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ADSORPTIVE REMOVAL OF AMPICILLIN FROM AQUEOUS SOLUTION BY USING MAGNESIUM OXIDE

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ABSTRACT:

In this research the effect of various experimental factors on adsorption of ampicillin onto magnesium oxide as shaking times, adsorbent dosage, initial ampicillin concentraion and pH were studied at room temperture. The adsoprtion data was fitted to the Freundlish isotherm than Langumair isotherm and the corresponding parameters were calculated. Three kinetic models, namely pseudo first order, pseudo second order and intra-particle diffusion models were selected to analyse the adsorption process. The results indicated that the adsorption followed a pseudo second order and confirms that adsorption of ampicillin on magnesium oxide was a multistep process.

INTRODUCTION:

The β-lactam antibiotics have been reported to account for over 65% of the world antibiotic market[1]. Ampicillin is one of this antibiotics group, and can be introduced into liquid wastes from different sources hospitals, pharmaceutical products and homes, considering the general contribution of hospitals to municipal waste waters. In general the antibiotics are poorly absorbed by the human body, and thus are excreted either unchanged or transformed, via urine and faces and reached the surface water and groundwater[2]. When antibiotics get into the arable land, they could possibly impact vegetation growth and development as well as soil microbial activity[3]. It was found that the bacteria isolated from sewage bioreactors have been shown to exhibit resistance to some antibiotics including erythromycin, tetracycline, ciprofloxacin and ampicillin[4], and the highest environmental risk patterns were assessed for ampicillin[5].

The removal of antibiotics from wastewater is one of the most important environmental issues to be solved today, various treatment techniques and processes have been used to remove pollutants from contaminated water. Among all the approaches proposed, adsorption is one of the most popular methods and is currently considered as effective, efficient and economic method for water purification[6]. A survey of literature revealed that metal oxides as other adsorbents (activated charcoal, clays

and zeolites) in natural materials or synthesis materials are widely used as adsorbents due to their adsorptive efficiencies or reactive surfaces sufficiently favorable for adsorbing toxic metals,[7-10] bacteria[11] and organic pollutants[12-16] from contaminated water.

Magnesium oxide occurs in two types of oxides, the two oxides differ from one another in density. Both are practically insoluble in water and alcohol but soluble in dilute acids. In the presence of water the oxide is converted to the hydroxide, and therefore, the chemistry and pharmacology are the same as those of magnesium hydroxide[17].

Magnesium oxide is an important material for various applications including catalysis[18] aste remediation, chemisorbent and as antibacterial agent[19,20]. Magnesium oxide can be regarded as a good adsorbent[21] due to its high adsorption capacity, non-toxic in nature, limited solubility in water, high concentration of low-coordinated sites and structural defects on the surface[22].

So the aim of the present study is to study the kinetics and equilibrium states of adsorption of ampicillin (Fig. 1) on magnesium oxide. A systematic study is conducted in order to observe the effect of contact time, adsorbent dose, adsorbate concentration and pH on the adsorption process.

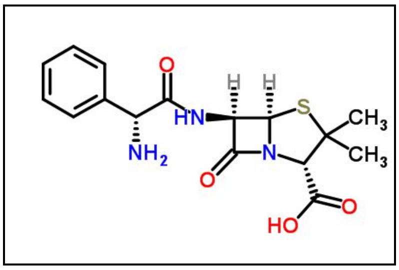

Fig. 1: structure of ampicillin

MATERIALS AND METHODS:

1-Materials:

All chemicals used in this study were used as received without further purification. The following chemicals were used: pure ampicillins, sodium phosphate dibasic and magnesium oxide and were supplied by Loba Company. Hydrochloric acid, sodium hydroxide and potassium phosphate monobasic were purchased from (Sigma–Aldrich).

2-Equipment:

UV-2100 Spectrophotometer Unicom™ with 1 cm quartz cell was used for ampicillin analysis. The pH measurements have been performed with pH/cond level-1and the meter was standardised by using buffer solutions of pH 4 & 9. A magnetic stirrer and a mechanical shaker were also used.

3-Preparation of Adsorbate solution:

The stock solution of pure Ampicillin was prepared at room temperature by dissolving 1 g in one liter of distilled water by the help of magnetic stirrer.

A calibration curve of absorbance against ampicillin concentrations was obtained by using standard ampicillin of known concentrations.

The initial and final concentrations of ampicillin were determined by measuring the absorbance at 256 nm[23].

