Study the adsorption of diphenhydramine – HCl on Iraqi bauxite

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Abstract

Drug overdose and poisoning are common clinical problems and could occur with Diphenhydramine hydrochloride (DFH) (one of anti histaminic drug). It therefore important to study the adsorption of the DFH on pharmaceutical adsorbents which could serve as possible antidotes for the emergency treatment of DFH overdose or poisoning when they occur. The rate and extent of adsorption of DFH on some pharmaceutical adsorbents, bauxite were investigated spectra photometrically also the effect temperature, pH, presence of sucrose as additive have been studied as well, adsorbent's weight and partical size.The equilibrium adsorption contact times were determined for clay surface. Adsorption isotherms have been analyzed by the freundlich model. The apparent thermodynamics parameters were calculated and the obtained values support the endothermic process. The optimum pH required for maximum adsorption was found to be (6) . These studies indicate that bauxite could be effective antidotes for the anti histaminic drug used in cases of overdose and poisoning because of High binding capacities exhibited by the clay used.

1- Introduction

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 or untoward reactions [1]. Reaction to drug caused by an allergic sensitivity is not considered drug poisoning. Virtually all drugs, especially in Large doses of when taken over long periods of time, can initiate a toxic condition [2,3]. The major principles applied in the emergency treatment of accidental poisoning by drug are dilution, emesis and adsorption [4]. In cases where so specific antidotes exist, prevention of further adsorption of drug from the oral route is by use of oral adsorbents. This could be of immense benefit in the management of drug overdose or poisoning the use of standard adsorbents such as bauxite in the prevention of further adsorption of drug, are recognized in clinical practice. The safety, the high adsorptive capacity, there low density and the high specific surface, have been accepted for

along time, and they account for most of the current uses of the clay [5]. Diphenhydramine hydrochloride figure (1) (N, N-dimethyl – (diphenyl methoxy) ethylamine is synthesized by a simple reaction of benzydrybromide and 2-dimethylamino ethanol [6,7], Diphenhydramine hydrochloride is a first generation (typical) anti histamine used to treat a number of conditions including allergic symptoms, itchiness, the common cold, insomnia, motion sickness and extra pyramidal symptoms [8].

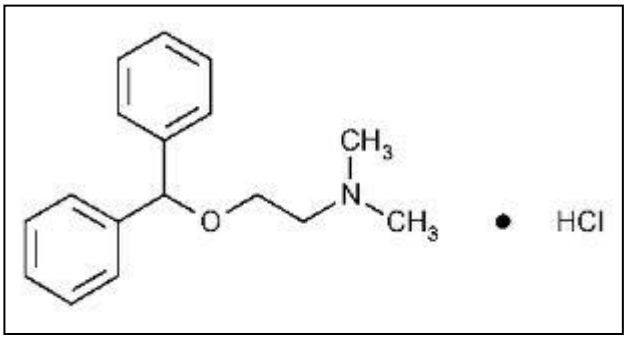

Figure (1) : Diphenhydramine hydrochloride structure

The aim of this work to study the effect of different factors on the adsorption of this drug on bauxite surface in different aqueous solutions.

2- Experimental

2.1 Materials

The drug employed in this study (diphenhydramine hydrochloride was obtained from (the state Enteprose for the drugs Industries and Medical Appliances) in Samarra – Iraq (SDI). The molecular weight is equal to 255.355 g/mol, the maximum absorption λ max = 257.8 nm, the bauxite clay employed in this study was obtained from (the general company for geological survey and mining), Baghdad. The clay in powder form was washed several times with excessive amount of distilled water and then dried at (120 ºC) in an oven (D – 6450) for three hours and then kept in airtight containers. The adsorbent used in this work was sieved (Retsoh Gmband Co.); KG Germany) by using a test sieve. The particle size of 75 μm was used for adsorbent in the experiments of this research.

