A study of Adsorption of Theobromine from Aqueous Solution on Attapulgite and Bentonite

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Abstract

This study is concerned with the adsorption of Theobromine from solution on the surfaces of attapulgite and bentonite, which are provided locally in Iraq. The purpose of this study into search for an active surfaces to be used as an antidote in treating of poisoning by this drug if taken beyond its usual dosage. UV-spectrophotometric technique has been used to produce quantitative adsorption data at different conditions of pH, ionic strength and temperature.

The calculated data were in accordance with Freundlich equation and the adsorption isotherms are of S-curve type according to Giles classification. The results obtained show greater adsorption uptake of the drug on bentonite than attapulgite.

The adsorption phenomenon was examined as a function of temperature ***(25, 37.5, 45^{o}C)***. The extent of adsorption of Theobromine on the clays was found to decrease with increasing temperature (exothermic process). The basic thermodynamic functions have also been calculated.

The amount of drug adsorbed on the clays at different pH values showed an increase in the following order pH 3.5 > 2.5 > 2.0 > 1.2. This behavior was discussed depending on the ionic character of the surfaces of adsorbents.

The adsorption process is affected by the electrolyte concentration. The results indicated an increase in adsorption of Theobromine in the presence of sodium hydrochloride.

Introduction

Adsorption is an important surface phenomenon usually describes the concentrating of a particular component at an interface relative to an adjacent solution or other bulk phase (1). It is a phenomenon in which the available surface is the determining factor (2). Adsorption is a spontaneous process and hence is attained by a decrease in free energy change and entropy of the system. This process is influenced by a number of factors: concentration of adsorbate (2), surface area of adsorbent (3) solubility of adsorbate, temperature, pH, ionic strength, (4-9) and the chemical state of adsorbate and adsorbent molecules (10).

The molecular and thermodynamic characteristics of adsorption (i.e. capacity, affinity, isotherm shape and enthalpy) are essential to understanding binding processes and providing mechanistic evidence for the selection and ranking of adsorbents that have application in reducing or preventing toxicity in animals (11). Medical uses of adsorbents, particularly, in the treatment of poisoning were a matter of several

publications. Charcoal was the most solid surface employed as a physical antidote in the treatment of acute poisoning by toxic substances and drug overdosage (12). Active surface materials other than charcoal have also been studied and found of clinical significance in the treatment of acute poisoning by drug overdosage and poisons, like kaolin (13), talc (14), attapulgite (15), smectite (16), and bentonite (17).

The Aim of Present Work:

The aim of this work in to investigate the capability of locally available clays for prevention of toxicity by Theobromine in different conditions of temperature, pH and ionic strength.

Materials and Methods

Instruments:

1- UV-Visible spectrophotometer Cintra 5.
2- Dunboff metabolic shaking Incubater GCA/ precision Scientific.
3- pH-Meter, HM-73, TDA Electronic Ltd.
4- Hettich Universal (D-7200), Centrifuge tubes.
5- Electronic Balance, Sartorius Lab. L420 B, $\pm$0.0001.

Materials:

Hydrochloric acid and sodium chloride were supplied by Fluka. Theobromine was obtained from "The state Enterpise for Drug Industries and Medical Appliances". Attapulgite and bentonite were obtained from "The General Company for Geological survey and mining". The weight percentages of the clays components are described in Table (1).

Table (1) The main components of the clays

Compound	*Attapulgite wt.%*	*Bentonite wt.%*
SiO_2	52.3	54.6

Al_2O_3	14.1	14.6
Fe_2O_3	7.35	4.88
CaO	8.20	4.77
MgO	0.74	6.00
Na_2O	3.40	0.65
TiO_2	0.70	-
SO_3	0.87	1.20
K_2O	1.30	-
Loss on Ignition	9.66	12.5
Total	98.6	99.4

Methodology

The clays were washed with excessive amounts of distilled water, dried at 160^{o}C for three hours. The clays were ground and sieved to a particle size of 75 μm. wavelength of maximum absorbency (λ_{max}) was recorded for Theobromine dissolved in aqueous media and found 275nm Figure (1).

