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Adsorption of Folic Acid on Iraqi Bentonite and Kaolin from Aqueous Solution

Raid J.M. Al-Timimi[1] *PhD*, **Hiba S. Jassim**[2] *MSc*, **Ghassan M. Suleiman**[2] *PhD*

[1]Dept. of Chemistry and Biochemistry, College of Medicine, Al-Nahrain University, [2]Section of Biochemical Technology, Dept. of Applications Sciences, University of Technology, Baghdad, Iraq.

Abstract

Background Using specific antidotes for the treatment of acute poisoning that is due to drug overdose by drugs adsorption is of significant importance in physical pharmacy for the preparation of physical antidotes.

Objective The adsorption of folic acid from aqueous solution was investigated on two adsorbents (bentonite and Iraqi kaolin).

Methods The present study involves studying adsorption of folic acid on Iraqi clays (bentonite and kaolin) from aqueous solution. Adsorption isotherm of folic acid on both surfaces used obeyed Freundlich isotherm. UV- Spectrophotometric technique was used to obtain the quantities of adsorption data at different conditions of temperature.

Results The quantities adsorbed of the folic acid for bentonite and kaolin was increased at 37°C. Adsorption characteristics were described using Freundlich isotherm. The value of ΔG° showed the spontaneous nature of the folic acid adsorption on both adsorbents.

Conclusion This result indicated the surface heterogeneity leading to different adsorption forces from site to site and different affinities toward drug molecules.
Thermodynamic parameters have been calculated at different temperatures. The adsorption of folic acid increases with increase in temperature and positive value of ΔH° indicates endothermic nature of the adsorption process. Negative values of free energy at all studied temperatures indicate that the adsorption process is spontaneous and favorable for folic acid. Positive value of entropy suggests increased randomness at the solid/solution interface.

Keyword Adsorption, folic acid, bentonite, kaolin, thermodynamic parameters.

Introduction

Folic acid or folate is a vitamin B_9 soluble in water, identified as an anti-anemia and growth factor. It is produced by plants (green leaves, algae) and micro-organisms (bacteria, yeast). In mammals, folic acid and its derivatives, serve as acceptors and donors of carbon units and are involved in amino acid and nucleotide biosynthesis, also prevents neural tube defects such as spina bifida [(1)], in addition the action of mechanisms of folic acid acts role as a methyl donor in a range of metabolic and nervous system biochemical processes, as well as being necessary for DNA synthesis.

Vitamin B_9 is essential for numerous bodily functions. Humans cannot synthesize folates *de novo*; therefore, folic acid has to be supplied through the diet to meet their daily requirements. The human body needs folate to synthesize DNA, repair DNA, and methylate DNA as well as to act as a cofactor in certain biological reactions.

There is a complex interaction between folic acid, vitamin B_{12} and iron. A deficiency of one may be "masked" by excess of another so the

three must always be in balance [2]. The risk of toxicity from folic acid is low, because folate is a water-soluble vitamin and is regularly removed from the body through urine. One potential issue associated with high dosages of folic acid is that it has a masking effect on the diagnosis of pernicious anemia (vitamin B_{12} deficiency), and a variety of concerns of potential negative impacts on health. Drug poisoning has been defined as a condition produced by any substance which when swallowed, inhaled, injected, or absorbed precutaneously is capable of causing death, injury, toxic reactions. One of perspective methods for emergency treatment of accidental poisoning by drug is adsorption.

In cases where no specific antidotes exist, prevention of further adsorption of a drug from the oral route is by use of oral adsorbents. Using adsorption method, the adsorbents have to answer to number of requirements, to be active, stable, and accessible cheap, and the most important is that the exchange ions should be harmless. The use of natural adsorbents clays in the prevention of further adsorption of drug, are recognized in clinical practice.

The thermodynamic parameters associated with the adsorption processes can be calculated from the variation of thermodynamic equilibrium constant (K) with change in temperature, during the adsorption reaction, at pH=8.