2.2 Method

Adsorption experiments were carried out by shaking (0.4g) of bauxite used in separate form with (10ml) from aqueous solution of DFH drug of desired concentration at various temperature (10,25,37.5,45 ºC) pH (5.2) and ionic strengths (0.1 , 0.2 , and 0.3M sucrose solution in water) for 50 minutes (the required time to reach the equilibrium concentration). A thermo stated shaker bath(GFL(D-3006),Fed-Rep. Of Germany) was used to keep the temperature constant. At the end of the adsorption period, the rotation was

stopped and the solution was filtered by using filter paper (what man No. 42 Germany). The clear supernatants were assayed for drug, spectrophotometrically (CECIL,CE7200,England,190-900nm) after the appropriate dilution. The adsorbed amount of the drug was calculated from the concentration in solutions before and after adsorption according to the equation (1)

$$Qe = \frac{V(Co - Ce)}{W} \qquad (1)$$

Where : Co and Ce are the initial and equilibrium liquid-phase concentration of drug solution (mg/L), respectively, Qe is the quantity of adsorbate in (mg) held by weight of adsorbent in (g), V is the Volume of drug solution (L) and W is the weight of clay sample used (g).

3. Results and Discussion

In aqueous solution DFH had λ max Value of 257.8 nm Fig. (2) , At this beer's Law Fig (3) was obeyed of DFH. The study to know when equilibrium was attained showed that with bauxite as adsorbent. adsorption equilibrium was attained within (50 min) table (1) fig (4) for the drug under study.

3.1 Adsorption Isotherm of aqueous drug solution

It is generally possible to express the results of experimental sorption measurements in the form of equilibrium sorption isotherms Figure (5 , 6 , 7) , table (2) displays the isotherms of adsorption related to DFH drug from aqueous solution on bauxite surface. It was seen that these isotherm fitted the Freundlich adsorption isotherm. Experimental data was also applied to the Langmuir adsorption isotherm (equation 2), but the linear state of the Langmuir adsorption isotherm was not obtained. This consistency is seen in the Freundlich Linear adsorption isotherm drawn according to equation (3) figure (8) [8]

$$Ce / Qe = 1/ab + 1/ a Ce \qquad (2)$$

$$\text{Log } Qe = \log KF + \frac{1}{n} \log Ce \qquad (3)$$

Where (Ce) is the equilibrium concentration of drug in solution (mg/L) , (Qe) is the amount of drug sorbed per unit of sorbent (mg/g) , (a) is a constant related to the area occupied by mono- layer of sorbent, reflecting the sorption capacity (mg/g), (b) is a dried measure for the intensity of the sorption process (L/mg) , (K) and (n) constants peculiar to adsorbent and adsorbate were determined from the intercept and slope of Freundlich adsorption isotherm.

The (K) constant is concerned with the ability of the adsorbent to adsorb and the (n) – Constant is concerned with tendency of the adsorbate to be adsorbed. In order to prove the applicability of Freundlich isotherm as shown by the linear relationships of Logarithmic forms of Qe and Ce Figure (8). The R^2 Values computed by Linear regression for the two types of isotherms are presented in table (3) for the sorbent .

3.2 Effect of Temperature and Parameters Thermodynamic

The adsorption of DFH drug on bauxite clay surface at different temperatures has been carried out and shown in figures (5), (6) and (7). Variable temperature will help in evaluating the basic thermodynamically Functions (ΔH, ΔG, ΔS) of the adsorption process.

Adsorption of DFH on bauxite used in this work increases with increasing temperature.

To calculate the heat of adsorption (ΔH) we used the following equation

$$\ln X_m = -\frac{\Delta H}{RT} + \text{Constant} \qquad (4)$$

Where X_m is the maximum uptake of adsorption at certain Value of equilibrium concentration, (Ce) that was fixed for all temperature of the study. The change in free energy (ΔG) could be determined from the equation :

$$\Delta G = -RT\ln K^{-} \qquad (5)$$

Where (R) is the gas constant (8.314 $J.Mol^{-1}.deg^{-1}$) .

(T) is the absolute temperature, and (K^{-}) is the equilibrium constant for the adsorption at certain value of equilibrium [10]. The change in entropy (ΔS) was calculated from Gibbs equation[11].

