is one on the most important by-products in olive cultivation.These leaves are used as an extract or as a powder for the whole range. Available on fresh leaf or dried form. Olive leaves contain a variety of potentially

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bioactive compounds with antibacterial, antioxidant, antihypertensive, cholesterol-lowering, and anti-inflammatory properties [5-7]. Arrhythmias and increases blood flow. Hydrogels are three-dimensional, hydrophilic, polymeric networks capable of retaining large amounts of water, characterized by a soft consistency, and thus resemble living tissues. Hydrogels can be chemically stable and "reversible, stabilized by molecular entanglement, typically by swelling a single–network hydrogel in a solution containing a mixture of monomer, initiator, and activators. A variety of hydrophilic polymers or their precursors have been used to synthesize hydrogels; the main categories include natural polymers and their derivatives (polysaccharides and protein) and those containing hydrophilic functional groups (such as –COOH, –OH, $–CONH_2$, SO_3H) synthetic polymer [7,8].

Hydrogels are being prepared for a variety of medical and tissue engineering applications. Medicines, tissue engineering. Drug delivery systems have improved therapy periods and drug activity. The system enhances drug active treatment time, the efficiency of eliminating various pollutants, and also utilizes water purification [9]. An example of the drugs used in this research is acetaminophen (paracetamol), or N-acetyl-para-aminophenol (APAP) is one of the most commonly used antipyretic and analgesic drugs worldwide [10-11]. Compounds related to paracetamol were first known in the 1880s when a patient accidentally administered acetanilide instead of naphthalene, resulting in a marked reduction in fever [12].

In this regard, according to the best of our knowledge, this is the first report for the synthesis of Poly (Acrylic acid, acryl amide) / olive leaf plant and characterized by Fourier transform infrared spectroscopy (FT-IR), Thermal Gravimetric Analysis (TGA), and Field emission scanning electron microscopy (FESEM). In the adsorption studies, was tested for the quantity of adsorbent of paracetamol from aqueous solutions, at different values of pH, quantity of adsorbent mass, contact time and initial drug concentration.

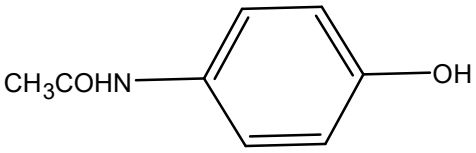
MATERIALS AND METHODS

Olive leaf plant from farms of Iraq – Diwaniyah. Acrylamide (AAm) (CDH Himedia and purity 99.000%). Acrylic acid (AA) (CDH Himedia and purity 99.000). N,N-Methylene-bis –acrylamide(MBA)(CDH Sigma Alderich and purity 99.900). Potassium persulfate (KPS) (CDH Fluka and Purity 99.900).

Paracetamol solutions preparation

The physicochemical characteristics and formula for paracetamol (PC) are shown in the Table 1. Deionized water was used to create paracetamol solutions (Millipore Direct Q4 Water Purification System). When necessary, pH changes were done by adding sodium hydroxide or 0.1 M hydrochloric acid to solutions. Each and every

Table 1. Chemical structures and selected properties of the adsorbates [13].

Compound	Paracetamol
Molecular structure	
IUPAC name	N-(4-hydroxyphenyl)- acetamide
Chemical formula	$C_8H_9NO_2$
Molecular weight	151.16 g.mol^{-1}

reagent was bought from Merck in Darmstadt, Germany. A Crison Model Digilab 517 pH metre was used to measure the pH.

Synthesis of Poly (Acrylic acid -acryl amide) / olive leaf plant

Part1: Cross linked hydrogels were prepared by the free radical polymerization method in the presence of nitrogen gas including dissolving) 1 (g of acrylamide (AAM) and dissolving it in 5 ml of D.W then 10 ml of acrylic acid is added to it and mixing is done until the two components are completely dissolved, and a magnetic stirrer is used for this purpose.

