Pak. J. Chem. 1(3): 132-137, 2011 Full Paper
ISSN (Print): 2220-2625
ISSN (Online): 2222-307X DOI: 10.15228/2011.v01.i03.p05

Adsorption of Some Drugs onto Surface of Iraqi Kaolin Clay

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ABSTRACT
Drugs overdose poses a serious threat on human health and may be occur with (ciprofloxacin, chloroquin, piperazine, phyllocontin, digoxin and diazepam).The objective of this study was to examine the adsorption of these drugs onto the Iraqi kaolin clay surface,which used for the temporary treatment of these drugs overdose when this occur.In this work a UV-Visible spectrophotometer has been used to determine the adsorption isotherms which were of type (S_3,S_4) according to Giles classification and these isotherms were analyzed by the Freundlich and Langmuir equations using linearized correlation coefficient,the characteristic parameters for each isotherm have been determined.The effect of temperature, acid function and initial drug concentration were chosen as an experimental parameters. The results showed that the adsorption process attained equilibrium within seventy minutes.
Thermodynamic parameters such as ΔH, ΔG and ΔS were calculated.The adsorption process was found to be exothermic and non-spontaneous for (ciprofloxacin, chloroquin, piperazine, phyllocontin and diazepam while for digoxin was endothermic and non-spontaneous.

Keywords: kaolin, adsorption, isotherms, pharmaceuticals

1. INTRODUCTION
Kaolin is a naturally occurring clay resulting from weathering of aluminous minerals such as feldspar with kaolinite and its principal constituent[1]. Kaolin is also a common mineral, considered "generally regarded as safe" by U. S. Food and Drug.Administration, it is used as anti-caking agent in processed foods and an additive to cosmetics, toiletries, ceramics, rubber and health products, is also used as an "inert" carrier in some pesticides and enhances the performance of some microbial products[2].

Drug poisoning has been defined as a condition produced by any substance which when swallowed, inhaled, injected or absorbed precutaneously in capable of causing death, injury, toxic or untoward reactions, the major principles applied in the emergency treatment of accidental poisoning by drug are diluted, emesis and adsorption ; in cases where no specific antidotes exist, preventation of further absorption of a drug from the oral route is by use of oral adsorbents, this could be of immense benefit in the management of drug overdose and / or poisoning[3]. The use of some pharmaceutical adsorbents in the preventation of further absorption of drugs are recognized in clinical practice[4-6].

The aim of this study was to extent the previous works of adsorption onto the Iraqi kaolin clay(7-8) surface and to investigate that inexpensive adsorbent for the treatment of (ciprofloxacin, chloroquin, piperazine, phyllocontin, digoxin and diazepam) drug overdose and poisoning, the influence of experimental conditions such as acid function, initial concentration of drug and temperature were studied.

2. EXPERIMENTAL

2.1 *Materials*
The drugs used in this work were supplied by international Egypt company for drugs industries, table:1, shows some physical properties and λmax of these drugs.

Table-1: λmax, melting point and molecular weight of the drugs

drugs	λmax		melting point C°	molecular weight
	Obs.	Lit.		
ciprofloxacin	277,254	254	120	331.4
chloroquin	221,5	210,370	184	515.9
piperazine	253,5	253	154	232.3
phyllocontin	254,5	254,5	100-105	420.4
digoxin	219,5	210,250	115-122	781
diazepam	230	230,330	131-135	284.7

Iraqi kaolin clay was obtained from bahar–Al-Najaf region in Al-Najaf governarate, Iraq, which characterized by XRD study, Table-2 shows the chemical analysis of the kaolin sample.

*Corresponding Author Received May 6th 2011, Accepted May 21st 2011

Table-2: Chemical analysis of Iraqi kaolin clay sample

Constituent	Wt%
SiO_2	48.57
Al_2O_3	35.05
CaO	0.6
MgO	0.77
K_2O	0.08
Fe_2O_3	1.34
TiO_2	1.19
Moisture	0.08
Loss on ignition	12.32

2.2 *Methods*

The kaolin clay was washing with distilled water and drying at 150C° for two hours in the oven then cooled and grinding.It was sieved to 100 μm size and stored in descicator.Two type of experiments were carried out, the first was to investigate the time to attain equilibrium, while the second was to find out the extent of adsorption. To estimate the time to reach equilibrium, 30 ml of standard solution of each drugs were added into 50 ml volumetric flasks to which (0.1g) of kaolin was add.The mixtures were put in the shaker bath set at 20 C° for 30 minutes,then the aliguots was decantation and centrifuged at 1000 rpm for 3 minutes, portions of the clear solution to measure the absorbance at the λmax of each drug, using a spectrophotometer (shimadzu, 1700).From the Beer's plot for each drug obtained earlier at the λmax, the a mount of free drug in solution was calculated and from the results,the time to attain equilibrium for each drug was 70 minutes.