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

Table (4) shows the basic thermodynamic values of adsorption of the drug on bauxite used in this study. Thermodynamic equation showed endothermic heat of adsorption accompanied with increase in entropy. The change in free energy (ΔG) of the adsorption process was found to posses negative values indicating a spontaneous adsorption process.

3.3 Effect of pH

The adsorption of drug from aqueous solution is highly dependent on the pH of solution which affects the surface charge of the adsorbent, and the degree of ionization and speciation of the adsorbate species [12].

Hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M) were used to adjust the acidity of the drug solution that are taken orally are retained for some time prior and shaking at (37.5º C) (body temperature). Figure (9) table (5) demonstrates the influence of pH on the adsorption uptake on fixed drug concentration (100 mg/L) by bauxite used at (37.5º C). The adsorption of DFH on bauxite increased with increasing pH of the solution. At low pH, a competition exerted by the hydronium ions is expected to cause a significant reduction in adsorption of the drug In addition, the solubility of the adsorbate (drug) may be affected by the change of the pH value causing an increase in adsorption affinity towards the surface. Moreover, the increase in adsorption uptake of the drug with increasing pH value could be attributed to the possible changes in properties of the surface [13].

3.4 Effect of additives

The effect of additives on adsorption uptake of DFH on bauxite surface was studied at variable concentration of sucrose (0.1 0.2 and 0.3M). The increasing of concentration of sucrose in the solution causes decrease in the adsorption of DFH drug on the clay surface at pH 5.2 and 37.5 ºC. This behavior may be due to the inhibition effect of sucrose used on adsorption extent. Thus, the molecules of sucrose will compete drug molecules for the active sites which could be found on the surface. Moreover, the attraction between the sucrose molecules and the surface is greater than that attraction between the drug molecules and the surface, therefore, will leads to decrease in the adsorption extent. These results agreed with the earlier investigation [14]

3.5 Effect of Adsorbent Weight

The dependence of adsorption of the drug on the amount of bauxite was studied by varying the adsorbent dose from (0.1 to 1g) at temperature (37.5 ºC) pH (5.2) and fixed concentration (100 mg/L). The results are given in table(7) and figure(11). The figure indicates that adsorption increased with increasing sorbent dose due to greater availability of the exchangeable sites or surface area.

3.6 Effect of Particle Size

The effect of particle size of adsorbents on the adsorption of DFH was studied at fixed concentration of the adsorbate (100 mg/L) and fixed weight of the adsorbents. Table (8) and figure (12) represents the variation in Qe values with the particle size of the adsorbent. The Data indicates that the adsorption of drug increased with decreasing the surface area of the adsorbent. These results are in an agreement with other studies [15].

4. Conclusion:-

It is found that the contact time for the maximum adsorption of the drug on bauxite clay surface was 50 minutes ,and the adsorption isotherm of the drug under study on bauxite obeyed Freundlich isotherm as the adsorption increases with increasing the concentration at equilibrium. This result indicated the surface heterogeneity leading to different adsorption force from site and different affinities toward drug molecule .The adsorption capacity of the clay was found decrease as the sucrose concentration of solution increased. The thermodynamic study of this work relieved that the adsorption of this drug was found to exhibit an endothermic process on the clay surface. The adsorption capacity of DFH on bauxite increases as the pH increases. The adsorption of DFH increases with adsorbent's quantity increasing than stable at fixed rang. The adsorption of DFH increases as the surface area decreases.