Part2: Then a solution of the cross linking agent MBA (methyl di acrylamide) is added to the mixture prepared by dissolving 0.05g in 2 ml of D W. Then the potassium sulfate initiator solution (KPs), which was prepared by taking 0.05 and dissolving it in 2 ml of D.W, was gradually added to the reaction mixture. Then the olive leaf plant is brought to the mixture prepared by dissolving it 0.1g in 20 ml of D.W and left on the magnetic stirrer for half an hour, then we put it in the ultrasonic device for the purpose of dissolution

Part3: Finally, the plant is added in the form of drops and the mixture is transferred to the water bath for an hour to complete the polymerization, then the polymer is extracted and washed several times with D.W to get rid of the unreacted substances. It is dried at a temperature of 66 °C for 72 hour with the ground to be ready for experiments added in the form of drops and the mixture is transferred to the water bath for an hour to complete the polymerization, then the polymer is extracted and washed several times with D.W to get rid of the unreacted substances. It is dried at a temperature of 66 °C for 72 hour and ground to be ready for experiments [14] as in Fig. 1.

RESULT AND DISCUSSION

Characterization

Fourier transform infrared spectroscopy (FT-IR)

Fig. 3 shows the (FT-IR)spectrum before drug loading. The chemical structure was confirmed by FT-IR, possibly showing a consequent functional group chang, and wavenumber the composite hydrogel matrix we found a large difference in peaks between hydrogel and hydrogel matrix. We found a large difference in the peaks belonging to the two drugs between the hydrogel and the hydrogel matrix, the difference indicates the interface between the drug and the adsorbent surface (hydrogels). The Spectrum occurs before

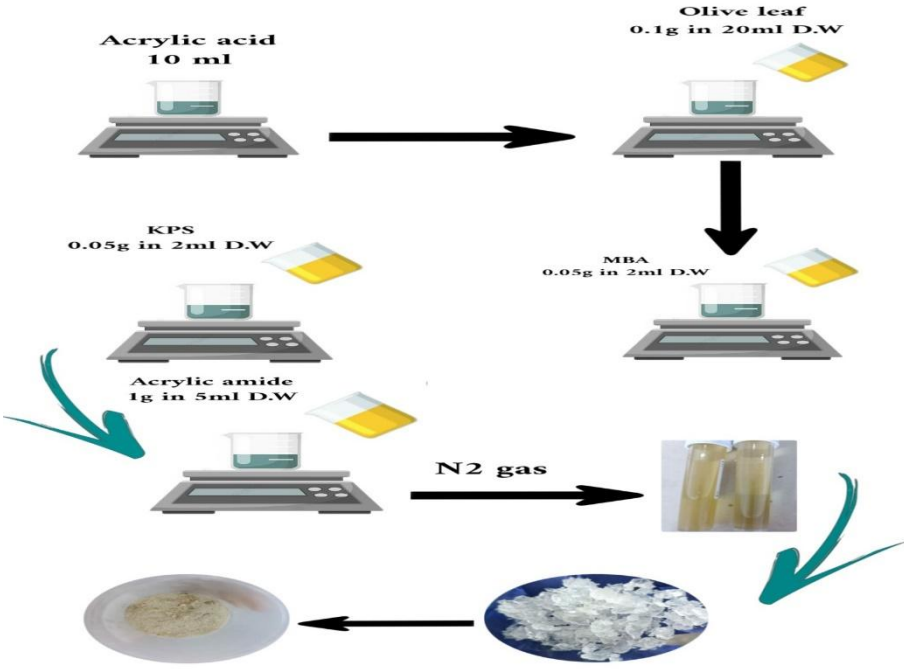


Fig. 1. Methods synthesized of hydrogel P(AAC- -AM)/OL.

the charged broadband stretching vibration is sandwiched between) 3400(and) 3100(cm^{-1} and the hydroxyl groups. Other bands in the (2630 -2517) cm^{-1} indicate asymmetric and symmetrical stretching.