To obtain adsorption isotherm for each drug, ten solution were prepared in the range of concentration, (3-30)mg/l for ciprofloxacin and chloroquin while (10-100)mg/l for piperazine, phyllocontin, digoxin and diazepam.

Sample of (30 ml) of each concentration of drugs were put in flask and (0.1g) of kaolin was added,the flasks were put in thermostated shaker for a period 70 minutes at different temperature (17,27,37,47C°) and different acid function (4,7,10) which was adjusted with buffer solution by using (HANA, pH-meter 112),after that the solution was filtered and centrifuged for 30 minute (3000 rpm). The supernatants were assayed for drug spectrophotometrically, the adsorbed of each drug was calculated from the equation (9)

$$Q_e = (C_o - C_e)\, V_{sol.} / M$$

Where C_o and C_e are the initial and equilibrium concentration of drug solution (mg/l), Q_e is the equilibrium adsorbed amount of drug (mg/g),$V_{sol.}$ is the volume of drug solution (L) and M is the weight of kaolin used (g).

3. RESULTS AND DISCUSSION

3.1 *Adsorption isotherms*

The amount of drug adsorbed (Q_e) was plotted against the equilibrium concentration (C_e) for each drug is given in Figs.1,2,3, the results showed that the amount adsorbed of each drug increases with the increase of initial drug concentration, that mean the adsorption process is to be dependent on the initial concentration.

Langmuir and Freundlich are the most frequently employed models to describe the equilibrium adsorption isotherm. The linearized Freundlich equation is:

$$\text{Log } Q_e = \log k_f + 1/n \ \log \ C_e$$

Where k_f and n are the Freundlich constants which are indicated of adsorption capacity and adsorption intensity respectively. So the Langmuir equation is:

$$C_e/Q_e = C_e/K_2 + 1/ K_1K_2$$

Where K_1 and K_2 are the Langmuir constants which are represented the capacity and binding energy of adsorption. Figs.(4,5,6,7,8,9) shows the Freundlich and Langmuir isotherms plots obtained from the adsorption studies.The R^2 values (goodness of fit) for the two types of isotherms for these drugs are presented in Table-3. As seen from Figs.4-9 and table.3. The kaolin clay at 17C° fits quite well into the Langmuir adsorption model for piperazine and pyllocontin, while poorest fitting for ciprofloxacin, chloroquin, digoxin and diazepam. However it was also seen that the experimental data obtained for the Freundlich model show the best fitting of diazepam, ciprofloxacin and chloroquin,while poorest fitting of piperazine, digoxin and phyllocontin.

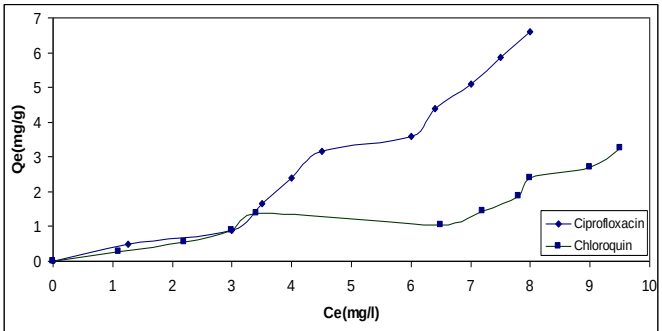

Fig:1 adsorption isotherm of ciprofloxacin and chloroquin on iraqi kaolin clay at 17C° and PH=7

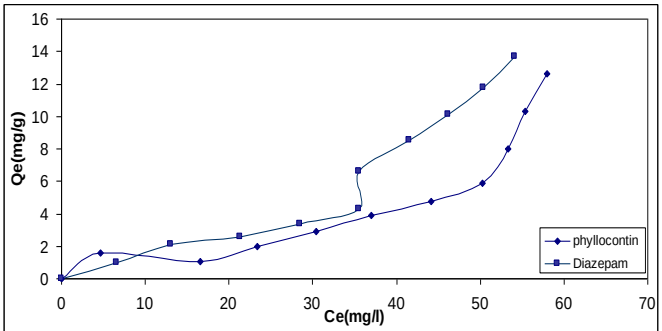

Fig: 2 adsorption isotherm of phyllocontin and diazepam on iraqi kaolin clay at 17C° and PH=7