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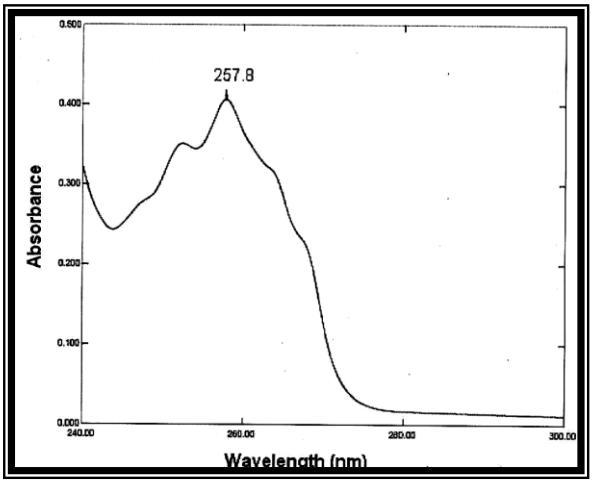

Fig.(2):UV/Visible scanning spectrum of diphenhydramine hydrochloride

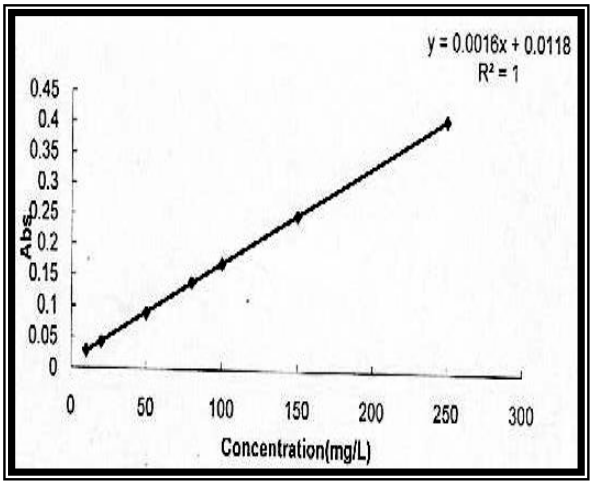

Fig .(3):Calibration Curve of diphenhydramine hydrochloride

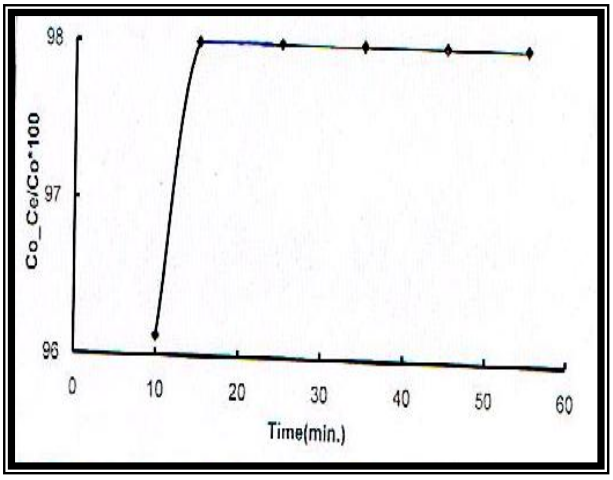

Fig.(4):Effect of contact time on adsorption uptake of DFH on bauxite (Co=100mg/L)