Adsorption is usually a decrease in free energy change and entropy of the system. This process is affected by a number of factors such as concentration of adsorbate, surface area of adsorbent, temperature, ionic strength, pH [3], solubility of adsorbate in water and hydrophilic characteristics i.e. the effect of hydrogen bond. The increase in the solubility of solute in water and hydrophilic properties causes a decrease in the adsorbed amount [4].

The adsorption at different types of adsorbents such as kaolin, activated charcoal, attapulgite, talc, magnesium trisilicate and bentonite has been studied [3,5]. The Kaolin (high adsorption capacity) and bentonite can reduce both undesirable and desirable components, such as aroma and flavor compounds [5,6].

Therefore, the Bentonite is considered as a good adsorbent material for heavy metal ions such as Pb^{2+} in aqueous solution due to its typically elevated surface area, high availability and low cost [7]. Bentonite consists of one octahedral alumina sheet lying between two tetrahedral layers of silica. The negative charge of bentonite is attributed to the isomorphs replacement of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer [8].

The adsorption data are tested for a number of isotherm equations (Langmuir equation and Freundlich equation). Moreover, the current study has been to visualize the pattern of adsorption of this drug on the two different adsorbents to various situations such as, pH, temperature, and contact time.

Langmuir behavior assumes a rapid reversible adsorption, and interaction only between adsorbate molecules and a surface site of adsorbent.

The Langmuir equation could be expressed as:

$$C_e/Q_e = 1/K + a/k \, .C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where Q_e is the amount of adsorbate (mg/g), C_e is the equilibrium concentration (mg/L), and a, k are constants related to adsorption capacity and energy of adsorption respectively or sometimes called Langmuir constants.

Freundlich Isotherm is one of the most important isotherms that deal with adsorption at solid-liquid interface. Most of surfaces are heterogeneous, so the change in potential energy is regular, and the adsorption sites are not equivalent in energy hence the multilayer formation is highly expected.

Freundlich equation could be written as follows:-

$$Q = k_F \, C_e \, 1/n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$\log Q = \log k_F + 1/n \log C_e \quad \ldots\ldots\ldots\ldots\ldots(3)$$

Where Q is the adsorbate quantity (mg/g), C_e is the concentration of adsorbate at equilibrium (mg/L), k_F, and n is the adsorption capacity and

an empirical parameter, respectively and also called Freundlich constants [9].

Methods

The instruments used were UV - VIS Spectrophotometer (UV-1800) Shimadzu, thermo stated Shaker bath/GFL (D-3006), Germany, pH Meter/HM -73, TDA Electronics Ltd., Centrifuge / eppendorf 5804 R, electronic Balance/Sartorius Lab. BP 3015. The material used is NaOH (Emscope laboratories Ltd). The drug used was folic acid that is obtained (Hopkin & Williams, Ltd.) England. The molecular formula of folic acid is $C_{19}H_{19}N_7O_6$, and its molecular weight is 441.4. It has a melting point of 250°C, a density of 1.68 g/cm^3. Folic acid is practically insoluble in water. It dissolves in diluted acids and in alkaline solutions [10] (Fig. 1).

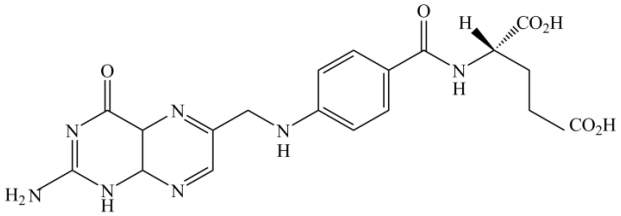

Fig. 1. Structural formula of folic acid [10].

Adsorbents

Iraqi kaolin (Fig. 2) was obtained from (Dwaikhla) opened mine (north of Rutba) in the Iraqi Western desert supplied by the ''General Company for Geological Survey and Mining'', Baghdad, Iraq.