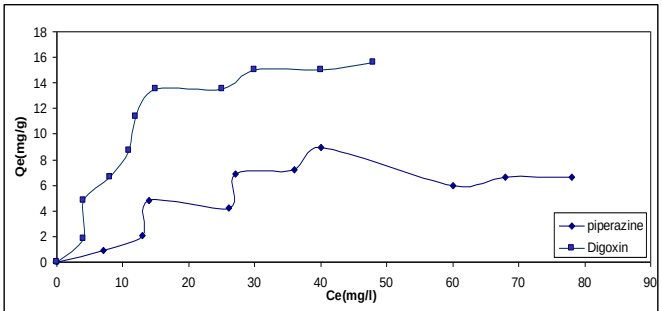

Fig:3 adsorption isotherm of piperazin and digoxin on iraqi kaolin clay at 17C° and PH=7

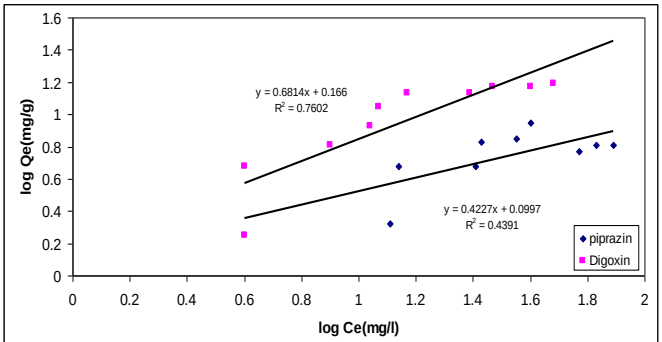

Fig:4 linear Freundlich adsorption isotherm on Iraqi kaolin clay at 17C° and PH=7

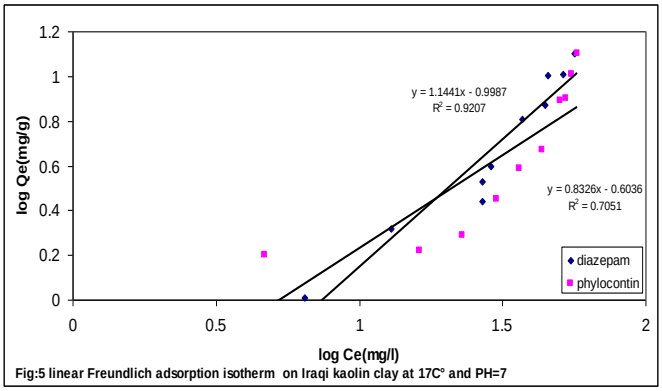

Fig:5 linear Freundlich adsorption isotherm on Iraqi kaolin clay at 17C° and PH=7

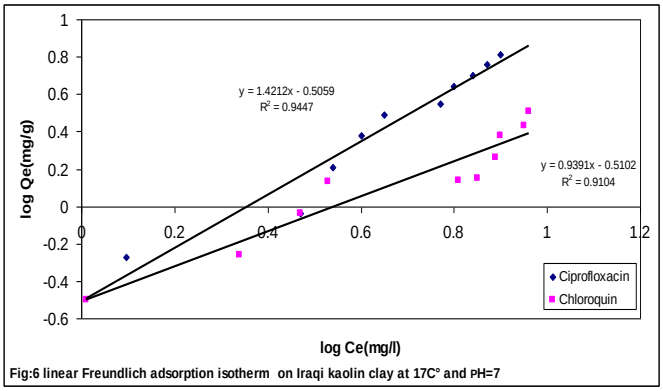

Fig:6 linear Freundlich adsorption isotherm on Iraqi kaolin clay at 17C° and PH=7