4-Preparation of Buffer solutions:

The buffer solutions were prepared and the pH of buffer solution measured by pH meter and adjusted by addition of sodium hydroxide or hydrochloric acid if required.

pH (1.2): 4.55 ml hydrochloric acid of analytical grade (11 moles/dm^3) was taken in 500 ml volumetric flask and 1.0g of sodium chloride added. The volume was made up to the mark with distilled water.

pH (4): 5.04 grams of disodium hydrogen orthophosphate and 3.01 g of potassium dihydrogen orthophosphate were dissolved in water to produce 1000 ml.

pH (7.5): 0.6 grams of potassium dihydrogen orthophosphate, 6.4 grams of disodium hydrogen orthophosphate and 5.85 grams sodium chloride were dissolved in sufficient amount of distilled water to produce 1000 ml.

pH (9): 17.4 grams of potassium dihydrogen orthophosphate were dissolved in 800 ml of water and the pH was adjusted if necessary with 1 moles/dm^3 sodium hydroxide and diluted to 1000 ml with water.

5-Adsorption experiments:

Adsorption equilibrium experiments were carried out by adding adsorbent 2.5 g to 50 ml ampicillin solution with the desired concentration and pH at room temperature using a shaker at 200 rpm. After the equilibrium time the suspension was filtered and the final concentration of ampicillin was measured. The percent adsorption calculated by the below equation (1):

$$\text{Percentage Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \quad ..(1)$$

The amount of ampicillin adsorbed onto magnesium oxide, q_e (mg/gm), was calculated by the following relation:

$$q_e = \frac{(C_o - C_e)\,V}{W} \quad \ldots\ldots\ldots (2)$$

where C_o and C_e are the initial and equilibrium liquid-phase concentrations of ampicillin respectively (mg/L). V the volume of the solution (L) and W the weight of the magnesium oxide used (g/L).

The procedure of kinetic experiments was basically identical to those of the equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of ampicillin were similarly measured.

RESULTS AND DISCUSSION:

1-Effect of contact time:

The experiments were carried out to determine the equilibrium time of ampicillin removal for the initial concentrations 200 and 400 mg/L respectively at time intervals ranging from 30-150 minutes using 2.5 g of magnesium oxide and 200 rpm. The results are cleared in Fig. (2) and the optimum shaking time were

found to be two hours, which were used for all further adsorption studies.

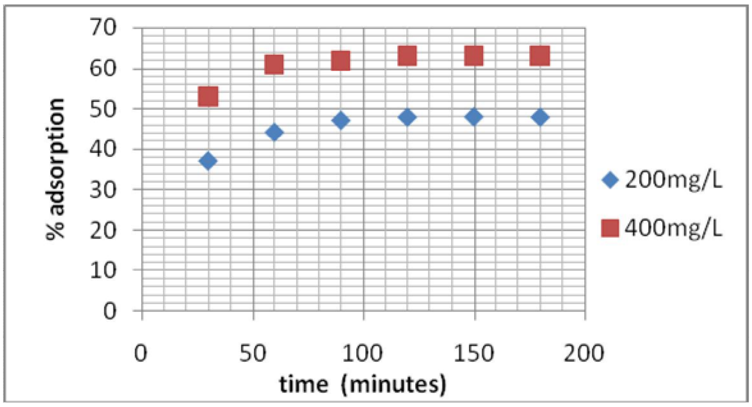

Fig. 2: Effect of contact time on adsorption
(Magnesium oxide 2.5 g, 200 mg/L ampicillin and 400 mg/L ampicillin)

2-Effect of adsorbent dose:

The experiments were performed to find out the optimal dosage of adsorbent for adsorption of ampicillin from the aqueous solutions. The manganese oxide dose was varied from 0.5-2.5 g/50 ml and equilibrated for 2 hours at an initial concentration of 400 mg/L. The adsorption percentage increases upon increasing adsorbent doses. The results given in Fig. (3) indicate that the optimum adsorption occurs at a dose of 2.5 g magnesium oxide.

