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Three Locally Clays as A Surfaces for Adsorption of Cephalexin Monohydrate from Aqueous Solution: Thermodynamic and Desorption Equilibrium

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Abstract

The adsorption of cephalexin.H_2O from aqueous solution on attapulgite, bentonite and kaolin has been studied at the human body temperature (37.5˚C) and at 5, 27, 47˚C in 0.1M hydrochloric acid (pH ≈1.2). The value of pH ≈1.2 has been chosen to simulate the pH of stomach fluid. The clays show the following order: Bentonite > attapulgite > kaolin, for their activity to adsorb cephalexin.H_2O. The charged clay particles can attract molecules either by electrostatic forces, for the molecules of oppositely charged, or by inducing dipole formation in the neutral molecule. The L-shaped adsorption isotherm indicated that drug molecules arrangement in a flat geometry on the clay surface. The results indicated the applicability of Langmuir isotherm for adsorption of drug on three clays. The amount of cephalexin.H_2O adsorbed on the three clays was increased with increasing pH value from 1.2 to 5. At the acidic pH, the competition between cephalexin.H_2O molecules and hydronium ions results in a reduction in adsorption process. At fixed temperature and pH, the adsorption of cephalexin.H_2O on the three clays was increased with increasing the ionic strength of solution. The data showed a little increase in the amount of drug adsorbed by attapulgite and bentonite with increasing temperature, so the adsorption process appeared endothermic. The reverse was observed with adsorption of cephalexin.H_2O on kaolin surface (exothermic). The extent of desorption of cephalexin.H_2O from the clays increased when the concentration of drug increased. This result may refer to the difficulty of desorption of the drug at low concentrations, which reflects a relatively higher adsorbate - adsorbent interaction.

Keywords: clays, cephalexin monohydrate, desorption equilibrium, thermodynamics.

1. Introduction

Adsorption is a phenomenon happened on the surface which usually refers to the concentrating of special kinds of materials at the interface of solution or other phases [1]. It is a phenomenon in which the available active sites on the surface is the determining factor [2,3]. The thermodynamic and molecular properties of adsorption process such as affinity, capacity, shape of isotherm, and the enthalpy change) are the basic parameters to understand the binding processes and to provide mechanical information for the selection solid adsorbents that have many applications in preventing toxicity in animals [4-6]. However, there are many phenomena where adsorption is essential to occur. In industry, for example, analysis and separation of gases, petroleum processing [7], decolorisation [8], taste improvement and deodoration of drinking water [9], all these processes occur through the adsorption phenomena on solid surfaces such as clays and activated charcoal. Medical uses of adsorbent surfaces, particularly, in the treatment of poisoning with different materials was discussed in several publications. Charcoal is high efficient surface was used as an antidote for treatment the poisoning with drug overdosage and toxic substances [10,11]. Another Active surface material were also studied and found of clinical importance in the treatment of poisoning by toxins and drug overdose, such as kaolin [12], soils [13], talc [14], alumina and silica [15], montmorillonite [16] and smectite [17]. The present study was performed to explore the validity of three locally available clays (attapulgite, bentonite and kaolin) as antidotes in treatment of poisoning by cephalexin monohydrate if taken beyond its usual dosages. In physical pharmacy the adsorption and desorption of drugs is very important to prepare sustained release tablets and physical antidotes.

2. Experimental

Preparation of Clays Powder

The used clays were supplied by the Company of Geological Survey and Mining, Iraq. The three clays were washed by distilled water to remove approximately all the soluble materials. Washed clays were then dried for 3 hours in an oven at 160 ^{o}C and kept in containers. The dried clays were ground and sieved by using sieve of (200-mesh). The size of particles that used for three clays in all experiments is 75 μm.

Preparation of cephalexin monohydrate solutions

Different concentrations of cephalexin monohydrate were prepared by serial dilutions. The absorbance of solutions at 256nm were plotted vs. the cephalexin.H_2O concentration. The linear calibration curve was obtained and show the applicability of Beer-Lambert's law.