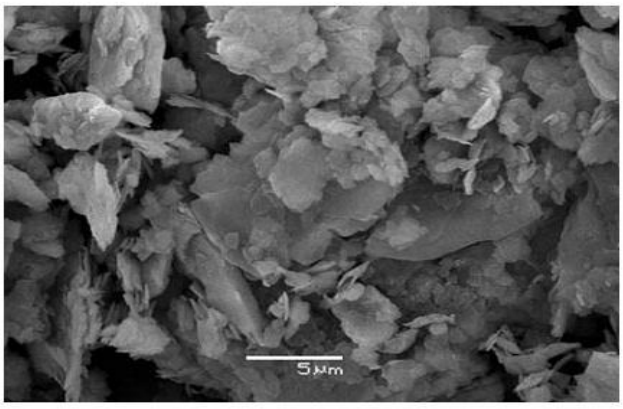

Fig. 2. The shape characterization of kaolin [3]

The weight percentages of the Iraqi kaolin clay were: SiO_2 (54.68%), Al_2O_3 (30.19%), Fe_2O_3 (1.02%), TiO_2 (1.00%) and loss on ignition (10.94%).

Bentonite

The bentonite clay (Fig. 3) size 75 µm used in this study was supplied by Geological scanning company and has the following composition (by percentage weight): SiO_2 (56.77%), Al_2O_3 (15.67%), Fe_2O_3 (5%), CaO (4.48%) MgO (3.42%), K_2O (0.60%), Na_2O (1.11%), L.O.I (12.49%).

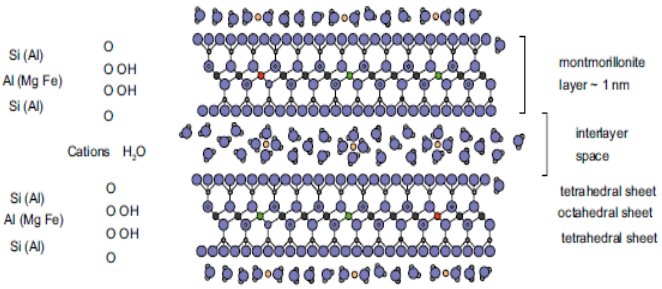

Fig. 3. The Structural formula of bentonite [12]

Kaolin and Bentonite adsorbents were in powder form. Each of them was washed several times with excessive amounts of distilled water then dried at (170°C) in the oven for three hours and kept in airtight containers. Each adsorbent was ground and sieved using Retch test sieve 150µm. A stock of (500ml) aqueous solution of folic acid drug (0.0005 mg L^{-1}) was prepared and its (λ max) was determined. The maximum absorbance (λ max) was (210) nm (Fig. 4).

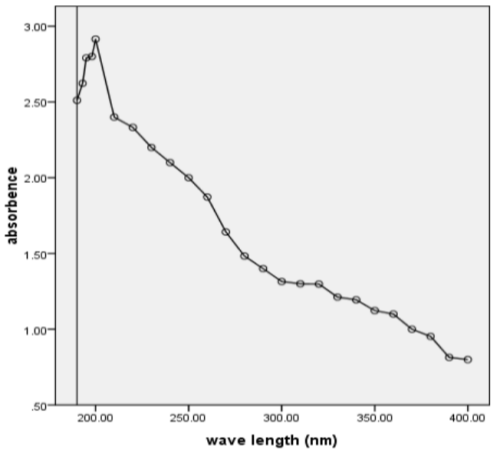

Fig. 4. UV Spectra of aqueous solution of folic acid at pH=8 and temperature 37°C

Various drug solutions with different concentrations were prepared by diluting the stock solution with distilled water (0.0001, 0.00015, 0.0002, 0.00025, 0.0003 and 0.00035 mgL^{-1}).

In order to obtain the calibration curve for aqueous solutions of Folic acid at pH = 8 the absorbance values of these drug solutions were measured at the specific (λmax) using UV-Vis double beam Spectrophotometer and plotted versus the concentrations of these drug solutions (Fig. 5).