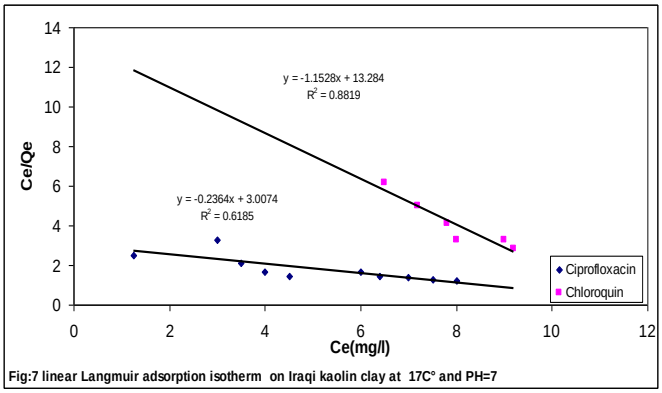

Fig:7 linear Langmuir adsorption isotherm on Iraqi kaolin clay at 17C° and PH=7

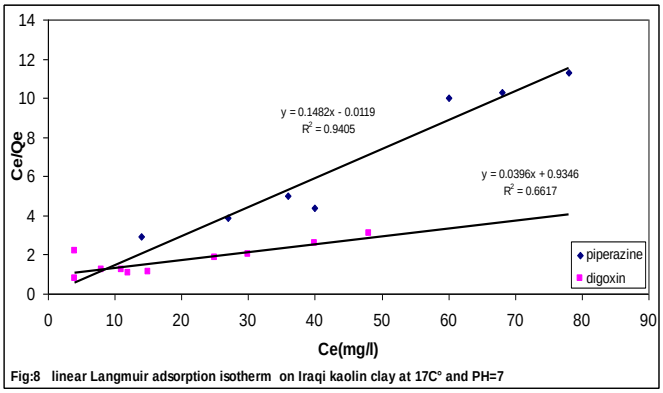

Fig:8 linear Langmuir adsorption isotherm on Iraqi kaolin clay at 17C° and PH=7

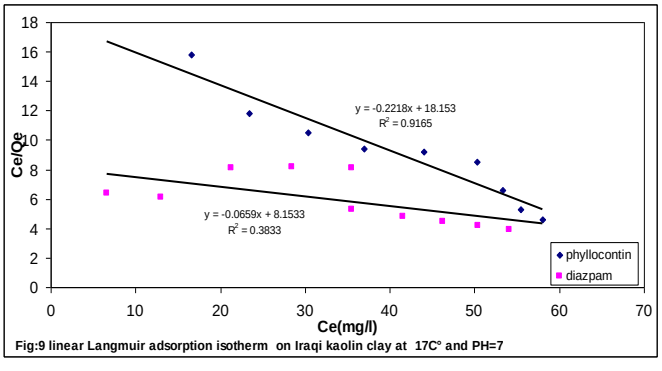

Fig:9 linear Langmuir adsorption isotherm on Iraqi kaolin clay at 17C° and PH=7

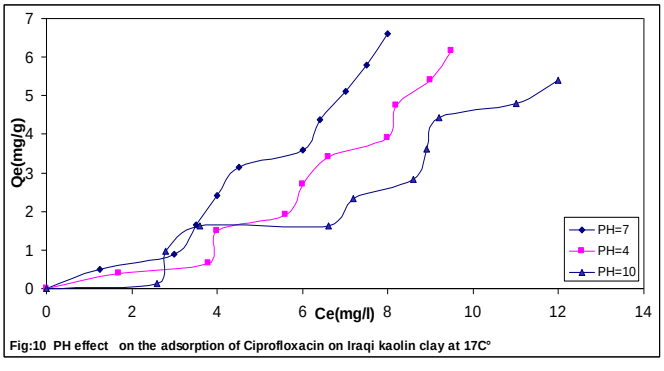

Fig:10 PH effect on the adsorption of Ciprofloxacin on Iraqi kaolin clay at 17C°

Fig. 1-10

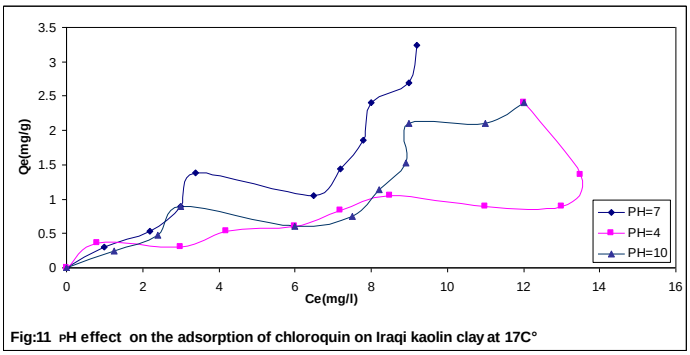

Fig:11 pH effect on the adsorption of chloroquin on Iraqi kaolin clay at 17C°