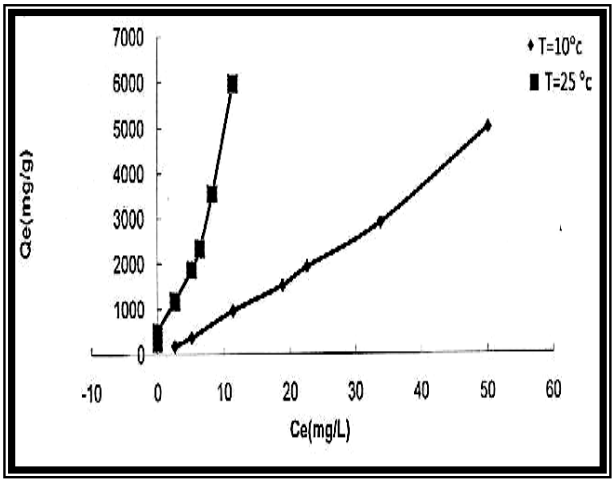

Fig.(5):Adsorption isotherms of DFH bauxite at pH=5.2

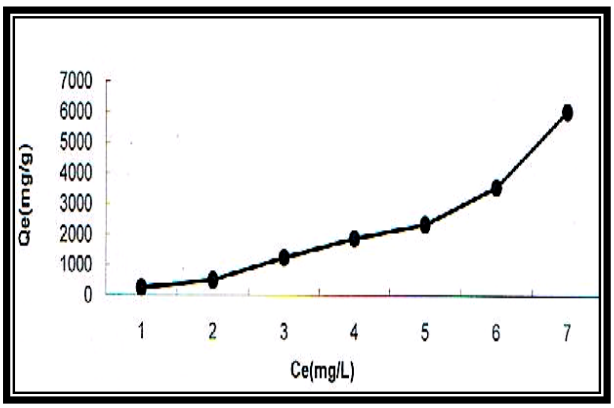

Fig.(6) Adsorption isotherm of DFH on bauxite at T=37.5°C and pH=5.2

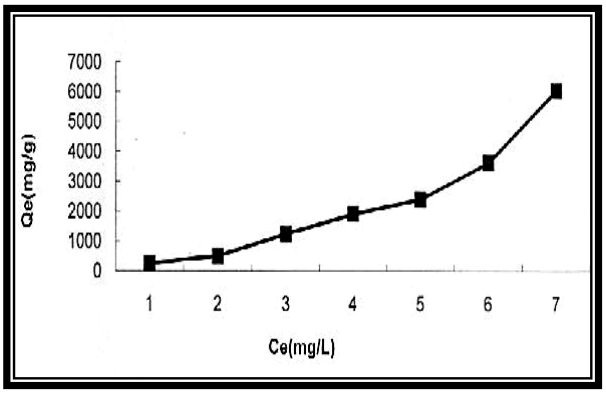

Fig.(7): Adsorption isotherm of DFH on bauxite at T=45°C and pH=5.2

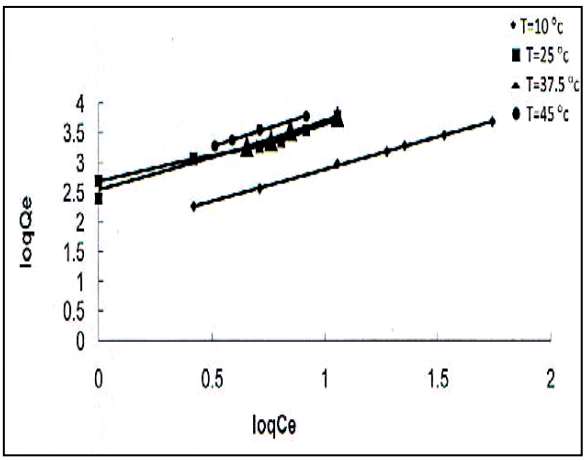

Fig.(8):Freundlich lines of the adsorption of DFH on bauxite

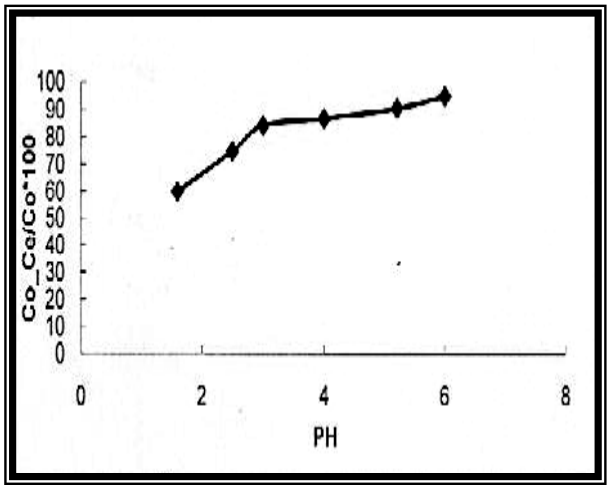

Fig.(9):Effect of PH on adsorption uptake of DFH on bauxite (Co= 100mg/L)