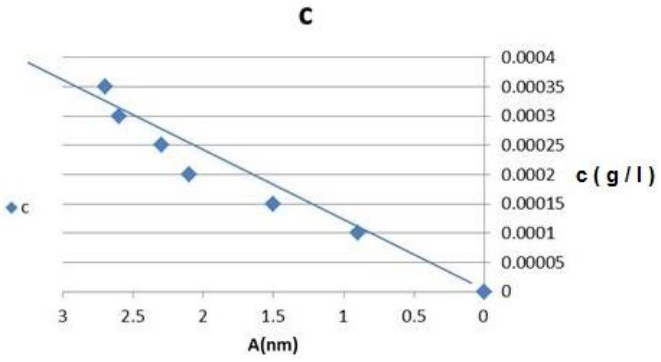

Fig. 5. Calibration curve for aqueous solutions of Folic acid at pH=8 and temperature 37°C.

The time to reach equilibrium state, that is required for full saturation of adsorbent surface at 37°C by the adsorbate has been determined by the following procedure: 500 ml initial concentration (0.0005 mg/L) of adsorbate solution was shaken with (0.5 g) of each adsorbent. The absorbance of adsorbate solutions were measured by UV/Visible spectrophotometer at different intervals 10, 20, 30, 60 …minutes until reaching equilibrium (no further uptake of adsorbate by adsorbent as the time proceeds).

A systematic procedure was followed to determine the adsorption isotherms for each pair of adsorbent -adsorbate systems. A volume of (50ml) of six different concentrations of drug solution (0.0001, 0.00015, 0.0002, 0.00025, 0.0003 and 0.00035 mg/L) was shaken with (0.5 g) of adsorbent at a certain temperature in a thermostatic shaker. The speed of shaking was 60 cycles per minute. After the equilibrium time (30 min) elapsed, the mixtures were allowed to settle and the clear liquids were centrifuged at 3500 round per minute (rpm) for 20 minutes. The absorbencies of the filtrate solutions were measured at (λmax). The equilibrium concentrations of the prepared solutions can be determined from the calibration curve using their absorbencies. Adsorbed amount of the drug was calculated at certain conditions from the concentration of solution before and after adsorption according to equation (1):

$X_m = (C_o - C_e)\ V / m$……..(1), where C_o and C_e are the initial and equilibrium concentrations of drug solution (mg/L) respectively, V is the volume of solution in liter, X_m= the maximum quantity of adsorbate (in mg) that is adsorbed on the adsorbent at certain value of C_e that was fixed for all temperatures used in the study, (m) is the weight of adsorbent in grams.

X_m can be determined from equation (2):

$Q_e = X_m / m$……(2), where Q_e= is the quantity of adsorbate (in mg) held by (0.5 g) of adsorbent.

The equilibrium constant (k) for the adsorption process at each temperature is calculated from equation (3):

$K = (Q_e)\ (0.5\ g)/(C_e)\ (0.05\ L)$……..(3), where (0.5 g) represents the weight of the clay that has been used, (0.05 liter) represents the volume of the drug solution used in the adsorption process.

The change in free energy (Δ*G*°) could be determined from equation (4):

$\Delta G° = -\ RT\ \ln K_c$ ……..(4), where R is the universal gas constant (8.314 kJ/mol K), T is the temperature (K) and K_c is the distribution coefficient. Gibbs free energy change of adsorption (Δ*G*°) was calculated using ln K_c values for different temperatures.

The heat of adsorption (Δ*H*°) may be obtained from equation (5):

$\ln Xm = -\Delta H°/RT + \text{constant}$ …….(5)

The change in entropy (ΔS°) can be determined from equation (6):

$\Delta G° = \Delta H^o - T\Delta S^o$ ……(6)

Results

Temperature effects and thermodynamic parameters

The general shapes of the adsorption of folic acid on kaolin and bentonite at three different temperatures (30, 37 and 40°C) are given in fig. 8 and 9. Figures show that the adsorption of folic acid increases at 37°C temperature.

