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# **Removal of Diclofenac from Contaminated Water using Organoclay as Reactive Material**

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### **Abstract**

This study is concerned with the adsorption of Diclofenac (DIC) from polluted water using modified bentonite. Hexadecyl trimethyl ammonium bromide (HTAB) was used to alter the hydrophilic nature of the bentonite to a hydrophobic one. Various effecting parameters were investigated such as: contact time, pH, agitation rate, adsorption dosage,acidity pH, mixing time time, and initial adsorbate concentration (Co). The best result obtained for the removal of Diclofenac is 98% which occurred at 30 ppm initial concentration, acidity pH 7, 100 min mixing time, and o.3g/100ml (DIC) dosage. Langmuir isotherm model eas found the more suitable model to represent the adsorption process.On examining the kinetics of the adsorption process, the pseudo-second-order kinetic model well describes the experimental data. Finally, thermodynamic investigations show that the adsorption process is endothermic, spontaneous as well as exhibited characteristics of physisorption.

*Keywords***:** *Diclofenac; adsorption; Modified – bentonite; isotherm; Kinetics*

## **1.Introduction**

The issue of drug contamination in the water system and the subsequent heightened health risks stemming from improper drug disposal in aquatic habitats have emerged as significant concerns, mostly due to their adverse environmental consequences[1]–[3]. The primary sources of pharmaceutical residues in the environment are the

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human, veterinary, and pharmaceutical sectors. The release of therapeutic agents into surface water, groundwater, or drinking water can pose risks to individuals. This can occur through various means,including the direct release of veterinary medications,improper disposal of drugs,discharge of effluents from manufacturing plants, hospitals, and private residences, as well as the improper disposal of unused medications.[4], [5]. Because

these chemicals remain in the environment for a long time, are resistant to microbes, and may act together in harmful ways, they can have bad effects on aquatic life, even at very low levels [5], [6]. These effects can include disrupting hormones, halting reproduction, and affecting the ecosystem as a whole. In addition, it is very likely that organisms are constantly exposed to a variety of these substances throughout their lives, as pharmaceutical compounds are regularly discharged into the surrounding ecosystem.[7], [8]. Pharmaceutical drugs with anti-inflammatory properties are commonly used due to their effectiveness in managing various forms of aches and pain. Anti-inflammatory medications such as naproxen, diclofenac, piroxicam, and celecoxib have been around for a long time and are still in use. This is a big reason why aquatic ecosystems are so polluted[9], [10]. Diclofenac (DIC), a nonsteroidal anti-inflammatory drug is one of the most important medications, frequently used to treat pain and inflammation caused by migraines, arthritis, gout, and other diseases. [11], [12]. DIC is commonly encountered in biosolids, surface water bodies, and wastewater systems. The aforementioned drug exhibits toxicity towards bacteria, invertebrates, and algae, and certain scholars have established a correlation between its usage and alterations in animal physiology [13], [14]. DIC waste has been treated in several different ways, including electrochemical degradation [15], ozonation [16], advanced oxidation [17], nanofiltration [5], and photocatalytic degradation [18]. Adsorption has been employed to handle DIC waste<sup>[19]</sup>, [20]. Recent results revealed that the use of adsorption technique improved effectiveness in reducing the leakage of pollutants into the water system. [20], [21]. An active carbon prepared from Apricot seed was used to remove DIC from an aqueous solution [2]. Another study used commercial activated carbon to remove diclofenac from synthetic water [22]. Maia et al (2019) used commercial organoclay to remove DIC [14].