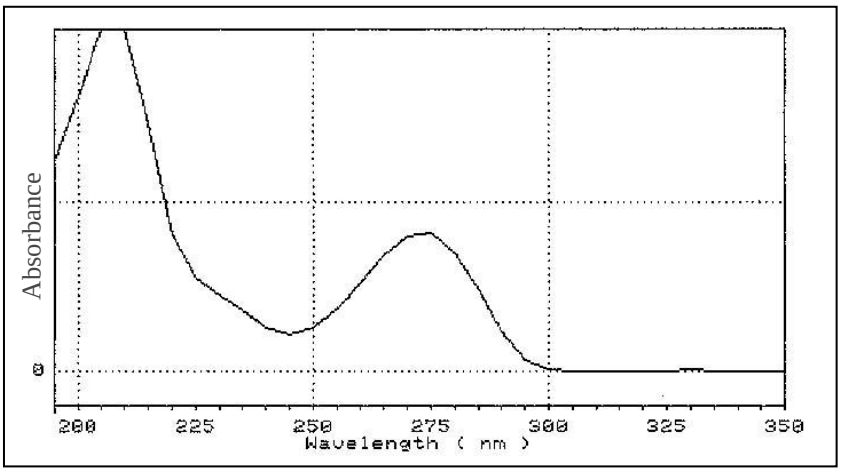

Figure (1) U.V. spectra of Theobromine

This value was utilized for estimation of quantity of drug adsorbed. Solutions of different concentrations were prepared by serial dilution at 275nm and plotted against concentration values. The calibration curve in

the concentration range that falls in the region of applicability of Beer-Lambert's law were employed.

Adsorption Isotherm

Solutions of Theobromine (25 ml) of known concentrations (1×10^{-5}-10×10^{-5} M) at pH ≈1.2 were added to stoppered flasks containing 0.5g of clay. The flasks were shaken in a thermostatically controlled water bath at a speed of 60 cycle/min. till equilibrium is attained (120 min). This time is sufficient for the adsorption process to reach equilibrium. After the equilibrium time elapsed, the suspensions were either centrifuged at 3000 rpm for 20 min. or filtered using double filter papers. The clear supernatants were assayed for drug, after appropriate dilution, spectrophotometrically. Equilibrium concentrations were obtained by comparing the experimental data with the calibration curve.

The quantity of drug adsorbed was calculated according to the following equation (18):-

$$Q_e \text{ or } \frac{x}{m} = \frac{V(C_o - C_e)}{m} \quad \text{.....(1)}$$

Where:

x : the quantity adsorbed.

m : weight of adsorbent (g).

C_o : initial concentration (mg/L).

C_e : equilibrium concentration (mg/ L).

V : volume of solution (L).

Effect of Temperature

Adsorption experiment was repeated in the same manner at temperatures of 25, 37.5 and 45 ^oC to estimate the basic thermodynamic functions.

Effect of pH

Adsorption experiment was carried out as mentioned previously as a function of pH using a fixed concentration of Theobromine. Hydrochloric acid was used to adjust the pH range from 1.2 to 3.5. The pH of the suspensions at the commencement of the adsorption was measured as well as after filtration at the end of the experiment using pH-meter.

Effect of Ionic Strength

The effect of 0.154, 0.2 and 3.5 M sodium chloride solutions containing different concentrations of Theobromine in electrolyte solution were added to flasks containing 0.5 g of clay. The procedure described for the adsorption experiment was followed.

Results and Discussion

Adsorption of Theobromine:

The adsorption of Theobromine from aqueous solution on attapulgite, and bentonite has been studied at the human body temperature (37.5˚C) and at other two temperatures (25 and 45˚C) at pH $\approx$1.2. The value of pH $\approx$1.2 has been chosen to simulate the pH of stomach fluid (15,19).

The general shapes of Theobromine adsorption isotherms are shown in Figure (2), where the quantities adsorbed on attapulgite and bentonite are plotted as a function of equilibrium concentration at the constant temperature.

The results showed an increase in adsorptive capacities of the two clays as the concentration of Theobromine increased. The clays were found of reasonable surface activity in adsorption from solution of some materials and drugs (19,20). The greatest amount of adsorption was exhibited by bentonite followed by attapulgite. Bentonite, among other clays, has structural properties that favour the intercalation of organic

molecules within the interlayer space, giving rise to the formation of adsorption complexes (21).