The study of the temperature effects on adsorption helps in finding the basic thermodynamic functions (Δ*H*°, Δ*G*°, Δ*S*°) of the adsorption processes. Table (1) gives X_m values at different temperatures at pH=8. Most of the absorption process after digestion process ends at the small intestine pH = 8. Table 1 shows the effect of temperature on the maximum adsorbed quantities of folic acid on kaolin and bentonite; where X_m is the maximum uptake of adsorbate at certain value of (C_e) for all temperatures.

Table 1. Effect of temperature on the maximum adsorbed quantities of folic acid on kaolin and bentonite

Adsorbent	T.°C	T.k	1000/T. k^{-1}	X_m(mg)	In X_m
Kaolin	30	303	3.30	0.000006	-12.02
	37	310	3.22	0.000006	-12.02
	40	313	3.19	0.000005	-12.20
Bentonite	30	303	3.30	0.000005	-12.20
	37	310	3.22	0.0000065	-11.94
	40	313	3.19	0.000006	-12.02

Plotting (In X_m) versus 1000/T produced a straight line with a slope = - ΔH/R as shown in fig. 6 and 7.

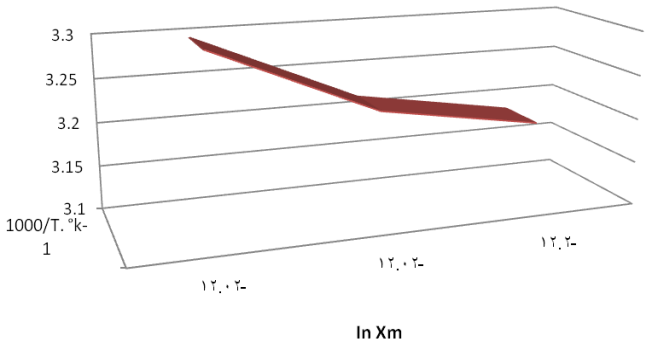

Fig. 6. In Xm plotted against reciprocal absolute temperature for the adsorption of folic acid on kaolin at pH=8 and different temperatures (30, 37 and 40°C).

Table 2 shows the basic thermodynamical values of adsorption of folic acid on kaolin and bentonite. The negative values of the ΔG for the adsorption of folic acid on bentonite and kaolin indicated that the adsorption process of folic acid is spontaneous. The positive values of ΔH at different temperature indicated an endothermic reaction. The positive values of ΔS for the adsorption of folic acid on bentonite indicated increase in the degree of freedom of the adsorbed species.

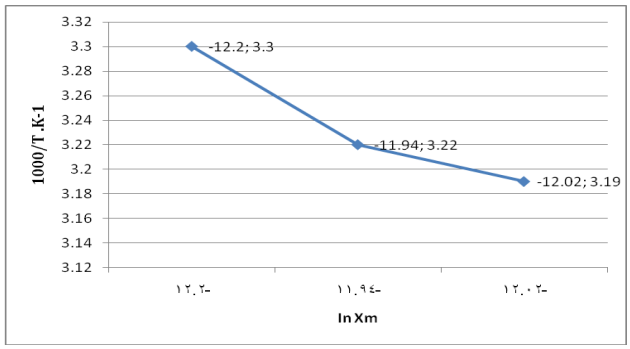

Fig. 7. In Xm plotted against reciprocal absolute temperature for the adsorption of folic acid on bentonite at pH=8 and different temperatures (30, 37 and 40°C).

Adsorption isotherms

Adsorption isotherm is the equilibrium relationship between the concentration in the liquid phase and the concentration in the

adsorbent phase in the adsorbent particles at given temperature. The experimental data obtained are analyzed by the adsorption isotherms of folic acid on bentonite and kaolin at pH=8 and different temperatures. In the present study, Freundlich models were used to analyze the data. The adsorption isotherm in fig. 8 and 9 indicated a frundlich isotherm according on Giles classification.