Different adsorbents have been employed in adsorption methods to remove pollutants like heavy metals, dyes, or antibiotics from municipal and industrial wastewater.[23], [24]. Activated carbon is one of the substances that is most frequently utilized as adsorbents for the elimination of diclofenac [19]. However, there are several obstacles to employing activated carbon as an adsorbent, one of which is the high preparation cost [25], [26]. The use of bentonite as an adsorbent for the removal of hazardous compounds has received a lot of interest recently because it is an affordable material [13], [27]. The utilization of clays in pharmaceutical formulations induces modifications in the efficacy of the medication as a result of the interplay between the drug and clay constituents. Interactions between clay minerals and medications have the potential to either enhance or diminish the bioavailability of drugs upon administration [24]. Surfactants, such as HTAB [28], consist of molecules containing a hydrophilic quaternary ammonium group and a hydrophobic alkyl chain. Addition of surfactants to bentonite increases the interlayer distance and number of reaction sites. This method of modifying clay alters its surface characteristics, transitioning it from being hydrophilic to progressively becoming hydrophobic, simultaneously enhancing its absorption capacities.[29]. Recent research has shown that adding hexamethylammonium bromide (HTAB) to bentonite enhances the removal of antibiotics from aqueous solutions [30], [31]. The main objective of this study is to determine how well-modified bentonite acts as an effective and affordable adsorbent for the removal of diclofenac from contaminated aqueous solutions. Moreover, this study aims to know the effect of operating factors (Co, pH, clay dosage, contact time, and mixing time) on the efficiency of the removal process.

## **2. Materials and Methods**

## **2.1 Materials**

## **2.2 Cationic surfactant (HTAB)**

Hexadecyl trimethyl ammonium bromide is a commonly used surfactant with a positive charge. It has a 16-carbon tail and an ammonium group head with three methyl groups attached [29]. This surfactant was used without additional purification. The chemical formula and structure of HTAB are shown in Fig. 1.



**Fig. 1. The chemical formula and structure of HTAB**

**Adsorbent:** The study used Iraqi bentonite, which was obtained in the form of rock pieces from the General Company for Geological Survey and

Mining in Baghdad, as an absorbent material. The laboratories of the General Company for Geological Survey and Mining analyzed the chemical composition and physical properties of Iraqi bentonite. The composition is shown in Table 1. The surfactant used to denature natural bentonite (NB) was hexadecyltrimethylammonium bromide (HTAB). This surfactant, which was of analytical quality, was used without any further purification. **Adsorbate:**The General Corporation for Pharmaceutical Industries and Medical Supplies in Samarra, Iraq, supplied diclofenac. This material has been used in its original state without undergoing any additional processing.

**Table 1,**

**Chemical composition of Iraqi bentonite.**

<b>Component</b>	Composition wt%
SiO <sub>2</sub>	50.03
$Al_2O_3$	16
CaO	7.75
FeO <sub>3</sub>	6.27
MgO	3.13
Na <sub>2</sub> O	1.02
LO/1	11.43

# **2.3 Preparation of Modified bentonite**

The following steps prepared the modified bentonite: (i) Ten grams of natural bentonite (NB) were added to 200 mL ( i.e., weight ratio 1: 20 NB to water) of distilled water. (ii) The natural bentonite (NB) swelling well in distilled water after 2 hr. (iii) HTAB was added at a weight ratio of 0.37 g to each gram of bentonite and mixed for 2 hr. (iv) The resulting mixtures, modified bentonite, were washed with distilled water repeatedly to remove the excess salts and then dried in the oven at 105 ℃. (v) The dried mixtures were ground and sieved with a size range of 355 to 710  $\mu$ m [29].

# **2.4 Adsorption Experiment**

A series of batch experiments were conducted to investigate the adsorption behavior of Diclofenac (DIC) on the modified bentonite. The experiments were conducted using an orbital shaker to agitate a predetermined quantity of modified bentonite (MB) in a 50 mL solution of synthetic contaminants. The impact of several factors on the recovery of DIC from an aqueous solution was studied. These factors included contact duration (ranging from 30 to 300 minutes), initial pH of the solution (ranging from 2 to 11), agitation speed (ranging from 0 to 270 rpm), initial concentration of DIC (ranging from 10 to 200 ppm), and sorbent dosage (ranging from 0.1 to 0.8 g per 100 mL). Next, the Whatman filter paper was used to separate the adsorbent from the suspension. Diclofenac concentration (DIC) was determined using a dual UV spectrophotometer (UV model T80, England). The wavelength of the DIC was determined to be 276.2 nm in a previous study [14]. The calculation of the fraction of dissolved noganic carbon (DIC) removed by the microbial biomass (MB) was performed using equation (1) [32].

$$
R = \left[\frac{C_0 - C_e}{C_0}\right] \times 100\%
$$
 ... (1)

Where R is adsorption percentage,  $C<sub>o</sub>$  and  $C<sub>e</sub>$  (mg/l) are the concentrations of diclofenac (DIC) at initial and equilibrium conditions, respectively.