Equilibrium Times of Adsorption Systems

An initially 5×10^{-3} M of drug solution at 37.5 ^{o}C was shaken with 0.5 g of clay powder. The concentration of drug solutions was evaluated at different times using UV-Vis spectrophotometer (Pye-Unicam. PU 8600, Philips). The time required to attain equilibrium for attapulgite and bentonite systems are 2.5h while its 2h for kaolin system.

Adsorption Isotherm

25 ml of aqueous solutions of cephalexin.H_2O with concentrations range from 8×10^{-4} to 2×10^{-2} M were mixed with 0.5g clay. The mixture was shaken in a thermostatic water bath, (GFL (D-3006) at 60 cycle/min., then centrifuged at 3000 rpm for 20 min. The remain content of drug was assayed after dilution using UV-Vis. spectrometer. The remain concentration at equilibrium was obtained from the calibration curve.

The amount of drug adsorbed on the surface was calculated from equation [18] :-

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

Where: x is the adsorption quantity, m : weight of clay (g). C_o and C_e: initial and equilibrium concen. (mg/L) and V: volume of solution (L).

Effect of Experimental Parameters

The procedure described for the adsorption experiment was carried out at different temperatures (5, 27, 37 and 47 ^oC) and different pH values (using a fixed concentration of the drug in different media, 0.1M HCl (pH≈1.2),different phosphate and biphthalate buffer systems were used to adjust the pH range from 1.6 to 9). The effect of ionic strength was studied using different concentrations of sodium chloride (0.154, 0.3 and 0.5 M).

Desorption Procedure

Desorption process was performed by two different methods. In first method, the extent of elution of adsorbed drug was evaluated using a suitable solvent and 0.154M NaCl as elution media. The adsorption process was performed as mentioned previously at 37.5^oC. After equilibration, the suspensions were centrifuged, and the supernatant was decanted carefully and set aside for assay. A 25 ml portion of eluent was added; after shaking for 1 hour, the suspensions were centrifuged and the drug content determined [19,20].

The amount of drug desorbed was calculated according to the following equation [19]:

$$\text{The amount desorbed (mg/g)} =\frac{C_e\times V}{m} \qquad \text{.....(2)}$$

where C_e : concentration of drug desorbed at equilibrium (mg/L), V : volume of eluent (L)

In another method a solution of fixed concentration of drug (2×10^{-2}M) was prepared in a suitable solvent and the desorption process was repeated according to the above procedure. The elution process was repeated by adding 25 ml of eluent until no significant amount of drug was recovered after several washings [19]. Equation (3) was used to calculate the amount of drug released in each step of elution and the desorption percent was obtained as follows [19]:

$$\%\ \text{desorption} =\frac{\text{amount of drug desorbed}}{\text{amount of drug adsorbed}}\times100 \qquad \text{.....(3)}$$

3. Result and Discussion

The adsorption of cephalexin.H_2O from aqueous solution on three locally clays (attapulgite, bentonite and kaolin) was studied at the human body temperature (37.5˚C) and at 5, 27 and 47˚C in 0.1M hydrochloric acid (pH ≈1.2).The shapes of cephalexin.H_2O isotherms are shown in Figure (1), the quantities of drug adsorbed on attapulgite, bentonite, and kaolin are plotted against concentration at the above temperatures. The adsorptive capacities of the three clays was observed to increase as the concentration of cephalexin.H_2O increased until reaching a limited value. The clays were found of sensible activity in adsorption of different materials and drugs [21]. The greatest amount of adsorption was exhibited by bentonite clay followed by attapulgite and kaolin.

In clay minerals an atom of lower positive valence replaces one of higher valence, this causes an increase in negative charge. This negative charge is neutralizing by the adsorption of cations on the surfaces. In the solution, a compensating process may occur between the cations on the layer surfaces and the cations which are available in solution [22]. On the other hand, the behavior of clay in solution can be predicted by Gouy theory and the concept of electrical double layer [23]. In aqueous solution the particles of clay mineral are charged and can attract molecules either by inducing dipole formation in the neutral molecule, or by electrostatic forces for the molecules of opposite charge.