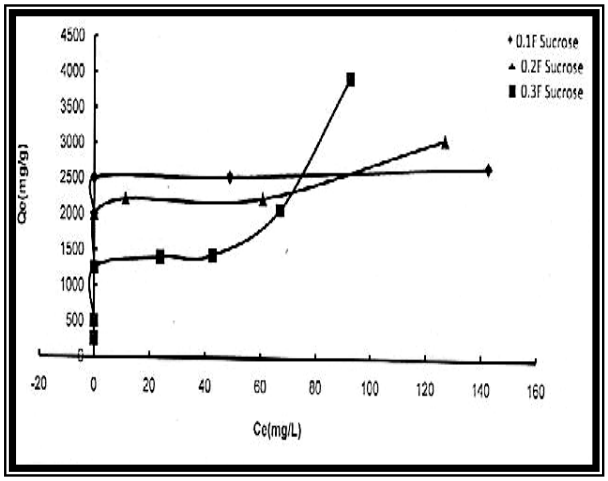

Fig.(10): The adsorption isotherms of DFH on bauxite with different concentration of sucrose (0.1 , 0.2 and 0.3M)

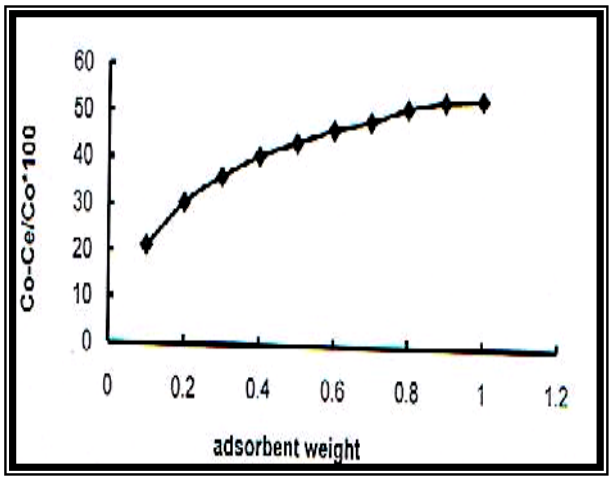

Fig.(11):Effect of weight of clay on adsorption uptake (percentage of removal) of DFH on bauxite (Co= 100mg/L)

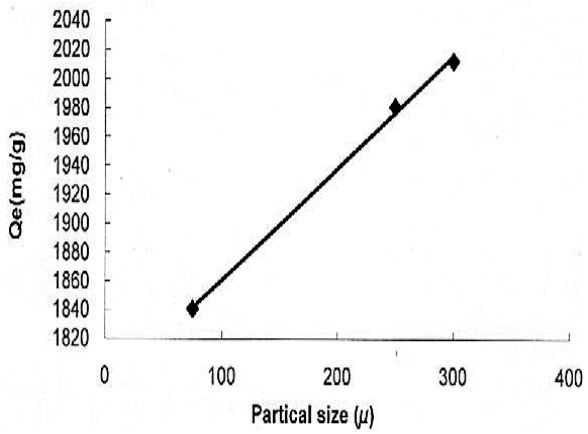

Fig.(12):The effect of particle size uptake on bauxite of DFH

Table (1) : Effect of contact time on adsorption of DFH on bauxite

Time (min.)	**Ce (mg/L)**	**Co – Ce/Co × 100**
10	3.875	96.125
15	2	98
25	2	98
35	2	98
45	2	98
55	2	98

Table (2) : Effect of temperature on adsorption uptake of DFH on bauxite

10 ^{0}C			**25^{0}C**		**37.5 ºC**		**45 ºC**	
Co (mg/L)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)
10	2.625	184.375	0	250	0	250	0	250
20	5.125	371.875	0	500	0	500	0	500
50	11.375	965.625	2.625	1184.375	0	1250	0	1250
80	18.875	1528.125	5.125	1871.875	4.5	1887.5	3.25	1918.75
100	22.625	1934.375	6.375	2340.625	5.75	2356.25	3.875	2403.125
150	33.875	2903.125	8.25	3543.75	7.000	3575	5.125	3621.875
250	55.125	4871.875	11.375	5965.625	11.375	5965.625	8.25	6043.75