Eq. (2) is used to determine the adsorption capacity,  $q_e$  (mg/g), at equilibrium conditions. [14].  $\overline{a}$  $(C^0 - C_e)V$ 

$$
q_e = \frac{q_e - q_e}{m} \qquad \dots (2)
$$

# **2.5 Characterization of modified Bentonite**

The morphology of the organic bentonite was examined using scanning electron microscopy (SEM). A Shimadzu FTIR 8400s was used to analyze the functional group present on the surface of the adsorbent and to characterize both native and modified bentonite. This was done using KBr pellets in the wavelength range  $400 - 4000$  cm<sup>-1</sup>.

## **3 Results and Discussion 3.1 Characterization 3.1.1 Characterization using FT-IR**

FTIR spectra were obtained by making measurements within the frequency range 400–  $4000 \text{ cm}^{-1}$ , as shown in Fig. 2. The experiment was performed using bentonite samples (natural and modified). Natural bentonite (NB) displays large absorption bands at 3631 and 3440 cm<sup>-1</sup>, which can be attributed to the stretching vibrations of the OH bonds in the Si-OH (silanol) and Al-OH groups, respectively [29]. In addition, it is important to note that the occurrence of a large peak at  $1031 \text{ cm}^{-1}$  can be attributed to the presence of Si-O-Si groups located inside the tetrahedral sheets. After the natural bentonite alteration process, it was observed that the asymmetric stretching mode of Si-O-Si changed from  $1028$  to  $1037$  cm<sup>-1</sup>. Moreover, it was discovered that the Si-O-Si deformation and bending modes, previously

observed at frequencies of 790, 528, and 455  $cm<sup>-1</sup>$ , respectively, were changed to frequencies of 786. 538, and 426 cm<sup>-1</sup> for MB. The appearance of the corresponding peak at  $1485 \text{ cm}^{-1}$  in modified bentonite, which is absent in natural bentonite, indicates the presence of CN vibration in tertiary amines. After the modification process, the absorption band related to the –OH group and the bending vibration of  $H_2O$  in natural bentonite (NB)

saw a remarkable shift from  $1650 \text{ cm}^{-1}$  to a lower frequency of  $1637 \text{ cm}^{-1}$ . This alteration signifies the removal of water molecules and change the hydrophobic characteristics of natural bentonite (NB). [33]. The modified bentonite exhibited peaks at  $2850$  and  $2920$  cm<sup>-1</sup>, which were attributed to the CH2 shear vibration band and CH3 symmetric stretching absorption band, respectively.



**Fig. 2. FTIR characterization bentonite ( natural (NB) and modified (MB).**

## **3.1.2 SEM Analysis**

Figure 3 displays the results of scanning electron microscopy (SEM) performed on the clay. The surface morphology of natural bentonite (NB) underwent noticeable changes after being treated with hexamethylammonium bromide (HTAB). Natural bentonite (NB) has a porous surface morphology that is characterized by uneven and rough optical properties. Additionally, it showcases a scattered block structure of varied sizes. In contrast to the modified state of bentonite, which exhibits a surface morphology that resembles fragile, thin cornflakes or copious crystals with a fine texture. This observation implies that the surfactant has primarily coated the surface of the bentonite. The reduction in specific disordered structures commonly present in bentonite is accountable for the fluffy visual aspect [29]



**Fig. 3. SEM images of (a) Natural bentonite (NB) (b) Modified bentonite (MB).**

## **3.2 Batch Experiments 3.2.1 Effect of Contact Time**

The study investigated the impact of varying time durations, ranging from 30 to 300 minutes, on the recovery of the pollutant. The other conditions stayed the same during the whole experiment. These included the starting concentration of Diclofenac (DIC) at 30 ppm, the pH level at 7, the speed of the stirring at 200 rpm, and the amount of adsorbent used at 0.3 mg/100 ml. Figure 4 illustrates the impact of contact time on the elimination of Diclofenac. The study revealed that, as time progressed, there was a corresponding increase in the quantity of DIC elimination. The initial removal efficiency exhibits a rapid rate, followed by a gradual decline until it stabilizes at a consistent level of 98% removal after 100 minutes [26]. The initial high adsorption rate of DIC can be attributed to the swift diffusion of DIC particles from the solution onto the exterior surfaces of the adsorbent. This phenomenon is facilitated by the abundance of polarization groups present in the composition of DIC pollutant molecules [2].