The isotherm shapes of cephalexin.H_2O adsorption are of L type as classified by Giles *et al.* [24]. L-shaped adsorption isotherm indicated that affinity between the drug and the clays is high [24]. Moreover, the adsorption of cephalexin.H_2O on kaolin was not limited to formation of one adsorption layer; a second plateau was obtained, which gives multilayer L_4 type of isotherms according to the classification of Giles. This refers to the heterogeneous surface nature of kaolin clay as given by some reports [25].

The experimental adsorption data were applied to the theoretical Langmuir isotherm (eq.4) [26]. The results showed the applicability of Langmuir isotherm as shown from Figure (2).

$$\frac{C_e}{x/m} = \frac{1}{ab} + \frac{C_e}{a} \quad \text{..... (4)}$$

Where a and b are Langmuir constants

The pH effect on the adsorption uptake of cephalexin.H_2O by three clays at 37.5˚C was investigated upon using buffer solutions (pH =1.2 -5). As shown from Figure (3), the adsorption quantities of the drug increase with increasing pH of solution. At the acidic pH, the competition between cephalexin.H_2O molecules and hydronium ions causes a reduction in adsorption of drug [27]. In addition, the solubility of cephalexin.H_2O is greatly decreased as the pH is increased from 2 to 5 result in increase of affinity towards the clay surface.

Figure (4) demonstrated the effect of ionic strength on adsorption uptake of cephalexin.H_2O on the three clays at variable concentrations of sodium chloride (0.154, 0.3 and 0.5M) (ionic strength (I) = 0.154, 0.3 and 0.5 M). It is observed an increase in drug uptake as the concentration of electrolyte increase. The higher interaction between electrolyte ions and aqueous molecules of solvent causes in the reduction of drug solubility and increase in cephalexin.H_2O adsorption. Also, the presence of ions and the electrostatic interactions in solution leads to change in the physical properties of the surface of clay [28].

The data and the shapes of cephalexin.H_2O adsorption isotherms at temperatures under study are demonstrated in Figure (1). A slight increase in the amount of drug adsorbed on attapulgite and bentonite was observed with increase in temperature, hence the drug uptake

process is endothermic. This means the interaction between the drug molecules and the clay surface, requires an appreciable energy to take place. Moreover, the mechanism of ion exchange may also take place at the clay-liquid interface [27]. On the other hand, the adsorption extent of cephalexin.H_2O on kaolin was decreased at the high temperatures, refers to exothermic process.

At different temperatures, the values of X_m were estimated to calculate the thermodynamic functions of adsorption of cephalexin.H_2O on the clays as illustrated in equations 5-7[29].

$$\ln X_m = \frac{-\Delta H}{RT} + constant \qquad \ldots\ldots\ldots\ldots\ldots (5)$$

X_m: is the maximum amount uptake by clay surface. When plot ln X_m vs. *1/T*, the straight line of slope $-\Delta H / R$ was obtained.

$$\Delta G^o = -RT\ln K \qquad \ldots\ldots\ldots\ldots\ldots (6)$$

Where ΔG^o change is free energy, R is constant equals to 8.314 $J.mol^{-1}.K^{-1}$. The entropy of system (ΔS) calculated from the equation: $\therefore \Delta S = \frac{\Delta H - \Delta G}{T}$ ……..(7)

Thermodynamic functions of cephalexin-attapulgite and cephalexin-bentonite systems show negative heat of adsorption and positive entropy (Table (1)). The hydrophobic bonding of water molecules which are surrounding the drug molecule and the adsorption sites of the surface was ruptured, thus the randomness of the system increased [27].