Other important bands too show sharps C=O stretching vibrations for both the carboxyl and amide groups at 1659 and 1613 [8]. The plot of the two drugs shows a peak belonging to C=O with a wavenumber shift in the range 3400-3200 due to the occurrence of hydrogen bounding between the drug and hydrogel surfaces, new band that appear in the drug map corresponds to the emerging peaks that realign the aromatic groups when present in structural drugs, The peak of (C=C) noticed at the pairs at)1550($cm^{-1}$and bending out of plane)941(cm^{-1} from the curved plane the pracetimol drug also appeared in the) 1319((C-N) stretch of the drug in Fig. 2. Paracetmol a and Fig. 3b we can observe the difference between the two mea[9-11].

Field emission scanning electron microscopy (FESEM)

Field emission scanning electron microscopy (FESEM) is an important for studying after and before surface topography drug compound loading. FE-SEM images obtained at a magnification of 500 nm of each hydrogel, matrix sheet surface for the two drugs in Fig. 3(A). It was

Observed that the surface hydrogel was uniformly granular with voids formed between the particles, and Fig. 4(B),clarified that the pracetimol drug loaded on the hydrogel seemed to have a

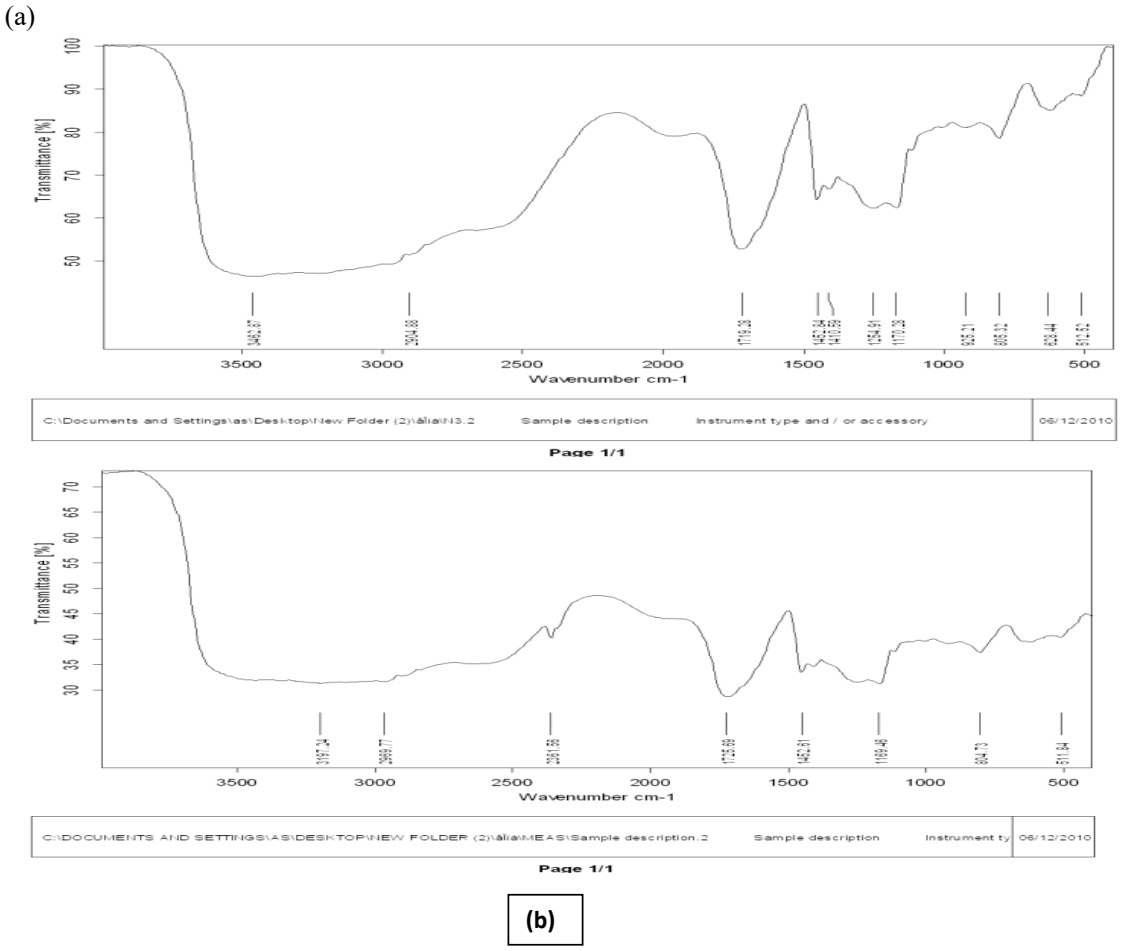


Fig. 2. FT-IR spectrum of a) hydrogel composite with olive leaf plant c) Hydrogel composite after adsorption.

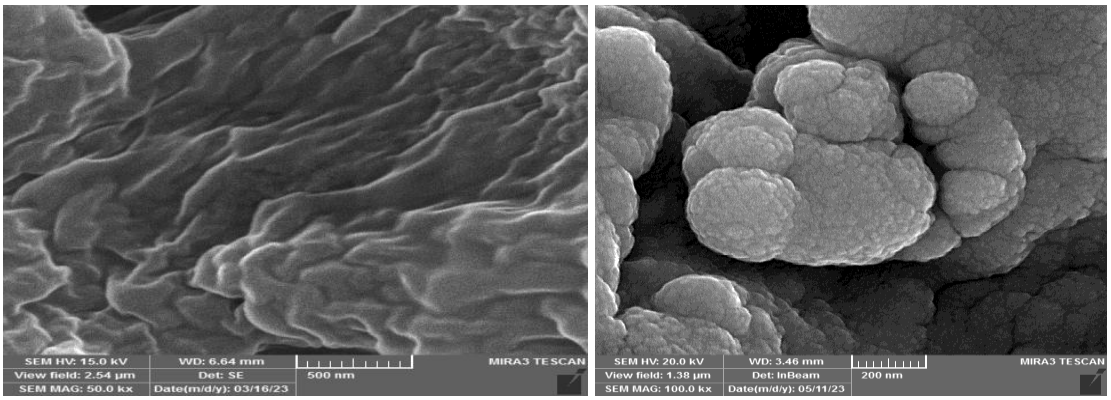
heterogeneous form, represented in Fig. 3(B) the hydrogel –loaded pracetimol drug appears as uniform granules that look like wave [12, 13].

Thermal Gravimetric Analysis

Its curvature (TGA) is suitable for the adsorbed hydrogel composite shown in Fig. 4. It shows that the sample goes through several stages during the pyrolysis process, if an initial weight loss of the polymer is observed at temperature 90°C, this is also due to the loss of water molecules from the adsorbed polymer, which loses 32.61% of the polymer weight in the thermal range 250-350 °C,indicating the dissociation of the carboxyl and amide groups in the cross-linked polymer, while the polymer weight dropped sharply, reaching 44.06% at the temperature range 350-550 °C, indicating polymer chain scission [14].

