# Equilibrium and Kinetic Studies of Adsorption of HCQ Drug onto Carrageenan/Carboxymethyl Cellulose-G-Poly Acrylic Acid Hydrogel

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**Abstract**
Carrageenan/Carboxyl Methyl Cellulose-g-poly acrylic acid (CG/CMC-g-P (AA) as super adsorbent hydrogel nano-composite using a free radical polymerization process of HCQ drug. The structure and morphology of the hydrogel nano-composites were studied using FTIR and FE-SEM, different parameter that affected of the adsorption method were studied, counting effect of solution pH, effect of weight of hydrogel and effects of solution temperature. Thermodynamic factor at different temperature (15, 20, 25 and 30°C), It was found that the adsorption method spontaneous. Thermodynamic factor for the adsorption method of drug, that negative value of the enthalpy indicates that the drug adsorption method is exothermic process.
Keyword: Adsorption, Removal, HCQ, Drug, Isotherm, Thermodynamic.

## 1. Introduction

Pollution, especially water pollution, is one of the most serious problems facing the environment, resulting from changes in the environment, which may be caused by physical, chemical, or biological changes. These environmental changes lead to water pollution with hazardous and toxic substances that are harmful to the environment due to industry and human uses. Pollution resulting from factory waste that flows into the waters of rivers and lakes can affect the pollution of marine organisms and the death of most marine life [1-4]. Pollution also affects the atmosphere, water, and soil [5, 6]. Therefore, many modern physical and chemical techniques are available to treat these pollutants. Among the most important techniques used in this field are adsorption, photo catalysis, ozone, and other techniques, but adsorption is one of the most important techniques used for its high efficiency and low cost in treating polluted water. Adsorption is the phenomenon of collecting a substance in the form of particles, atoms, or ions in its gaseous or liquid state on the surface of a solid [7-9].
Hydroxychloroquine has been used in very large quantities for the year (2019) to treat and prevent coronavirus disease (COVID-19. Hydroxychloroquine is taken to treat the disease COVID-19 as it is considered a very effective substance. It is recommended to take one dose every three days).
In this paper, a hydrogel was prepared, which is a highly efficient, available, environmentally friendly absorbent material with low economic cost and high efficiency in the removal of the drug from its aqueous solution. The several parameters that affect the adsorption process were studied under optimal conditions, and adsorption isotherms and thermodynamic parameters were studied.

## 2. Experimental Part

### Materials and Chemicals

Carrageenan, Carboxy Methyl, Cellulose and Acrylic acid, N, N- Methylene bis acrylamide (MBA), Potassium persulfate (KPS), HCQ drug, Sodium hydroxide (NaOH), Hydrochloric Acid (HCl) all chemicals obtain from Sigma-Aldrich.

### Preparation of Carrageenan/Carboxy Methyl Cellulose-g-poly acrylic acid

The surface of the cross-linked hydrogel (CG/CMC-g-P (AA)) is prepared, which involves dissolving 0.5 g of (k-caraa) in 40mL of distilled water, which is added in the form of drop-drop of distilled water and stirred for 10 minutes after which the temperature 70 oC until we get complete dissolving, then take 1 g of CMC .then 4ml of AA was added in the form of drops to the prepared solution with continuous stirring for 15 minutes, after that the crosslinking agent (MBA) was added, prepared from dissolving it (0.05g in 2mL of distilled water) in the form of drops. With continuous stirring for 15min, then add the KPS (Initiator) prepared from dissolving (0.05g) in 5mL of distilled water. All these processes are carried out in the presence of (N2). After that, the hydrogel washing several times by distilled water, then dry At 60 0C for 24 hr. The mechanism equations for preparing hydrogels can be shown in the Figure (1).

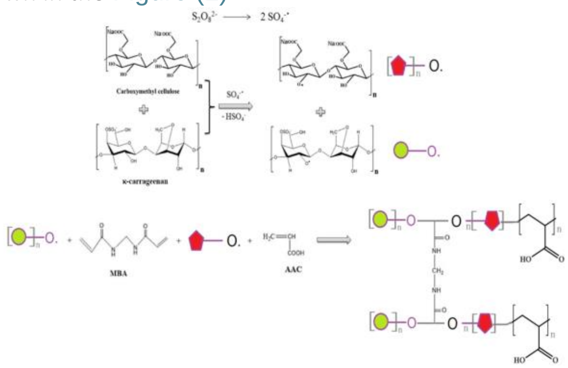

*Fig. 1: Preparation of (CG/CMC-g-P (AA))*

### Calibration curves of HCQ drug

The calibration curve of the HCQ drug was calculated via preparing a series of solutions of the HCQ drug with concentrations of about (1 – 50 mg/L) as illustrated in figure 2. The absorbance of these solutions was measured at the HCQ drug maximum wavelength 340 nm.