Figures 10 and 11 show a linear relationship between (log Q_e) and (log C_e), which indicates that the surface of adsorbent bentonite and kaolin are heterogeneous in character and involve the formation of multilayers.

Discussion

The adsorption system can be defined as an equilibrium one including the adsorbent being in contact with the bulk phase and also called interfacial layer [13].

The most important in the investigation of adsorption mechanism is the equilibrium adsorption isotherm. The properties such as surface property, the adsorption affinity of adsorbent and the maximum adsorption capacity can be determined from the adsorption isotherm and correlative constants [4].

Bentonite and kaolin is the clay mineral that was chosen as adsorbent for this study with folic acid as show in figure 1 have(C=O and NH) groups can be adsorbed on different site of each adsorbents.

From adsorption isotherms it can be concluded from Giles classification is S type depend on Freundlich Isotherm used to describe the adsorption characteristics for the heterogeneous surface and the formation of multilayers [14,15], this also indicates that bentonite surface is heterogeneous [15].

Table 2. Values of thermodynamic functions for the adsorption of folic acid on Bentonite and kaolin at temperatures.

Adsorbent	ΔH^o kJ.mol-1	ΔG^o kJ.mol-1	ΔS^o J.mol-1	pH	Temperature ^oC
Kaolin	+30281	-1007.65	+103.26	8	30
	+30981	-1030.93	+103.26	8	37
	+31748	-234.20	+102.17	8	40
Bentonite	+30734	-226.72	+102.18	8	30
	+30774	-180.41	+99.85	8	37
	+31280	-182.15	+100.51	8	40

It was found that the adsorption processes between the folic acid and negative site of hydroxyle group in the bentonite site surface [16], is attributed to the isomorphous replacement of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer. This negative charge is balanced by the presence of replaceable cations (Ca^{2+}, Na^{+}, etc.) in the lattice structure, which enhance adsorbing cationic pollutants [8].

The surface of the adsorbent becomes negatively charged which enhances the adsorption of positively charged functional groups of the adsorbate through the electrostatic force of attraction on the surface [17].

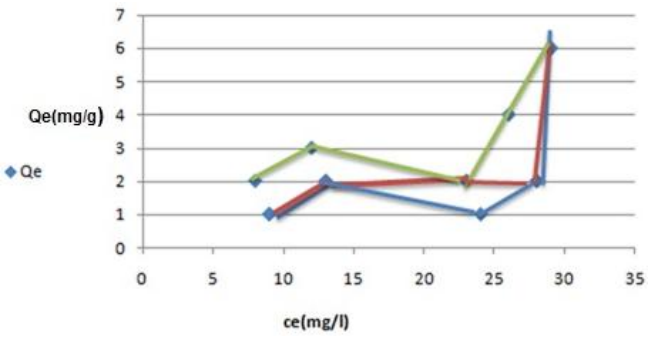

Fig. 8. Adsorption isotherms of folic acid on kaolin at pH=8 and different temperatures (30, 37 and 40°C).

Under alkaline solution at pH=8 the chemical structure of bentonite varies with the variation in pH. The natural bentonite is a net negative charge on the surface as pH reduces [15], while the kaolin clay carries the negative and positive charges [18].

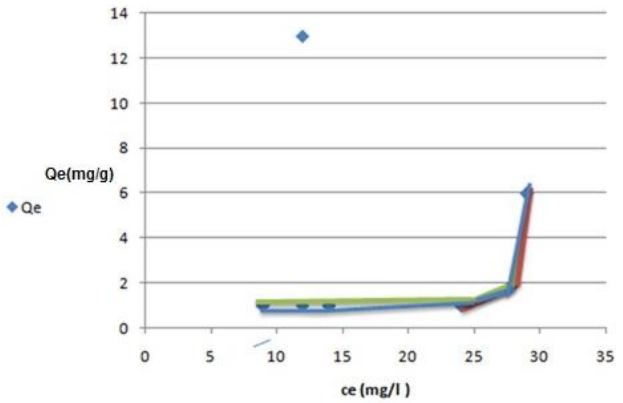

Fig. 9. Adsorption isotherms of folic acid on bentonite at pH=8 and different temperatures (30, 37 and 40°C).