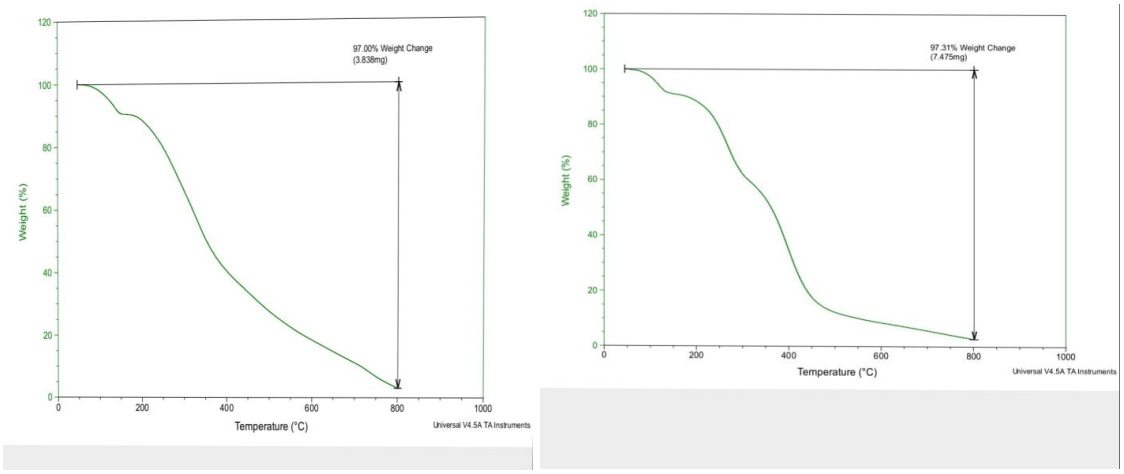
Contact Time

One of 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 pH of 6 weight of composite (0.1)



(a) (b)

Fig. 3. FE-SEM picture from (a) hydrogel composites in(500) nm and (b(hydroel composites after dasorpton in (200) nm.



(a) (b)

Fig. 4. TGA picture of (a) hydrogel composite (AAC- -AM) and (b) olive leaf plant.

g. As show in Fig. 5, how the adsorption shows the composition of the drug on the surface, since the drug of the adsorption increase with time until reached 60 min. After this time it stop, because all active sites from the composite are saturated because it's loaded with adsorbates [15, 16].

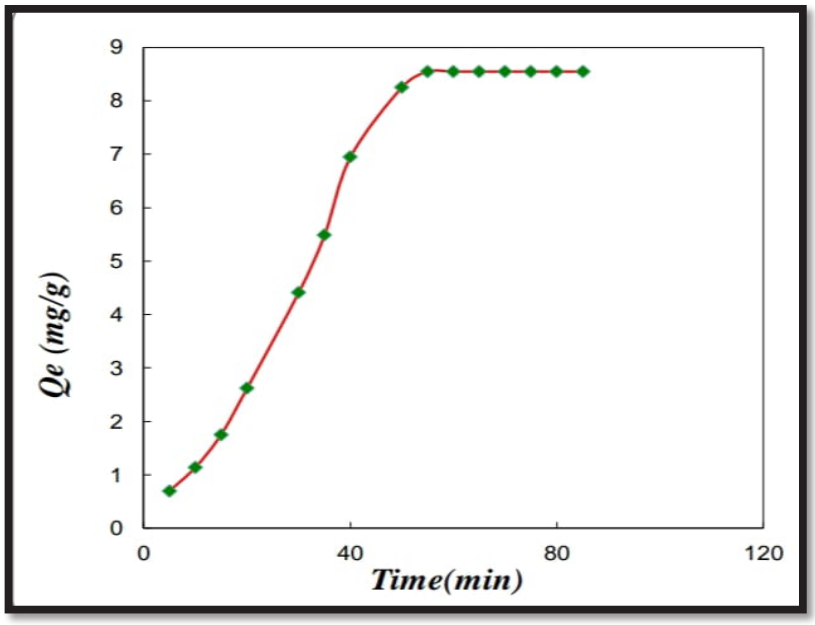


Fig. 5. Effect of contact time.