The extent of desorption of cephalexin.H_2O from the clays increased as the concentration of the drug in solution increased Figure (5). These results may refer to the difficulty of desorption of the drug at low concentrations, which reflects a relatively higher drug – clay interaction and the heterogeneity nature of surface. Easier desorption can be seen with increase the concentration of drug in solution [25].

The percent desorbed of drug after several washings with 0.1 M hydrochloric acid or 0.154 M sodium chloride was also determined. The results are listed in Table (2) by the concentration of drug released in each elution step. The results clarify the adsorption of cephalexin.H_2O on the three clays is of physical-chemical type characterized by van der Waals forces. Nearly half amount of cephalexin.H_2O adsorbed on bentonite and kaolin was recovered after seven and six washes respectively by 0.154 M NaCl or 0.1 M HCl, but 72.8 percent of the drug was retained by attapulgite. The low percent of cephalexin.H_2O desorbed from attapulgite as compared with that of bentonite and kaolin can be explained partially on the basis of the structure of clay surface and the mechanism of adsorption of drug on the surface [19].

Table (1) thermodynamic functions for adsorption of cephalexin.H_2O on three clays at 37.5 °C

Clay	*ΔH* *kJ .mol^{-1}*	*ΔG* *kJ.mol^{-1}*	*ΔS* *J.mol^{-1}.K^{-1}*
Attapulgite	+ 6.218	+ 1.506	+ 15.17
Bentonite	+3.566	0.603	+ 13.42
Kaolin	7.468	+ 5.235	40.91

Table (2) Percent desorption of cephalexin.H_2O from the clays by repeated elution

Clay	*Elutions No.*	*Desorption in 0.1 M HCl*			*Desorption in 0.154 M NaCl*		
		C_e mg/l	*Quantity desorbed mg/g*	*% desorption*	*C_e mg/l*	*Quantity desorbed mg/g*	*% desorption*
Attapulgite	1	355.05	17.75	25.9	331.05	16.55	23.8
	2	400.35	20.02	28.8	378.62	18.93	27.2
Bentonite	1	615.33	30.77	18.1	697.18	34.86	20.5
	2	946.38	47.32	27.8	996.08	49.80	29.3
	3	1097.30	54.86	32.3	1129.45	56.46	33.2
	4	1223.30	61.16	35.9	1238.90	61.93	36.5
	5	1292.71	64.63	38.0	1298.08	64.89	38.2
	6	1356.50	67.82	39.9	1338.72	66.92	39.4
	7	1402.88	70.14	41.2	1367.18	68.34	40.2
Kaolin	1	348.59	17.43	48.1	346.03	17.30	47.8
	2	375.30	18.76	51.8	398.30	19.91	55.1
	3	396.80	19.83	54.8	405.30	20.21	56.0
	4	413.05	20.65	57.1	-	—	—
	5	415.75	20.78	57.5	—	—	—
	6	416.55	20.82	57.6	—	—	—