**Fig. 4. Effect of time on removal percentage.** 

## **3.2.2 Effect of Solution Ph**

Measuring the pH in the aqueous solution is a crucial factor to consider in the adsorption process. The study investigated the impact of pH on the elimination of DIC throughout a pH range of 2 to 11. The remaining variables, including contact time (100 minutes), agitation speed (200 rpm), initial concentration (30 ppm), and adsorbent dosage (0.3 grams per 100 milliliters), were held constant A 0.1 M solution of hydrochloric acid (HCl) and sodium hydroxide (NaOH) were employed to adjust the pH of the solution. Based on the results depicted in Figure 5, the percentage of DIC removal stayed consistent at 98% across all tested pH values. This indicates that DIC removal is mostly unaffected by the pH levels of aqueous solutions. The observed phenomenon can be attributed to the use of a surfactant template, which creates an electrostatic attraction between the anionic groups of DIC and the quaternary ammonium groups present in the bentonite layers. [32]. Ibrahim Ziad (2020) showed similar patterns in the elimination of acidic dye using bentonite treated with cetyltrimethylammonium bromide [29].



**Fig. 5. Effect of solution pH on removal percentage.** 

# **3.2.3 Agitation speed**

To investigate the influence of agitation speed on the adsorption of DIC onto modified bentonite, a series of experiments were conducted using different agitation speeds, ranging from 0 to 270 rpm. Based on the data presented in Figure 6, it can be observed that the absorption DIC exhibited a positive correlation with the agitation speed. Notably, the highest absorption rate of DIC was achieved at an agitation speed of 200 rpm, reaching a peak value of 98%. The increase in DIC removal remains unaltered when values exceeding 200 rpm are applied. The observed phenomenon can be attributed to the resistance encountered by the adsorbate as it traverses the boundary layer within the liquid phase en route to the solid surface of the adsorbent, particularly at low agitation rates. Increasing the stirring speed leads to a decrease in the thickness of the boundary layer. The decrease in thickness reduces the resistance that occurs during mass transfer of the adsorbent, thus accelerating the adsorption process. The observed result is attributed to the increased film thickness on the solid surface, indicating that film diffusion is the limiting factor in the overall absorption rate [24].



**Fig. 6. Effect of agitation speed on removal percentage. (Co = 30 ppm, pH =7, time = 100 min and adsorbent dose= 0.3g/100ml).**

#### **3.2.4 Initial pollutant concentration**

The adsorption process of modified bentonite is significantly affected by the initial concentration of dissolved inorganic carbon (DIC). An investigation was performed using different initial concentrations of adsorbents, ranging from 10 to 200 ppm. Figure 7 shows the effect of starting concentration on the removal of dissolved inorganic carbon (DIC). The removal efficiency showed a positive correlation with the initial concentration, i.e. within the range of 10 to 30 ppm. The highest removal efficiency approaching 98% was achieved at an initial concentration of 30 ppm.. As a result, the effectiveness of removal has declined. The observed trend can be explained by the large proportion of available active sites on bentonite compared to the initial number of dissolved inorganic carbon (DIC) molecules at low adsorption concentrations. As a result, the removal efficiency is large. At larger initial concentrations, the amount of (DIC) surrounding the bentonite active sites will increase. As a result, the number of available adsorption sites on bentonite will decrease, resulting in decreased DIC removal effectiveness [11].