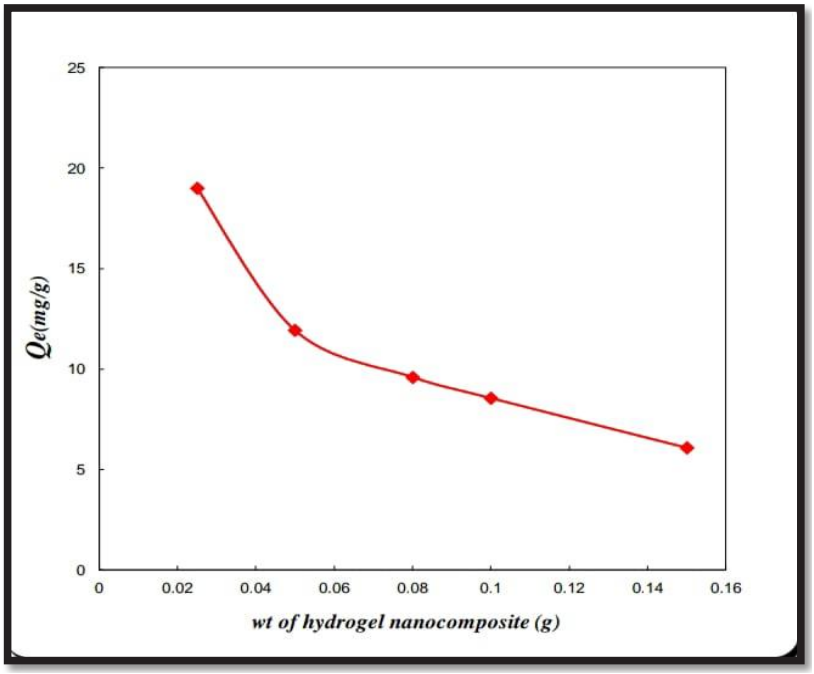


Fig. 6. Effect of weighthydrogel composite on Paracetamol drug(drug conc:100 mg/L, Temp :25°C).

Effect of weight composite

Effect of different weight ranges of hydrogel composites (0.15-0.025) with 100 mg/L of the drug, adsorption of drug from solution was observed to increase with increasing surface weight until reaching (0.1) g, which shows that it is possible to fill all active sites of the surface composite,too due to the saturation state and adsorbent that adsorption capacity decrease from 8.11-4.123 mg/g when weight of hydrogel composite increase from 0.025-0.15 g [17] as shown in Fig. 6.

Effect of pH solution

Pharmaceuticals' considerable impact on adsorption capacity. Metformin dosage of 100 mg/g, temperature of 25 °C, rotating speed of 150 rpm, the adsorbent mass of the composite material of 0.1 g, and contact duration of 60 min were used to determine the impact of pH on 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, which represents the ideal acid function. Fig. 4 therefore shows that when the acidity of the solution increases, the amount of adsorption increases in the range (2-6), and this can be understood. The sort of active group in the medicine and the composite (Fig. 7) should first be displayed for clarification. The composites feature a variety of functional groups, including oxygenate functional groups and epoxy (COC), carboxylic acid (COOH), carbonyl (C=O) and hydroxyl (OH). [18, 19], this group exhibits hydrophilic behavior and is sensitive to pH changes. It is susceptible to both protonation and deprotonation. [18, 19], 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 [20-22].

Adsorption isotherms

Adsorption Isotherm appears in the form of adsorbate Paracetamol drug adsorption at 25℃. The experimental adsorption was performed according to the arrangement of drug molecules on the surface of hydrogel composite based on multilayer and monolayer adsorption. In the present research, the equilibrium condition of drug in hydrogel composite and liquid phase solution of drug, three types of Adsorption isotherm like Freundlich isotherm, Langmuir isotherm and Temkin were study.