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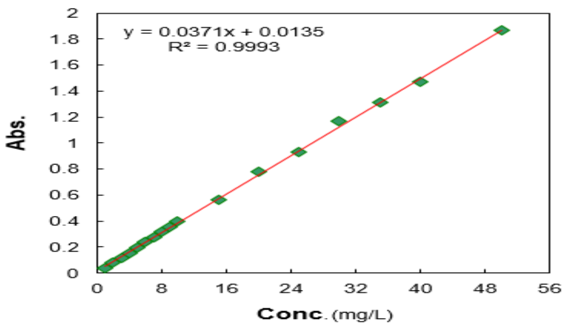


*Fig. 2: Calibration curve of the HCQ drug*

## 3. Result and Dissection

*FTIR*

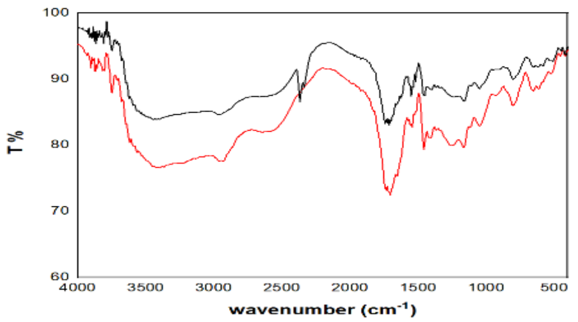


*Fig. 3: FT-IR spectra of (CG/CMC-g-P (AA)): (a) before, (b) after adsorption of HCQ drug*

*FESEM*

Figure 3 indicates the FT-IR spectrum before and after the drug adsorption process on the hydrogel surface. Where it was observed through the FT-IR spectrum, that no change occurred in the form of the (FT-IR) spectrum, meaning that no new beck appeared after the adsorption process, only a change in the intensity of the spectrum. This is clear evidence of the occurrence of physical adsorption and the success of the adsorption process [9, 10].

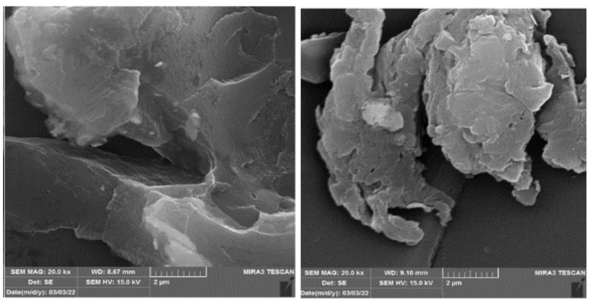

*Fig. 4: FE-SEM image of (CG/CMC-g-P (AA)) before and after adsorption*

Scanning electron microscopy (FE-SEM) technique was used to characterize the prepared surface before the adsorption process and after the adsorption process on a drug as shown in the Figure (4).

### Effect of solution pH

The effect of solution pH on the adsorption of HCQ drug on to (CG/CMC-g-P (AA)) was studied at range about pH (2-10) in the presence of primary concentrations (200 mg/L). The removal percentage R% of HCQ drug on (CG/CMC-g-P(AA)) little in pH 10 , the best removal percentage R% onto (CG/CMC-g-P(AA)) at pH 2 (86.9%) , which suggests that (CG/CMC-g-P(AA)) are excellent adsorbent for HCQ drug removal from large volumes of aqueous solutions as appear in Figure 5 [11, 12].

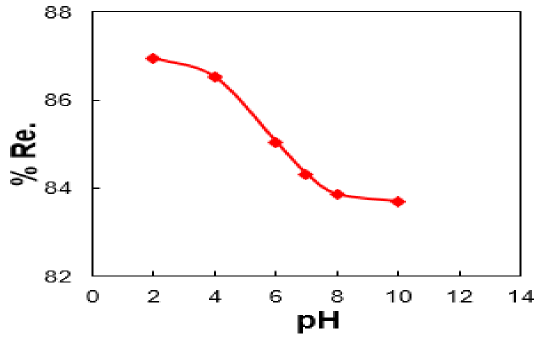


*Fig. 5: Effect of pH solution on the adsorption of HCQ drug onto (CG/CMC-g-P (AA)).*

### Effect of weight of (CG/CMC-g-P (AA))

The effect of the quantity of the (CG/CMC-g-P (AA)) was necessary to observe the minimum possible quantity, which shows the maximum adsorption stoichiometric. The weight of the (CG/CMC-g-P (AA)) range about (0.001 to 0.15) g of (CG/CMC-g-P (AA)). The results are appear in Figures 6.

A rise in the percentage removal R% of drug with increase weight of adsorbent, improving the number of adsorption sites available for adsorption as reported already in other cases. The rise in R% of drug with weight of adsorbent due to the introduction of more binding sites for adsorption [13, 14]. The best removal percentage R% reach about (85.04 %) when the weight of adsorbent about 0.05 g, It is observed through the result that the surface weight increases, the percentage of removal is not affected and remains almost constant, due to the fullness of all the effective sites of the surface [1, 2] .