Moreover, bentonite exhibits both high exchange capacity and high surface area which is consequently lead to a high degree of adsorption (22).

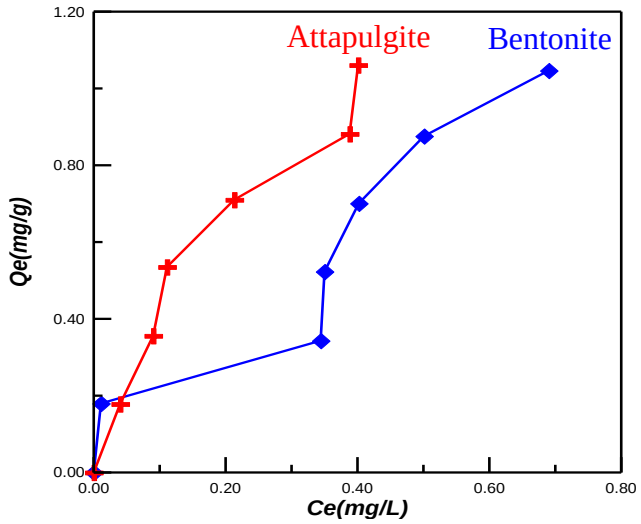

Figure (2) Adsorption isotherms of Theobromine on attapulgite and bentonite at pH ≈1.2 and constant temperature (37.5°C)

The shapes of Theobromine adsorption isotherms were found to coincide with the S-type isotherm reported by Giles *et al.* (23).

The S-type isotherm depends upon the Freundlich assumption about the heterogeneity of the surface. The presence of various planes, as powders leads to heterogeneous adsorption behaviour. Heterogeneity is a usual and a general feature of surface properties due to different unsaturated adsorption sites of different energetic behaviour (24).

The adsorption of Theobromine on clays, follow isotherms which are best represented by applying the Freundlich equation.

$$\frac{x}{m} = kC_e^{1/n} \quad \text{.....(2)}$$

Where $\frac{x}{m}$ is the quantity adsorbed in mg/g. C_e is the equilibrium concentration in mg/L, *n* and *k* are constants for the given adsorbent and solute.

The applicability of Freundlich isotherm is indicated by using the linear from of Freundlich equation.

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C_e \quad \text{.....(3)}$$

Figure (3) and Table (2) show the linear relationship of *log Qe* versus *log Ce* and constants for the given adsorbent and solute for the adsorption of drug on the clays.

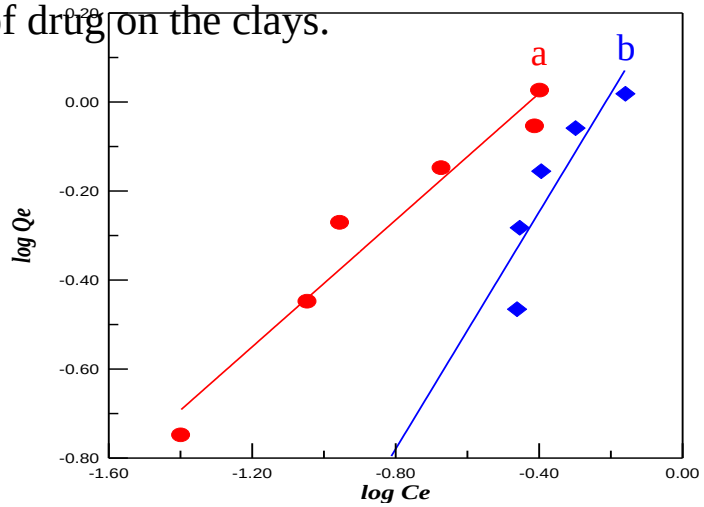

Figure (3): Linear form of Freundlich isotherm of Theobromine on: a- Attapulgite

b- Bentonite

Table (2) *constants for the given adsorbent and solute for the adsorption of*

Adsorbate	***Bentonite***			***Attapulgite***		
	n	K_f	**r**	**n**	K_f	**r**
Theobromine	1.4050	2.0137	0.7770	0.7513	1.9275	0.9530

The general shapes of Theobromine adsorption isotherms at three different temperatures are given in Figure (4).