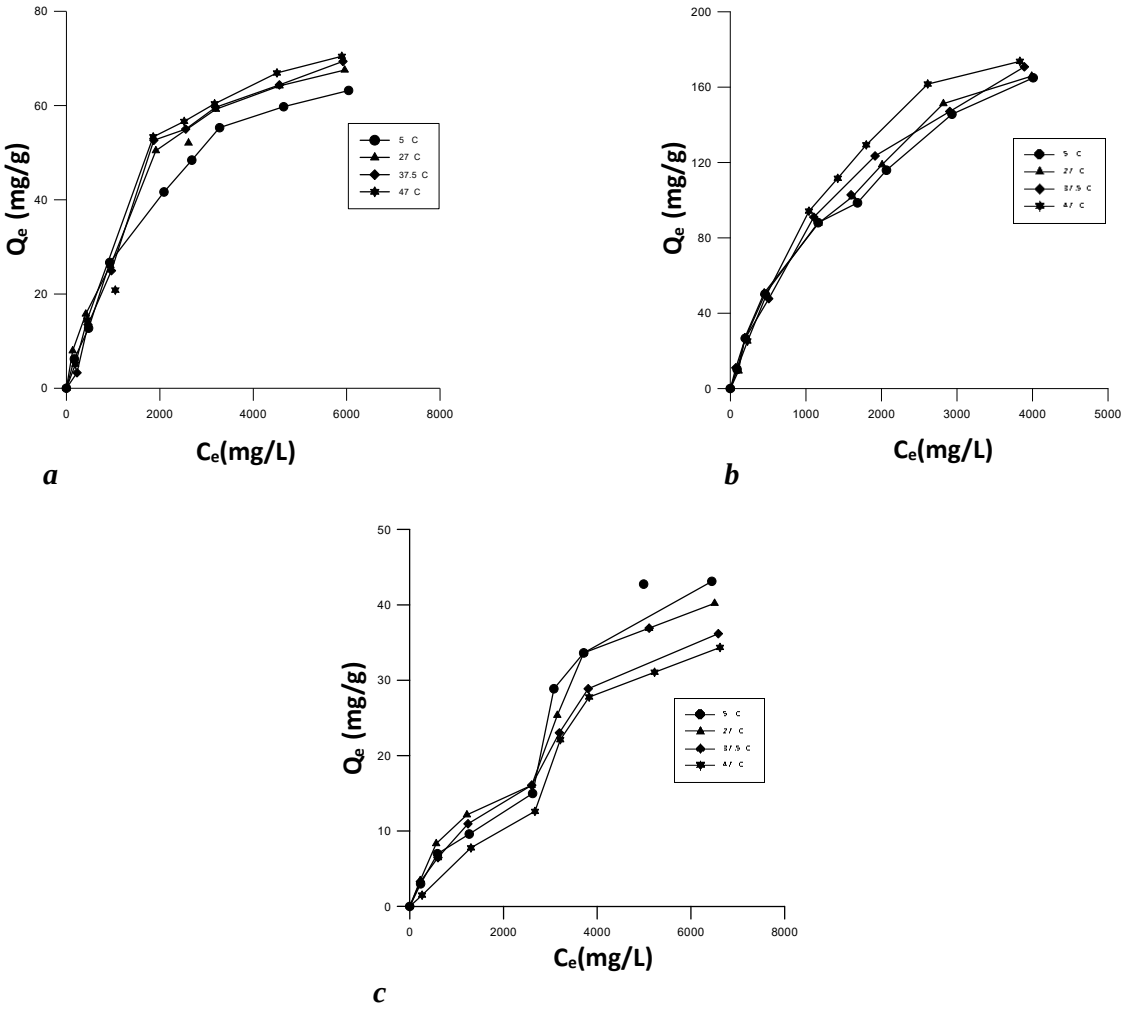

Figure (1): Adsorption isotherms of cephalexin.H_2O on : a- attapulgite, b- bentonite and c- kaolin at pH ≈ 1.2 and different temperatures

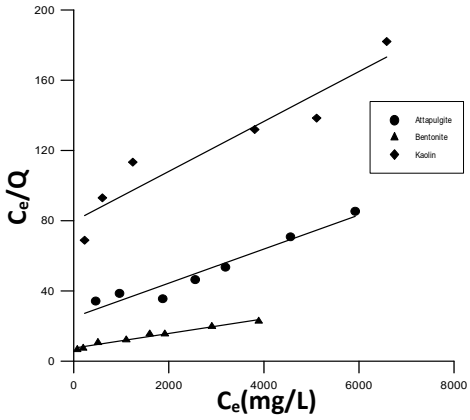

Figure (2): Linear form of Langmuir isotherm of cephalexin.H_2O on the clays

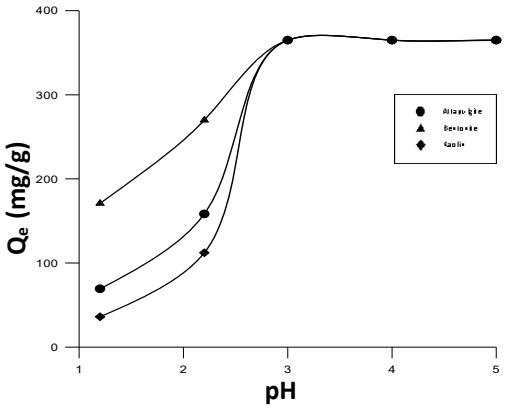

Figure (3): Effect of pH in adsorption uptake of cephalexin.H_2O on the clays at 37.5 ^oC