**Fig. 7. Effect of initial concentration on removal percentage.** 

#### **3.2.5 Modified bentonite dosage**

Research was conducted to examine the effect of different amounts of modified bentonite on the adsorption process. Doses ranged from 0.1 to 0.8 grams / 100 mL of DIC solution. The remaining parameters were kept constant at C<sub>0</sub> concentration  $= 30$  ppm, pH level 7, for 100 min, and a stirring speed of 200 rpm. The data shown in Figure 8 show a clear relationship between the dose of modified bentonite and the percentage of removal. As the dose of modified bentonite increases, the removal percentage also increases. At a dose of 0.3 g/100 ml of diclofenac solution, the bentonite clearance stabilizes at a constant value of 98%. Increasing the amount of adsorbent will enhance the number of active sites on the bentonite, leading to increased adsorption of DIC molecules and thus improving the removal efficiency of the adsorbent. The results of Khan and Hegde (2018) [33] are consistent with our results, where they showed that increasing the clay dosage enhances the adsorption efficiency. This can be attributed to the enlarged surface area of the modified bentonite, which facilitates the removal of cadmium from wastewater.



**Fig. 8. Effect of the adsorbent dosage on removal percentage%.** 

#### **Adsorption isotherms**

The adsorption equilibrium was examined using two specific adsorption isotherms: Langmuir isotherm and Freundlich isotherm. The Langmuir isotherm is derived from the concept of monolayer adsorption, which refers to the adsorption process that takes place exclusively on the surface of the adsorbent, where there are a limited number of adsorption sites. The mathematical representation of the Langmuir isotherm is defined by Equation 3. [26].

$$
q_e = \frac{K_L \, q_m \, C_e}{1 + K_L C_e}
$$
 ... (3)  
The linearized form of Eq. (3) is given by Eq. (4)

$$
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e}
$$
...(4)  
Equation (4) was used to determine the values of

Equation (4) was used to determine the values of  $K_l$  and  $q_m$ .

The Freundlich isothermal model is based on the hypothesis of diverse surface energies and the occurrence of multilayer adsorption. The Freundlich isotherm is represented by equation (5) [5].

$$
q_e = K_F c_e^{\frac{1}{n}}
$$
 ... (5)

The linearization form of the Freundlich model can be expressed as in Eq.(6).

$$
\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e) \quad ...(6)
$$

The constant parameters of the Freundlich isotherm, namely  $K_F$  and n, correspond to the adsorption capacity and adsorption density, respectively. Experimental data can be used to predict these values using equation (6). Figure 9 displays the correlation of the experimental data with the Langmuir and Freundlich isotherm models.



**Fig. 9. Linear form of the isotherm models for sorption of Diclofenac onto modified bentonite, (A) Langmuir, (B) Freundlich.**

Table (2) displays the values of  $q_m$ ,  $K_L$ , n, and  $K_F$  as well as the values of the correlation coefficients  $R^2$ .





Based on the values of the correlation coefficients  $(R^2)$ , it can be concluded that the Langmuir model provides a better fit to the experimental data compared to the Freundlich model. This indicates that diclofenac binds to modified bentonite in a monolayer manner.

The dimensionless constant  $R_L$  serves as a reliable indication of the Langmuir isotherm. The value of  $R_l$  can be determined by utilizing Equation (7). [34]:

$$
R_L = \frac{1}{1 + K_L C_o} \qquad \qquad \dots (7)
$$

 $R_L$  values are used to describe whether the adsorption is favorable when  $R_L < 1$ , linear when  $R_L = 1$ , unfavorable when  $R_L > 1$ , or irreversible when  $R_L = 0$ 

 $R_{L} = \frac{1}{1 + \mu}$  $\frac{1}{1 + K_L C_o} = \frac{1}{1 + 0.40}$  $\frac{1}{1 + 0.408(30)} = 0.075 < 1$ Then, the adsorption is favorable.