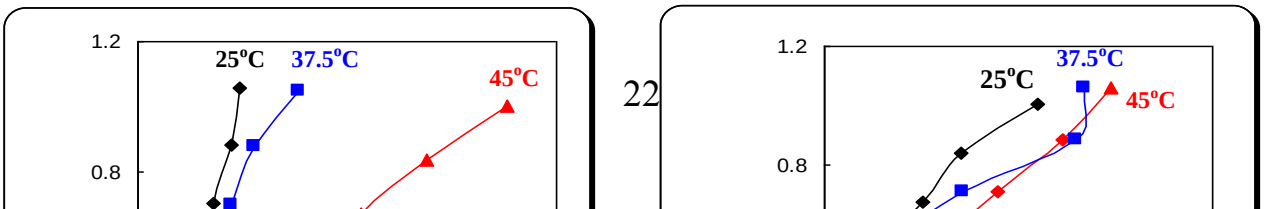

Figure (4): Adsorption isotherms of Theobromine on: a- attapulgite and b- bentonite at pH ≈1.2 and different temperatures (^oC)

The adsorption extent of Theobromine on clays was decreased with increasing temperature, indicating exothermic process. This could be interpreted as a result of weaking of attractive forces between the drug molecules and the solid surface with increasing temperature.

The reduction of adsorbate-adsorbent interaction with increasing temperature is reinforced by the temperature dependence of the solubility of drug molecules. The better molecules are solvated at higher temperatures, the smaller their tendency to adsorb onto the clay surface (5).The basic thermodynamic quantities of adsorption of Theobromine on the clays were estimated through calculating Xm values at different temperatures. The heat of adsorption (ΔH) may be obtained from Van't Hoff equation: $ln\,X_m = \frac{-\Delta H}{RT} + constant$, the change in free energy (ΔG) could be determined from equation (ΔG = −RTlnK) and the change in entropy (ΔS) was calculated from Gibbs equation The change in entropy (ΔS) may be obtained from Gibbs equation : ($\Delta G = \Delta H - T.\Delta S$). Table (2) and Figure (5) demonstrate these calculations.

Table (2) Effect of temperature on the maximum adsorbed quantity for adsorption of Theobromine on the clays

Adsorbate			***Bentonite***		***Attapulgite***	
	T(k)	**$10^3/T(k^{-1})$**	**X_m**(mg/g)	**$ln_{(}X_{m)}$**	**X_m**(mg/g)	**$ln_{(}X_{m)}$**
Theobromine			**Ce**= 0.33		**Ce**= 0.22	
	298.0	3.356	0.532	-0.631	0.881	-0.127
	310.5	3.221	0.342	-1.073	0.712	-0.339
	318.0	3.145	0.187	-1.677	0.623	-0.473

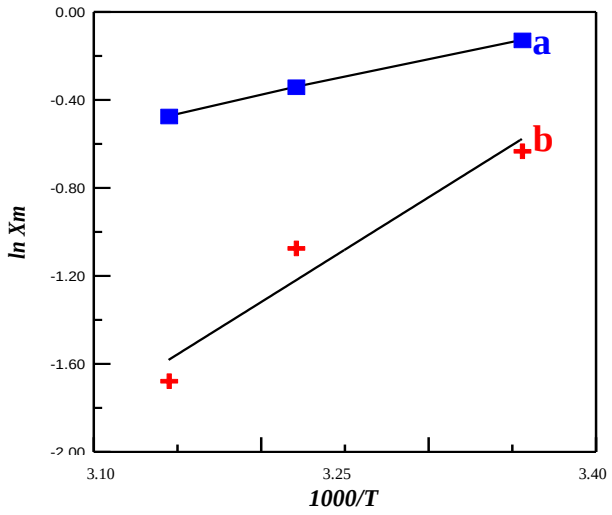

Figure (5): Plot of ln X_m against reciprocal absolute temperature for adsorption of Theobromine on: a- bentonite b-attapulgite

Table (3) shows the basic thermodynamic values of adsorption of Theobromine on the two clays. An adsorption of van der Waals type is suggested to take place as indicated by these values.