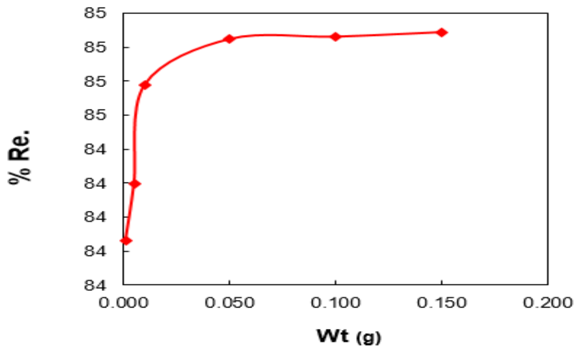


*Fig. 6: Effect of weight of (CG/CMC-g-P (AA))*

### Thermodynamic parameter

Figure (7) show when the temperature increases in the quantity of HCQ drug increase. This indicates that the adsorption process is exothermic [15, 16]. Table1 shows the thermodynamic factors of HCQ drug adsorption on the (CG/CMC-g-P (AA)); Gibbs free energy (ΔG) that negative value thus adsorption process (spontaneous). , Change of entropy (ΔS) positive value HCQ drug, change of enthalpy (ΔH) negative value that adsorption process of HCQ drug is exothermic [17] .

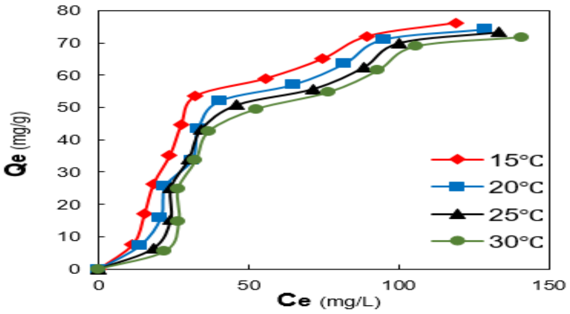


*Fig. 7: Adsorption isotherms of HCQ drug onto (CG/CMC-g-P (AA)) at several temperatures*

The change of enthalpy (ΔH) may be attained from Van't Hoff equation (equation (1)), (ΔG) could be calculate from eq. (2), and (ΔS) was estimation from (3)).

$$\ln X_m = \frac{-\Delta H}{RT} + \text{constant} \quad (1)$$

$$\Delta G = -RT \ln K_{eq} \quad (2)$$

$$\Delta G = \Delta H - T.\Delta S \quad (3)$$

Table (1) appear the basic thermo-dynamic parameter of the adsorption of drug on composite.

| Table (1): thermodynamic of drug on to (CG/CMC-g-P (AA)) | | | |
|---|---|---|---|
| ΔH (kJ.mol-1) | ΔG (kJ.mol-1) | ΔS (J.mol-1.K-1) | Equilibrium Constant (K) |
| -4.054 | -7.004 | -37.11 | 0.484 |

## Effect of Equilibrium Time and Adsorption kinetics

Kinetics adsorption of HCQ drug represent the amount of drug adsorbed by the (CG/CMC-g-P (AA)) per unit of time. It can be found via measuring the change in drug Qe (mg/g) of the (CG/CMC-g-P (AA)) on over time, which is presented in a rate constant of drug adsorption. The first order and the second order show by equation (4-7), were taken in to account to obtain the rate constant of drug adsorption by the (CG/CMC-g-P (AA)) .As shown in Table 2 and figure 8. The data appear that the kinetic adsorption of second order is more like-minded with the kinetic adsorption of drug on the (CG/CMC-g-P (AA)). This was done based on (R2) as show in Table 2 [18-23] .

dqt /dt = K1 (qe-qt) (4)

Dqt/dot = K2 (qe-qt) 2 (5)

Ln (qe-qt) =ln qe – [K1t] (6)

T/qt = 1/K2 qe + t/qe (7)

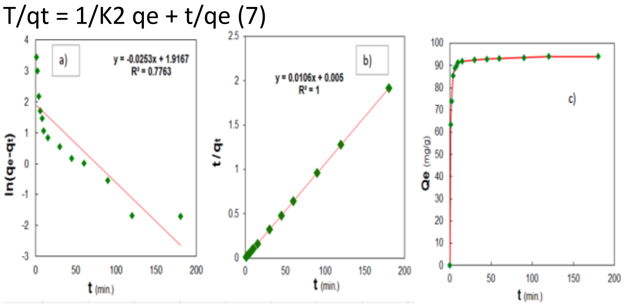


*Fig. 8: a) first-order, b), second-order and, c) equilibrium time on HCQ drug.*

| Table 2: Kinetic factors for the adsorption of HCQ drug | | | | | |
|---|---|---|---|---|---|
| First order | | | Second order | | |
| K1 | qe | R2 | K2 | qe | R2 |
| 0.025 | 6.798 | 0.776 | 0.0229 | 94.33 | 1.0000 |

# 4. Conclusion

The prepared hydrogel is an environmentally friendly surface prepared by free radical polymerization

The best removal percentage R% at pH 2 equal (86.9%)

The best removal percentage R% reach about (85.04 %) when the weight of adsorbent about 0.05 g.

Thermodynamic parameter for the adsorption process of drug, that negative value of the enthalpy adsorption method is an exothermic process.

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