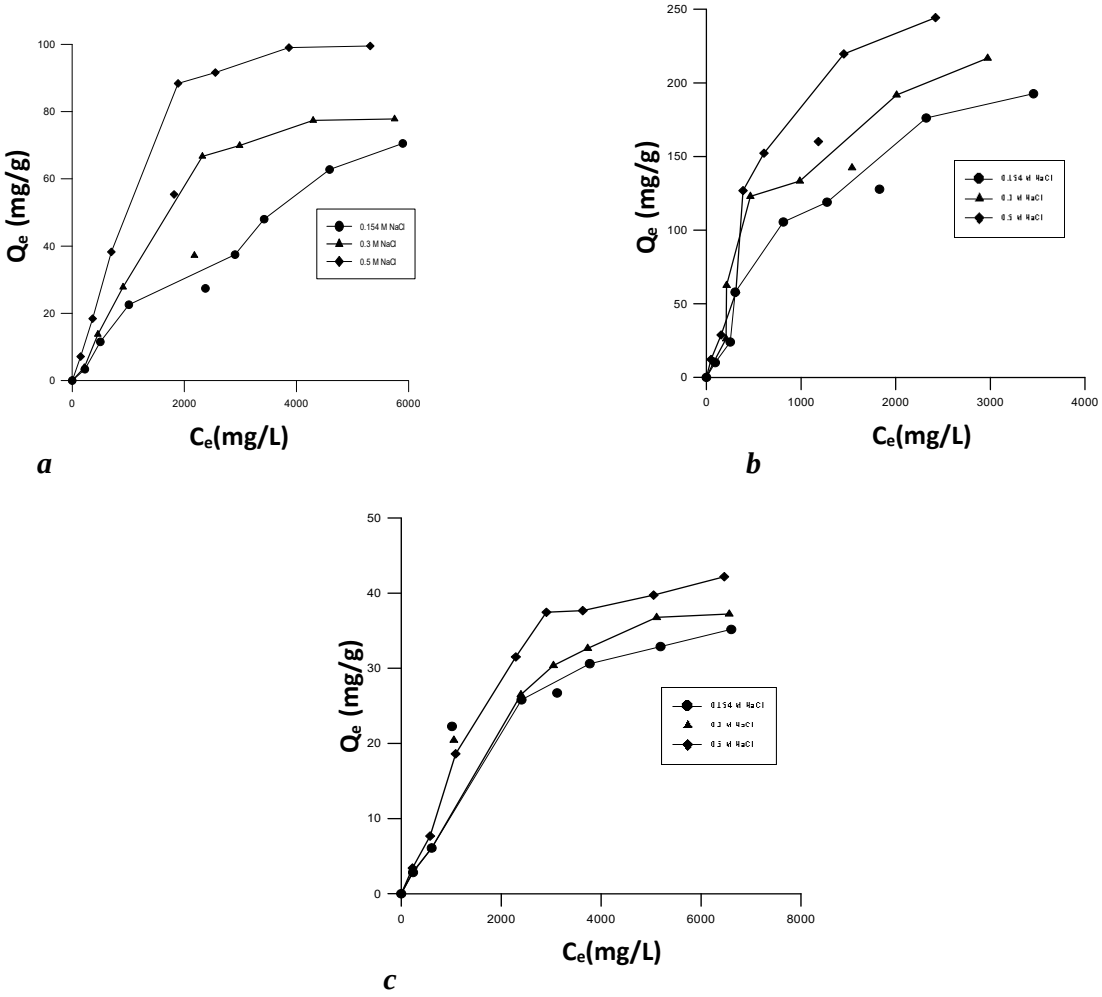

Figure (4): Adsorption isotherms of cephalexin.H_2O on: a- attapulgite, b- bentonite and c- kaolin at different concentrations of sodium chloride at 37.5 ^oC