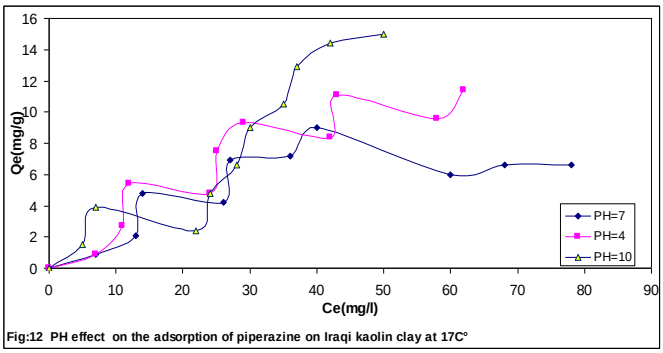

Fig:12 PH effect on the adsorption of piperazine on Iraqi kaolin clay at 17C°

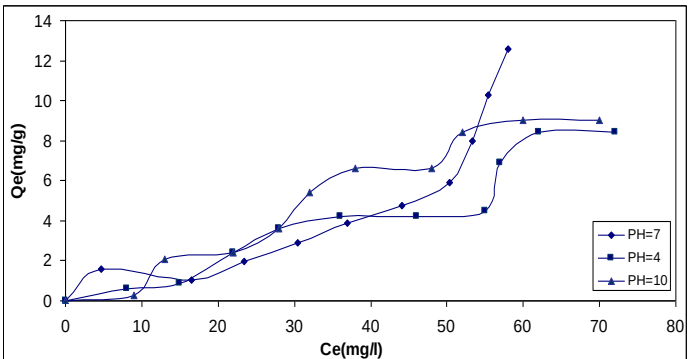

Fig :13 PH effect on the adsorption of phyllocontin on Iraqi kaolin clay at 17C°

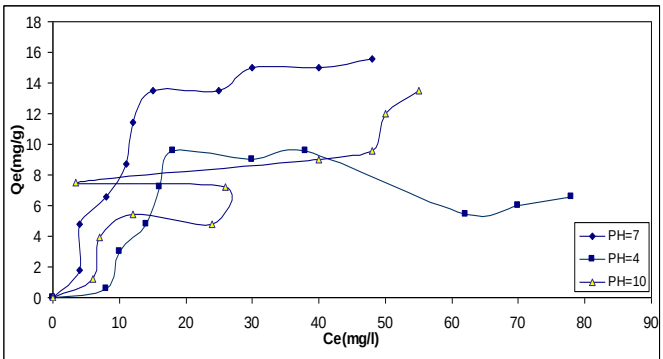

Fig:14 PH effect on the adsorption of digoxin on Iraqi kaolin clay at 17C°

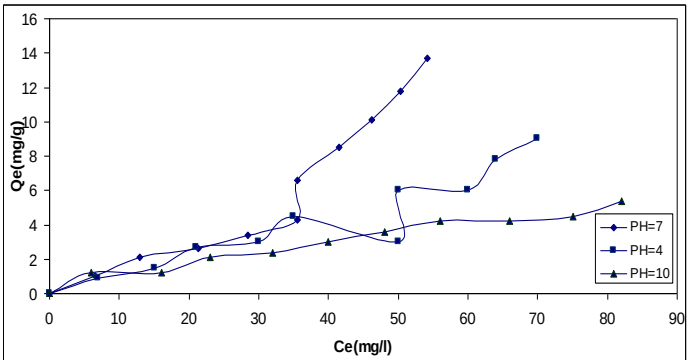

Fig:15 PH effect on the adsorption of diazepam on Iraqi kaolin clay at 17C°

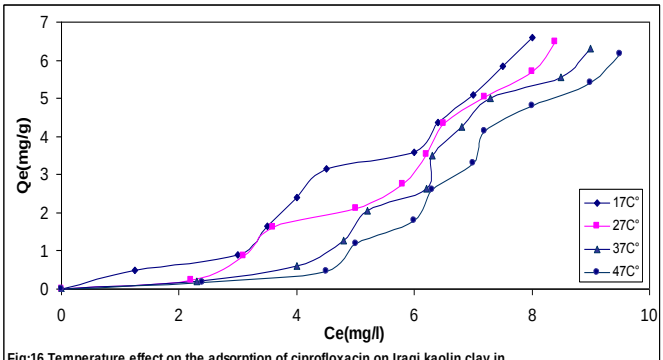

Fig:16 Temperature effect on the adsorption of ciprofloxacin on Iraqi kaolin clay in the rang (17-47C°)