#### **3.3 Adsorption kinetics**

Adsorption kinetic study is highly important in the design and evaluation of adsorbents for removing sorbates from the aqueous solution. The pseudo-first-order and pseudo-second-order models were employed to correlate the kinetics data. Equations (8) and (9) represent the

differential equations of pseudo-first-order and pseudo-second-order kinetics, respectively [35].

$$
\left(\frac{dq_t}{dt}\right) = K_1 \left(q_e - q_t\right) \tag{8}
$$

$$
\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{9}
$$

The linearized forms of Eqs. (8) and (9) are given by Eqs. (10) and (11), respectively.

$$
ln(q_e - q_t) = ln q_e - K_1 t \qquad \qquad \dots (10)
$$

$$
\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2}\right) + \left(\frac{t}{q_e}\right) \tag{11}
$$

As shown in Figure 10, the parameters for each model were determined by fitting the linearized form of these models to the experimental data. Table 3 displays all parameters with the empirical coefficients derived from the linear plot's slope and intercept using Microsoft Excel 2016 software. Regardless of the magnitude of  $\mathbb{R}^2$ , it is evident from Figure 10 and Table 3 that the sorption of DIC is likely to be second-order because the experimental value  $q_e$  (19.54 mg/g) was closer to the calculated value of  $q_e$  (19.72) mg/g) for the second-order model than for the first-order model (20.45 mg/g ). These results indicate that chemosorption or ion exchange mechanisms predominated in the sorption of DIC on modified bentonite. These findings align with the findings of other researchers such as [29], [36], and [37].



**Fig. 10. (A) Pseudo-first-order and (B) Pseudo-second-order kinetics models for adsorption of Diclofenac onto modified bentonite.**

Pseudo-first-order			Pseudo-second-order		
$\mathbf{v}_1$	Чe	$R^2$	$\mathbf{r}_2$	Чe	$\,R^2$
$(min^{-1}]$	(mg/g)		(g/mg. min)	(mg/g)	
0.0638	20.45	0.9675	0.00292	19.72	0.994

**Table 3, Adsorption kinetics parameters of pseudo first-order and pseudo second-order rate equations**

## **3.4 Thermodynamics study**

The thermodynamic properties of DIC adsorption on modified bentonite were studied by analyzing three thermodynamic parameters: enthalpy change  $(\Delta H^0)$ , Gibbs free energy change  $(\Delta G^0)$ , and entropy change (( $\Delta S^0$ ). The Gibbs free energy conversion  $((\Delta G^0)$  calculation was performed using equation (12) [36].  $\Delta G^o = -R \; T \; ln(K_c)$ ) … (12)

The values of  $K_c$  can be calculated by Eq. (13)  $K_c =$  $q_e$  $\mathcal{C}_{\bm{e}}$ … (13)

The relationship between the thermodynamic parameters, namely enthalpy change  $(\Delta H^o)$ , entropy change  $(\Delta S^{\circ})$ , and Gibbs free energy

change ( $\Delta G^o$ ), is defined by equation (14) [38].  $\Delta G^o = \Delta H^o - T \Delta S$  … (14) Substitution Eq. (14) in Eq. (12) gives  $ln K_c =$  $\Delta S^{\circ}$  $\frac{1}{R}$  –  $\Delta H^{\circ}$ … (15)

The equilibrium constant  $\ln(K_c)$  was calculated using equation (13) at different temperatures.

Using Equation 15, the enthalpy  $(\Delta H^o)$  and entropy  $(\Delta S^{\circ})$  were determined by slope and intercept analysis, respectively. Figure 11 shows a decrease in  $K_c$  values as the temperature increases from 30 to 50 °C. Table 4 presents the thermodynamic parameters <sup>o</sup>, ∆H<sup>o</sup> and ∆S<sup>o</sup> at different temperatures for the adsorption of diclofenac on modified bentonite.



Fig. 11.  $\ln K_d$  Versus  $\frac{1}{T}$  for the adsorption of DIC **on modified bentonite.**

**Table 4,**

**Thermodynamic parameters for the adsorption of Diclofenac onto modified organobentonite.**

$\Delta G^o$ (kJ/mol)			$\Delta S^{\circ}$ (J/mol. K)	$\Delta H^o$ (kJ/mol)
$30^{\circ}C$	40 $^oC$	50 $^oC$		
$-6.294$	$-5.208$	$-4.122$	$-108.6$	$-39.2$