Table (3): Constant of a Freundlich equation

Temperature	**Kf**	**1/n**	**R^2**	**R^2(Langmuir)**
10	1.0783	1.8176	0.9992	0.6422
25	1.0972	2.5502	0.9560	0.1432
37.5	1.2766	2.4366	0.9814	0.5887
45	1.2377	2.6575	0.9949	0.5734

Table (4) : Calculated thermodynamic parameters of DFH adsorption n clay surface (37.5 ^{0}C)

H (KJ.mole $^{-1}$) Δ	**G(KJ.mole $^{-1}$) Δ**	**S (J. mol^{-1}. K^{-1}) Δ**
0.1361	-7.6753	25.1577

Table (5) : The effect of pH on adsorption on uptake of DFH on bauxite

pH	**Ce(mg/L)**	**Co – Ce / Co *100**
1.6	40.125	59.875
2.5	43.875	74.875
3	15.75	84.25
4	13.25	86.75
5.2	9.5	90.5
6	5.125	94.875

Table (6) :The adsorption Values of DFH on bauxite surface with different Concentration of sucrose

Without sucrose		**0.1 M**		**0.2 M**		**0.3 M**	
Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)
0	250	0	250	0	250	0	250
0	500	0	500	0	500	0	500
0	1250	0	1250	0	1250	0	1250
4.5	1887.5	0	2000	0	2000	28.875	1403.125
5.75	2356.25	0	2500	11.375	2215	42.625	1434.375
7	3575	48.875	2528.125	60.75	2231.25	67	2075
8.25	6043.75	142.625	2684.375	127	3075	72	4450

Table (7) : Effect of weight on clay on adsorption uptake (percentage of removal) of DFH on bauxite

Adsorbent W. (g)	**Ce (mg/L)**	**Co – Ce/ Co *100**
0.1	393.75	21.25
0.2	347.5	30.5
0.3	344.375	36.125
0.4	312.5	40.625
0.5	291.875	43.625
0.6	267.5	46.5
0.7	263.125	48.375
0.8	243.75	51.25
0.9	236.25	52.75
1.0	233.75	53.25

Table (8) : The effect of particle size on adsorption uptake DFH on bauxite

Particle (µm)	**Qe (mg/g)**
75	1840.625
250	1981.25
300	2012.5

دراسة أمتزاز ثنائي فنيل هايدرامين هايدروكلورايد على سطح البوكسايت ا لعراقي

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***قسم الكيمياء – كلية التربية – ابن الهيثم – جامعة بغداد –العراق**

كلمات مفتاحية : أمتزاز ثنائي فنيل هايدرامين,هيدروكلوريك, بوكسايت

الخلاصة:-

ان زيادة جرعة الدواء و سميته من المشاكل الطبية الشائعة وقد تحدث مع ثنائي فنيل هيدرامين هيدروكـــــــــلورايد (DFH) لذلك اصبح من الضروري دراسة امتزاز هذا المركب على ســـطح دوائي و الذي يمكن ان يكون مضاد حيوي في الحالات الطارئة لمعالجة جرعة الدواء الزائدة او حالات التسمم عند حدوثها.

ان معدل ومدى امتزاز(DFH) قد تم بحثه بوساطة مطيافية الاشعة المرئية–فوق البنفسجية وكذلك تم دراسة تأثير درجة الحرارة والدالة الحامضية ودراسة وجود السكروز كمادة مضافة وتاثيرها فـــى سعة الامتزاز على سطح دوائي و تحديدا البوكسايت وقد تم تعيين الزمن اللازم لحدوث الاتزان علـــى سطح الطين المستخدم و دراسة ايزوثرمات الامتزاز و وجد انها تطابق انموذج فريندلش. واظهـــرت النتائج المستحصلة ان العملية ماصة للحرارة وان افضل قيمة ل(pH)يحصل عندها الامتزاز هـــي (6) . واكدت الدراسة ان البوكسايت هو سطح ماز جيد لمعالجة حالات التسمم بالدواء او في حالـــة تناوله بجرعات عالية .