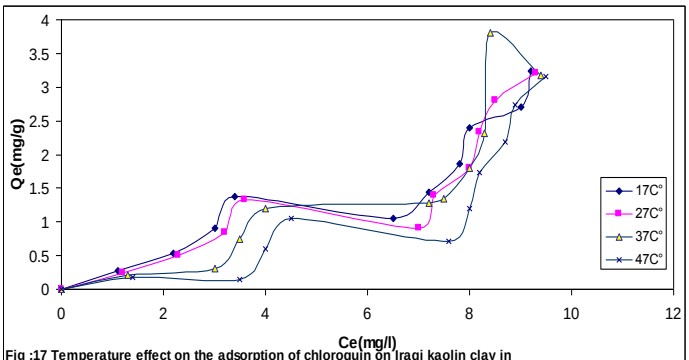

Fig :17 Temperature effect on the adsorption of chloroquin on Iraqi kaolin clay in the rang (17-47C°)

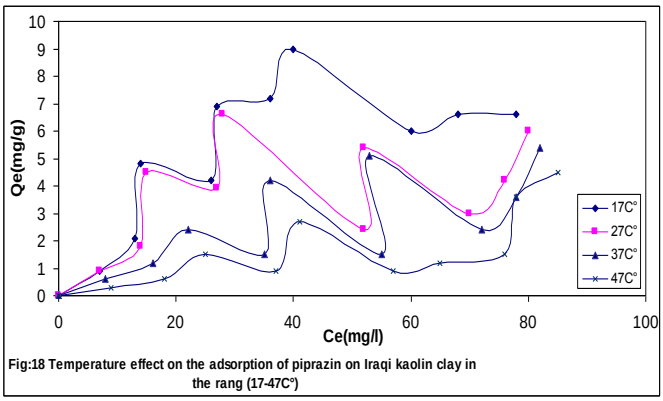

Fig:18 Temperature effect on the adsorption of piprazin on Iraqi kaolin clay in the rang (17-47C°)

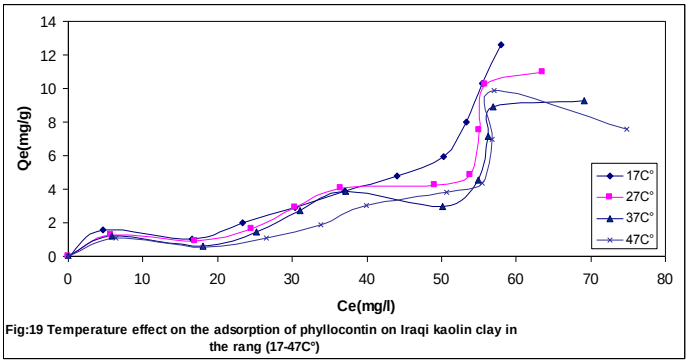

Fig:19 Temperature effect on the adsorption of phyllocontin on Iraqi kaolin clay in the rang (17-47C°)

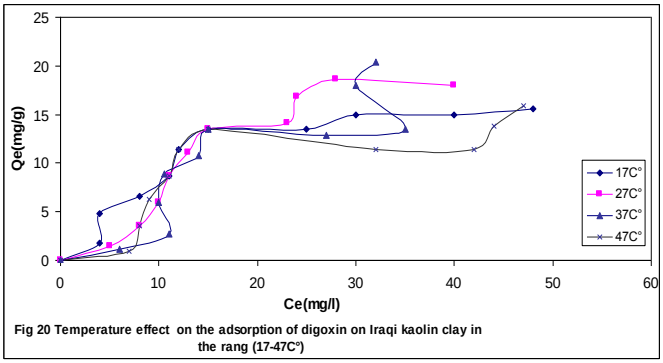

Fig 20 Temperature effect on the adsorption of digoxin on Iraqi kaolin clay in the rang (17-47C°)