The change in free energy  $\Delta G^o$  was calculated to be 6.294, 5.208, and 4.122 kJ/mol at 30, 40, and  $50^{\circ}$ C, respectively. The spontaneous and thermodynamically viable character of the adsorption process was indicated by the negative  $\Delta G^o$  values. The decrease in  $\Delta G^o$  values with increasing temperature indicates that adsorption at elevated temperatures is less feasible. The enthalpy of adsorption was determined to be -39.2 kJ/mol. The negative value of  $\Delta H^o$  indicates the exothermic nature of the adsorption, and its magnitude provides information on the type of adsorption, which can be physical or chemical.  $\Delta H^o$  values for physical adsorption are less than 40 kJ/mol, according to previous studies [39], [40]. The adsorption of DIC onto MB can therefore be classified as physisorption. It was determined that the So parameter for DIC adsorption was 108.6 J/mol K. The negative value of  $\Delta S^{\circ}$  indicates a reduction in randomization at the solid/solution interface during the adsorption process.

#### **4. Conclusions**

The modified bentonite demonstrated significant efficacy in the removal of diclofenac (DIC) from an aqueous solution, with a maximum removal rate of 98%. The percent removal of dissolved Diclofenac (DIC) was influenced by many parameters, like pH, Co, adsorbent dosage, agitation speed, and contact time. It was shown that variations in pH did not significantly impact the removal efficiency. The optimal values for these parameters, which resulted in the highest level of recovery, were determined to be a contact period of 100 minutes, an initial concentration of 30 parts per million (ppm), an agitation speed of 200 revolutions per minute (rpm), and an adsorbent dosage of 0.3 grams per 100 milliliters (g/100 mL). Based on the isotherm analysis, it was observed that the adsorption data exhibited a stronger correlation coefficient  $(R^2 = 0.9354)$  with the Langmuir isotherm model compared to the Freundlich isotherm model ( $\mathbb{R}^2 = 0.8692$ ). The results of the kinetic analysis confirm that chemisorption has been the dominant process  $(R<sup>2</sup>$  $= 0.994$ ). This is supported by the observation that the experimental data adhered to a pseudo-secondorder model rather than a pseudo-first-order model. Based on thermodynamic investigations, it was shown that the adsorption process is physisorption and had endothermic characteristics, as well as occurring spontaneously.

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# **ازالة الديكلوفيناك من المياه الملوثة باستخدام الصلصال العضوي كمادة تفاعلية**

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#### **المستخلص**

في هذه الدراسة ، تم ازالة المادة الدوائية الديكلوفيناك )Diclofenac )من المياه الملوثة عن طريق االمتزاز على البنتونيت المعدل. وقد تم تغيير البنتونايت من مادة محبة للماء إلى كارهة للماء باستخدام بروميد الأمونيوم ثلاثي ميثيل هيكساديسيل (HTAB). لقد استخدمت التجارب الدفعية لدراسة تأثير عدد من العوامل في كفاءة عملية الامتزاز. هذه العوامل هي: زمن التلامس ، ودرجة الحموضة (pH) للمحلول ، وسرعة الخلط ، والتركيز الابتدائي للملوث (Co) ، وكمية المادة الممتزة المستخدمة.وقد تم تحقيق أقصى إزالة للديكلوفيناك بحدود (٪98) عند القيم التالية للعوامل المؤثرة: زمن التلامس 100 دقيقة ، ودرجة الحموضة 7 ، وسرعة الخلط 200 دورة في الدقيقة ، وتركيز ابتدائي للمادة الملوثة 30 جزءاً في المليون ، والجرعة الممتزة 0.3 غم بينتونيت لكل 100 مل من المحلول الملوث.وتم استخدام الفحص المجهري الإلكتروني للماسح الضوئي (SEM) والتحليل الطيفي للأشعة تحت الحمراء لتحويل فورييه (FTIR) لتشخيص صفات المادة الممتزة )البنتونايت المعدل (.وقد وجد ان موديل Langmuir هو األنسب لتمثيل البيانات التجريبية التي تم الحصول عليها من التجارب العملية في المختبر.وقد تمت دراسة حركية عملية االمتزاز ووجد انها تتمثل بشكل جيد بتفاعل زائف من الدرجة الثانية. وكانت عملية االمتزاز من النوع الفيزياوي فضلا عن كونها ماصة للحرارة وتلقائية ، وفقًا لتحليلات الديناميكا الحرارية.