Freundlich isotherm was based on hetero-geneous and multi-layer adsorption. The linear equation calculated:

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

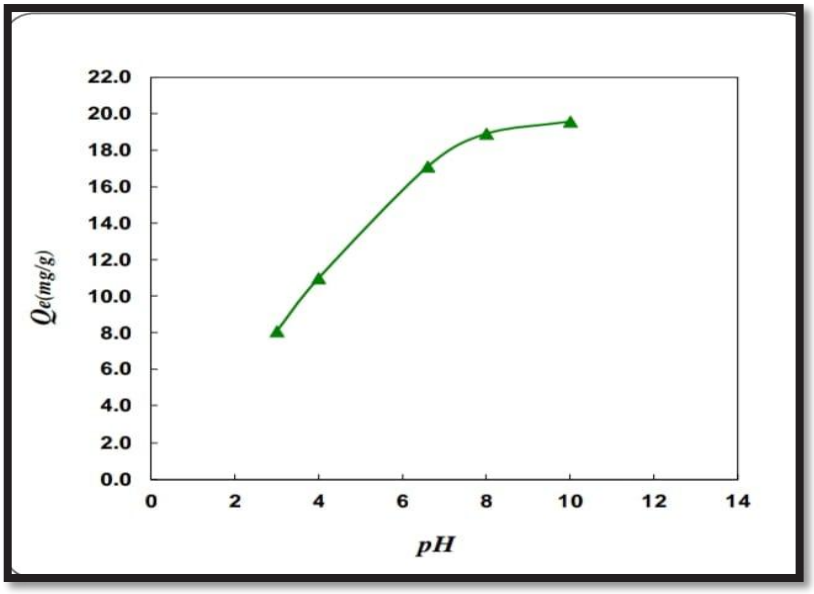


Fig. 7. Effect of solution pH of hydrogel composite 0.1g, pracetmol concentration (100) mg/L, Temperature 25 ℃.

Where n and kf can be determined from the linear representation of ln q_e vs. ln Ce. n was deviation from linearity of adsorption and 1/n is the heterogeneous factor. If kf ($L.g^{-1}$) is related to the binding energy as the Freundlich constant for adsorption. According to the values of R^2, the Freundlich isotherm fits this model better than the Langmuir isotherm. The n constant is further utilized to confirm the adsorption type. As a result, if n=1, adsorption is linear, if n 1, a chemical process, and if n 1, a beneficial physical process.

The Langmuir isotherm theory is based on two assumptions, that the adsorption energy is constant throughout the process and that the