Fig. 11-20

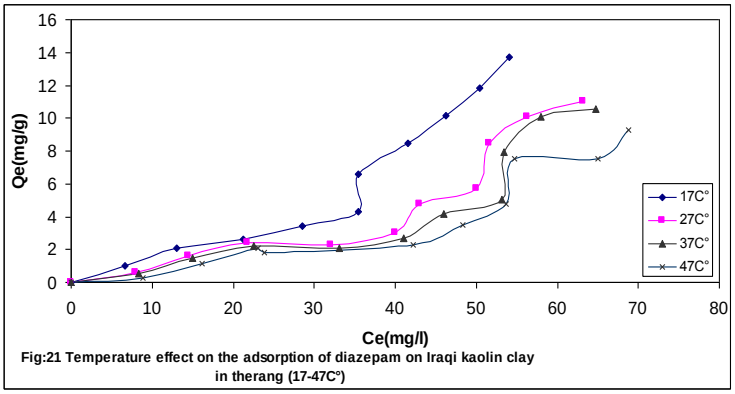

Fig:21 Temperature effect on the adsorption of diazepam on Iraqi kaolin clay in therang (17-47C°)

Table-3: Experimental constants and correlation factor of Freundlich and Langmuir isotherms at 17C° and H=7

Drug	Freundlich			Langmuir		
	n	K_f	R^2	K_1	K_2	R^2
ciprofloxacin	0.704	0.312	0.9447	-0.0786	0.3325	0.6185
chloroquin	1.065	0.308	0.9104	-0.0866	0.0752	0.8819
piperazine	2.365	1.258	0.4391	12.454	-84.0336	0.9405
phyllocontin	1.201	0.249	0.7051	-0.0122	0.0550	0.9165
digoxin	1.468	1.466	0.7602	0.0423	1.0699	0.6617
diazepam	0.874	0.1003	0.920	-0.0081	0.1226	0.3833

3.2 *pH Effect*

The effect of variations in pH on the adsorption of the (ciprofloxacin, chloroquin,piperazine, phyllocontin, digoxin and diazepam) on kaolin surface are shown in Figs(10,11,12,13,14,15), from these Figs. it is clear that pH values can play an important role of the adsorption of these drugs.

The results showed an increase in adsorption extent of ciprofloxacin with increasing pH value (pH 4>7>10), this effect is logical given the characteristics of the kaolin,which can remain stable in acid- base medium. Furthermore low pH value leads to an increase in hydrogen ion concentration in the system and the surface acquires positive charge, which caused electrostatic interaction between the drug molecule with the surface. While the extent of adsorption of chloroquin, phyllocontin, digoxin (pH 7>10>4) and for piperazine (pH 10 >4 > 7) showing different behaviour which was attributed to increase of negatively charge of the surface, a significantly strong electrostatic attraction appears.

So about diazepam adsorption the effect of pH variation follow (pH 7 > 4 > 10) which attributed to the charge of the drug which has a chemical structure that contains group more capable with the surface.

3.3 *Temperature Effect*

The initial concentration provides an important driving force to overcome all mass transfer resistance of all molecules between the aqueous and solid phases(10-11) in this study the effect of initial concentration of each drug on adsorption was investigated in the concentration rang of (3-100 $mg.l^{-1}$) and the equilibrium uptake capacity ($mg.g^{-1}$) at 17,27,37,47C° are given in Figs.(16,17,18,19,20,21) which shows the change of the equilibrium adsorption capacity of kaolin with initial drug concentration and temperature. It was indicated that Q_e values decrease with both increasing initial concentration of (ciprofloxacin, chloroquin, piperazine, phyllocontin, and diazepam) and increasing temperature showing the exothermic nature of the process, while the Q_e value of digoxin increases with increasing initial concentration and temperature showing the endothermic nature of the process and that indicates the absorption was happened besides adsorption process and that agreement with previous studies.

The thermodynamic parameters of the adsorption process at various temperatures were calculated to confirm the adsorption nature of the present study. Gibb's free energy was evaluated by the following equation:

$$\Delta G = -R\ T \ln K$$

Where R is the ideal gas constant (8.314 $Jmol^{-1}k^{-1}$) and T the temperature (K),K is the equilibrium constant.
Enthalpy and entropy of adsorption was calculated from the equations:

$$\text{Log } X_m = -\ \Delta H\ / 2.303\ RT + \text{constant}$$
$$\Delta G = \Delta H - T\Delta S$$

Where X_m is the maximum uptake of adsorption.