Spontaneity of a adsorption process can be determined by thermodynamic parameters such as free energy change (Δ*G*°), enthalpy change (Δ*H*°) and entropy change (Δ*S*°) [19].
The negative values of Δ*G*◦ indicate the feasibility and spontaneity of adsorption process. Further, the decrease in the values of Δ*G*◦ with the increasing temperature indicates the spontaneity of the process at higher temperatures [20] which does not require an external energy source for the system [19].

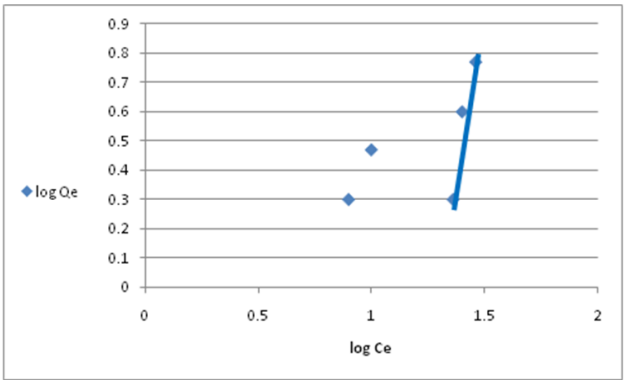

Fig. 10. Linear form of freundlich isotherm of folic acid adsorbed on kaolin at 37°C and pH=8.

The positive values of enthalpy change (Δ*H*◦) which indicate endothermic nature [20] was also confirmed from the increase of adsorbate adsorption efficiency on adsorbents as the temperature increased [19].
the positive value of Δ*S*◦ indicate a good affinity of adsorbate towards the adsorbent materials [20], that there is an increased at the solid/liquid interface during adsorbate adsorption onto the adsorbents and drug molecules remain randomly on the each surface [19 ,17].

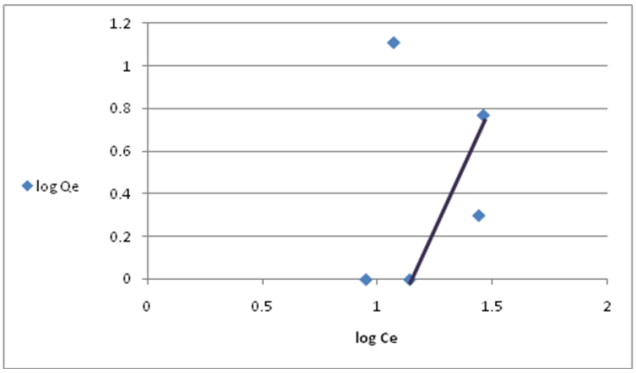

Fig. 11. Linear form of freundlich isotherm of folic acid adsorbed on bentonite at 37°C and pH=8.

In conclusion, Iraqi kaolin and bentonite showed ability to adsorb the folic acid drug from its aqueous media; therefore, both adsorbents can be used as antidotes for dealing with a case of drug overdose. Moreover, adsorption isotherms of the drug folic acid on Iraqi kaolin and bentonite depend on Freundlich isotherm model. These results indicated that the surface heterogeneity of the adsorbents leading to different adsorption strengths from site to site and different affinities towards drug molecules. Thermodynamic parameters such as enthalpy change (Δ*H*°), free energy change (Δ*G*°) and entropy change (Δ*S*°) showed that the adsorption process of folic acid on each adsorbents was endothermic and spontaneous.

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Author contribution
Both authors share the responsibility in preparing and completing this work.

Conflict of Interest
The authors declare no conflicts of interest.

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Correspondence to Dr. Raid J.M. Al-Timimi
E-mail: rjtimimi68@yahoo.com
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