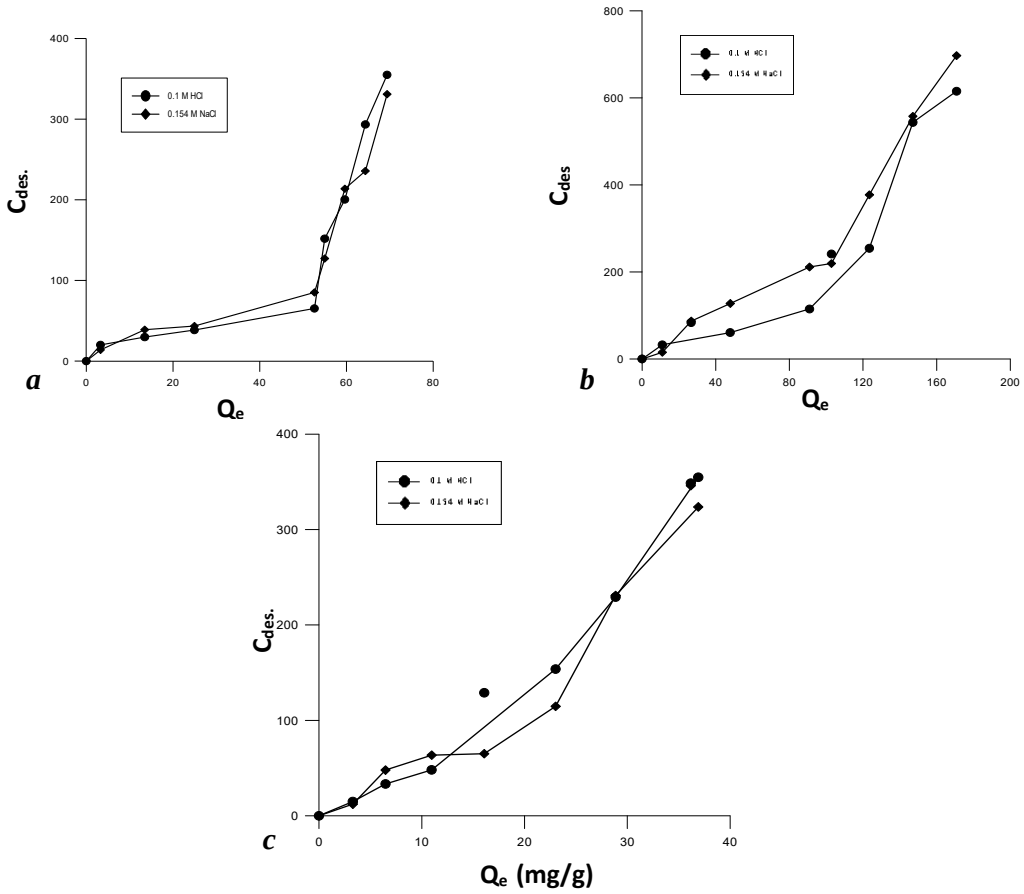

Figure (5): Concentration of cephalexin.H_2O desorbed from: a- attapulgite, b-bentonite and c- kaolin as a function of amount adsorbed

4. Conclusions

Due to higher activity of bentonite clay in adsorption of the drugs, it can be used as an antidote for treatment of acute poisoning by cephalexin.H_2O. Adsorption of the drug on the clays was pH dependent and it was reversible with low enthalpy value. The adsorption isotherms obeyed Langmuir equation and the extent of drug adsorption change positively with concentration of sodium chloride.

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