The positive ΔG values indicates the nonspontaneous nature of adsorption process that it means there is some sort of weak interaction (12).The negative ΔS values shows the decreased randomness at the solid /solution interface during the adsorption process.

Table-4: Summarize the values of the thermodynamic parameters at 17C°

drug	ΔH KJ.mol^{-1}	ΔG KJ.mol^{-1}	ΔS J.mol^{-1}.K^{-1}
ciprofloxacin	-2.642	0.464	-10.710
chloroquin	-1.225	2.593	-13.165
piperazine	-9.956	5.954	-54.865
phyllocontin	-14.552	3.681	-62.865
digoxin	1.532	2.709	-4.059
diazepm	-7.850	3.3114	-38.486

4. CONCLUSION

1) The present study has shown that iraqi kaolin clay can be used for the adsorption of ciprofloxacin, chloroquin, piperazine, phyllocontin, digoxin and diazepam drugs from aqueous solution
2) Freundlich and Langmuir model were used to describe the adsorption process of these drugs, Freundlich model have better correlation coefficient of ciprofloxacin, chloroquin and diazepam than piperazine, phyllocontin and digoxin, while Langmuir model fits quite well for phyllocontin, piperazine and poorest fitting for ciprofloxacin, chloroquin, digoxin and diazepam.
3) Thermodynamic parameters revealed that the adsorption of ciprofloxacin, chloroquin, piperazine, phyllocontin and diazepam onto the kaolin clay were found an exothermic process and non-spontaneous, while for digoxin was found an endothermic and non-spontaneous.

5. REFERENCES

1. ATTRA-Reduced –Risk pest control fact sheet: kaolin clay for management of Gtassywinged sharp shooter, http://attar.ncat.org/attar-pub/pdf/kaolin – clay grapes.pdf, **(2004)**.
2. Rasad, R. D., and Rangeshwaran, R., Shelf life and bioefficacy of Trichoderma harzianum formulated in various carrier materials. Plant Disease Research **(2000)**, 15(1):38-42.
3. Chukwenweniwe, J. E., and Aderemi, B. A., Invitro Adsorption of Fluoroquinolones on some pharmaceutical Adsobents, Tropical Journal of pharmaceutical Research, **(2006)** 5(1),533- 538.
4. Al-Bayati, R. A., Adsorption –Desorption Isotherm of one of Antidibetic Drug from Aqueous Solutions on Some Pharmaceutical Adsorbents, European Journal of Scientific Research, **(2010)** 40(4),580-588.
5. Orisakwe, O. E., Oluboyo, A., Foefule, S. O., Obi, E., llondu, N., Afonne, J., Agbasi, P., and Chiroma, D. H., Adsorption studies of Artesunate: Evaluation of Saline Carthartics as Additive in Management of Artesunate Poisoning, J. Health Sc., **(2001)** 47(5), 491-194, http://dx.doi.org/10.1248/jhs.47.491.
6. LanPhilip, K. N., Tian, Qi., Ip: Margaret and D.Gomersall charles, In vitro Adsorption of Gentamicin and Netilmicin by Polyacrylonitrile and Polyamide Hemofiltration Filters, Antimicrobial Agents and Chemotherapy., **(2010)** 54(2), 963-965, http://dx.doi.org/10.1128/AAC.01215-09.
7. Hassan, S. A., and Kadhim, L. H., Al-kufa Journal, Iraq, **(2007)** 8(2), 168-181.
8. Isha, S. A., Hassan, S. A., and Jahsim, K. G., IBN-Al-Haitham Journal for Pure and Appl. Sci., Iraq, **(2008)** 21(2), 57-75.
9. Murrell, J. N., and Bucher, E. A., "Properties of Liquids and Solution", Jhon wiley and Sons, New York, **(1982)** 255.
10. Juang, R. S., Wu, F. C., and Tseng, R. L., The ability of activated clay for the adsorption of dyes from aqueous solution, Environ. Technol. **(1997)** 18, 525-531, http://dx.doi.org/10.1080/09593331808616568.
11. Donmez, G., and Aksu, Z., Removal of chromium (VI) from wastewaters by Dunaliella species, Proces, Biochem. **(2000)** 38, 751-762, http://dx.doi.org/10.1016/S0032-9592(02)00204-2.
12. Daniels, F., and Alberty, A., Physical chemistry, 2nd, ed., **(1961)** 607.