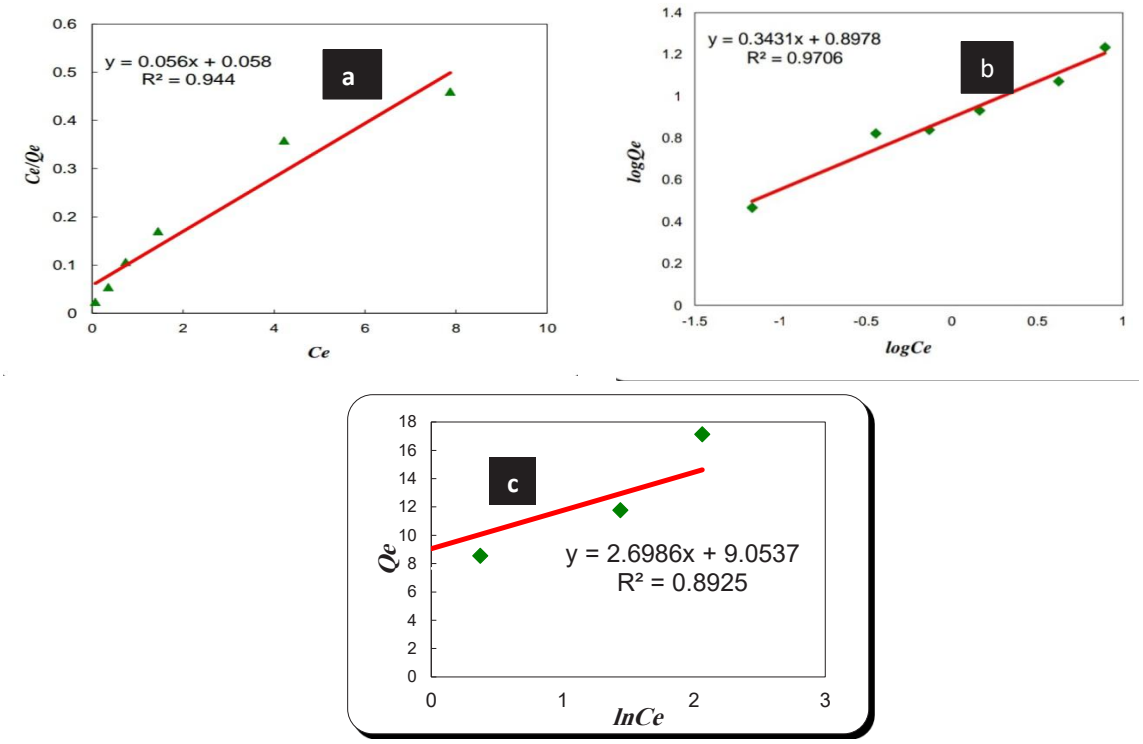


Fig. 8. Isotherms of paracetamol adsorption onto (AAC-AM)/OL at 25°C (a) isotherm Langmuir (b), isotherm Freundlish (c) isotherm Temkin.

Table 2. Langmuir, Freundlich and Temkin isotherm constants for the adsorption of Paracetamol on (AAC-AM)/OL.

isotherm adsorption	Parameters	Values
Langmuir	q_m (mg. g^{-1})	17.857
	K_L (L. mg^{-1})	0.9655
	R^2	0.9440
Freundlich	KF (L .mg^{-1})	6.974
	n	3.236
	R^2	0.9786
Temkin	KT (L. mg^{-1})	28.644
	B(J. mol^{-1})	2.6986
	R^2	0.8925

adsorbate occur on a homogeneous surface by monolayer adsorption, the equation calculates:

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

Where: C_e is the residual concentration of the solute at equilibrium (mg L^{-1}), q_e denotes the adsorption capacity of the adsorbent (mg. g^{-1}), q_m denotes the monolayer adsorption capacity (mg g^{-1}), and KL denotes the Langmuir constant (L. mg^{-1}), which is related to free adsorption.

Temkin isotherm model, taking into consideration the effects of indirect adsorbate interactions during the adsorption process, assumes that adsorption heat of all molecules in the adsorption layer decreases linearly with increasing coverage of adsorption surface only for an intermediate range of concentration. A general form of Temkin isotherm equation is given below:

$$Q_e = BInA_T + BInC_e \quad (3)$$

Qe: equilibrium adsorbed-amount (mg. g^{-1}), Ce: the equilibrium solution's adsorbate concentration (mg. L^{-1}), A_T Equilibrium binding constant of Temkin 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 2 and Fig. 8.

CONCLUSION

In this study, several methods have been used to synthesize and characterize the (AAC-AM)/OL. The produced nanocomposite's ability to quantity adsorption paracetamol simultaneously from aqueous solutions and simulated effluents was assessed. This hydrogel was recommended to be characterized by FE-SEM, TGA, and FT-IR spectra before and after the adsorption was completed to demonstrate the nature of the functional group. This study determined the optimum condition for the adsorption of paracetamol drug onto hydrogel composite appeared in pH=6, and 60 min. The ideal dose form of the adsorbent was 0.1 g. The adsorption capacity decreased when increasing the weight of the hydrogel composite, but the removal percentage increased when increasing the weight of adsorption. The opposite was shown with paracetamol; for linear sorption models, the Freundlich isotherm model best suited the equilibrium data. There were significant correlation coefficients (R^2) in the Freundlich isotherm. According to that the maximum adsorption capacity achieved were 103.093 mg g^{-1} for paracetamol. Adsorption processes and the Freundlich's isotherm model are represented by multilayers.

CONFLICT OF INTEREST

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

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