Table (3): Values of thermodynamic functions of adsorption process of Theobromine on the clays at 37.5 ^oC

Adsorbate	*Bentonite*			*Attapulgite*		
	ΔH $kJ.mol^{-1}$	*ΔS* $J.mol^{-1}.k^{-1}$	*ΔG* $kJ.mol^{-1}$	*ΔH* $kJ.mol^{-1}$	*ΔS* $J.mol^{-1}.k^{-1}$	*ΔG* $kJ.mol^{-1}$
Theobromine	-39.588	-102.000	-7.825	-13.566	-9.000	-10.765

The adsorption of Theobromine on clays is exothermic and spontaneous as indicated by the negative values of enthalpy (ΔH) and free energy change (ΔG). The adsorption of Theobromine on clays is exothermic in conjunction with a decrease in entropy. This result could be viewed through the fact, that the entropy change (ΔS) of the ordered constrained adsorbed layer is always less than that of dissolved solutes.

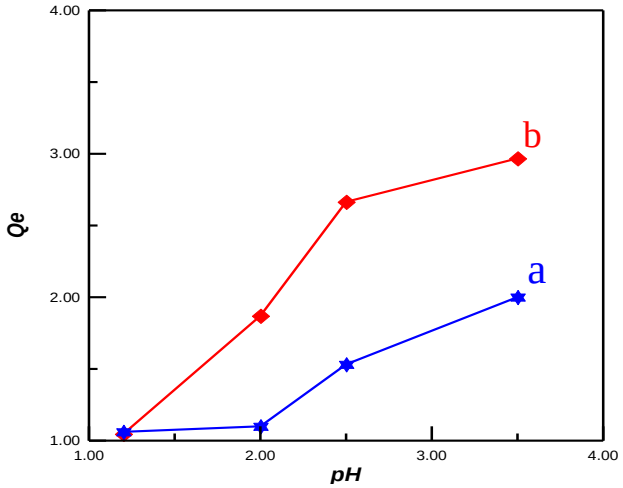

Figure (6) Effect of pH in adsorption uptake of Theobromine on: a- attapulgite and b- bentonite the clays at 37.5 ^{o}C

The results obtained from the adsorption of Theobromine on the clay Figure (6) showed an increase in adsorption quantities of the drug with increasing pH value. At low pH a competition exerted by the hydronium ions is expected to cause a significant reduction in adsorption of the drug (25).

The increase in adsorption uptake of Theobromine with increasing pH of solution could be attributed to the possible changes in properties of the clay surface (26). It was suggested that a marked increase in the adsorption of some drugs onto bentonite with increasing pH value, is due to an increase in density of the negative charge on the edges of bentonite particles. In addition, the solubility of Theobromine is greatly decreased as the pH is increased from 1.2 to 3.5 causing an increase in adsorption affinity towards the clay surface (27).

The effect of ionic strength on adsorption uptake of Theobromine on the three clays was studied at variable concentrations of sodium chloride (0.154, 0.2 and 0.35M). Figures (7) and (8) show the influence

of ionic strength on the amounts of drug adsorbed by attapulgite and bentonite at pH ≈1.2 and at 37.5˚C.

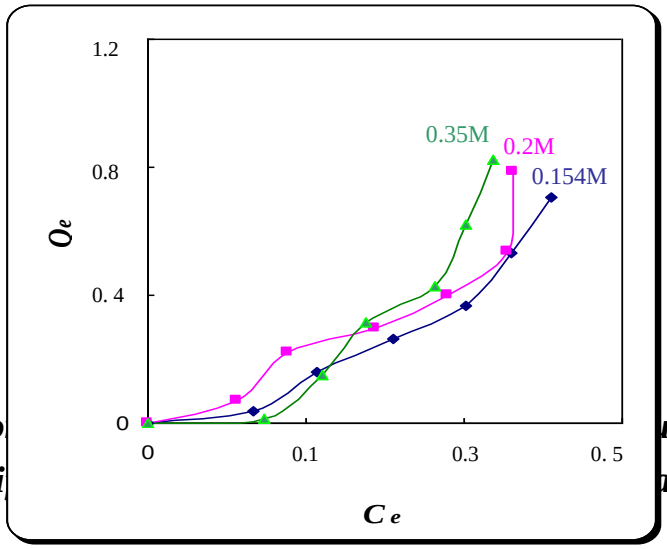

Figure (7) Adso… ulgite in the presence of di… t 37.5 °C

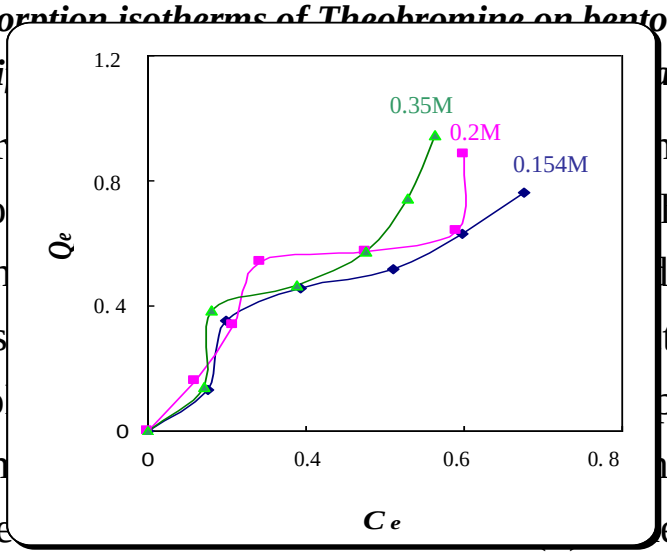

Figure (8) Adsorption isotherms of Theobromine on bentonite in the presence of di… t 37.5 °C

An over… ncreasing electrolyte concentratio… hown in Figures (7) and (8). Th… luction in adsorbate solubility as… trolyte ions with the aqueous so… perties of the clay adsorbent n… s in solution as a consequence… e solubility of ionic salts in aqueous media is normally higher than that of organic drug molecules (28). Therefore, a competition between them to interact with the solvent molecules leads to an increase in the attraction between the clay surface and the drug molecules (29).

CONCLUSIONS:

1-Bentonite surface appeared of highest activity in the adsorption from solution of drug.

2-Due to higher activity of bentonite surface in adsorption of the drug, it may be used as an antidote for treatment of acute poisoning by Theobromine.

3-The adsorption isotherms of Theobromine on attapulgite and bentonite obeyed Freundlich isotherm.

4-Theobromine-clays reactions exhibited low enthalpy values (exothermic).

5-Adsorption of the drug on the clays was pH dependent.

6-There was a positive correlation between the amounts of Theobromine adsorbed and the ionic strength of solution.

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دراسة امتزاز الثيوبرومين من محلوله المائية على سطوح الاتابلكايت والبنتونايت

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الخلاصة:

يعنى هذا البحث بدراسة امتزاز الثيوبرومين من محلولة المائي على سطوح الاتابلكايت والبنتونايت المتوفرة محليا، وكان الغرض من الدراسة هو البحث عن سطوح فعالة لمعالجة حالات التسمم بهذا الدواء فيما إذا تم تعاطيه بجرعات تفوق جرعاتها الاعتيادية. وقد تم استخدام تقنية مطيافية الأشعة فوق البنفسجية لمعرفة كميات الامتزاز عند ظروف متباينة من الأس الهيدروجيني ودرجة الحرارة والقوة الأيونية لمحلول الامتزاز.

أظهرت النتائج أن ايزوثيرم الامتزاز من نوع (***S***) طبقا لتصنيف ***Giles*** والذي يتفق مع معادلة فرندلش للامتزاز، كما بينت النتائج بان البنتونايت ذو قابلية اكبر لامتزاز الدواء من الاتابلكايت.

بينت الدراسة إن امتزاز الثيوبرومين على سطوح الأطيان عند ثلاث درجات حرارية ***(25, 37.5, 45^{o}C)*** يزداد مع زيادة درجة الحرارة (**امتزاز باعث للحرارة**) كما حسبت القيم الثرموديناميكية الأساسية لعملية الامتزاز.

وجد أن كمية امتزاز الدواء على هذه السطوح عند قيم مختلفة من الأس الهيدروجيني يزداد وفق للترتيب الآتي:

pH 3.5 > 2.5 > 2.0 > 1.2

إن امتزاز الثيوبرومين يتأثر بالقوة الأيونية للمحلول. فقد ازدادت كمية الدواء الممتز في المحلول بوجود كلوريد الصوديوم.