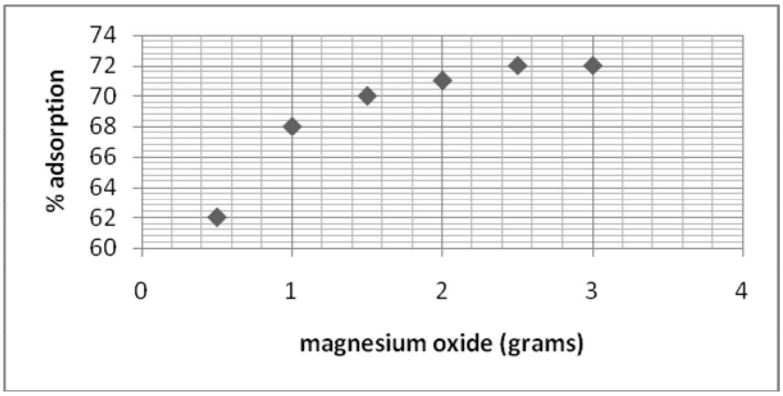

Fig. 3: Effect of magnesium oxide dose on adsorption
(Ampicillin 400mg/L, contact time 2 hrs)

3-Effect of initial concentration:

The effect of initial ampicillin concentration in the range 100-800 mg/L on the adsorption was studied. The experiments were carried out at a contact time 2 hrs., 2.5 g of magnesium oxide at 200 rpm. The results

revealed that the amount adsorbed increases when the adsorbent mass increases. The graph in the Fig. (4) shows that the optimum adsorption occurs at 400 mg/L of ampicillin.

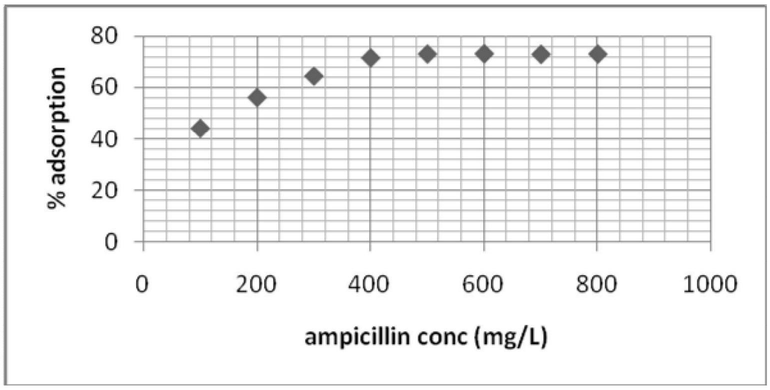

Fig. 4: Effect of ampicillin initial concentrations on adsorption (magnesium oxide 2.5 g, contact time 2 hrs)

4-Effect of pH:

The effect of pH on the adsorption of ampicillin on magnesium oxide was investigated by varying pH values in the range 1.2-9 (simulated buffer solution) at different initial ampicillin concentrations (600-900 mg/L). The removal efficiency was found to be highly dependent on hydrogen ion concentration of solution. The effect of pH on adsorption efficiency is shown in Fig. (5) which also illustrates the decrease of adsorption as pH value increases.

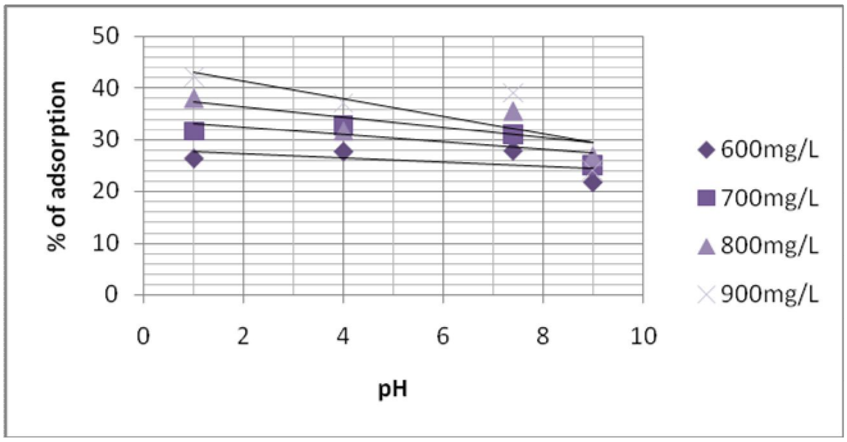

Fig. 5: Effect of pH on adsorption of ampicillin on magnesium oxide (Ampicillin 600, 700, 800 & 900 mg/L, magnesium oxide 2.5 g, contact time 3 hrs.)

5-Langmuir adsorption isotherm model:

Langmuir and Freundlish models were used for the desorption of the isotherms, the basic assumptions of both models are well known[24].

Langmuir adsorption model enables estimation of the maximum uptake values of the adsorbate. Langmuir model does not into take account the variation in adsorption energy, but it gives the simplest description of the

adsorption process. It is based on the physical hypothesis that the maximum adsorption capacity is related to a monolayer adsorption, that there is no interaction between adsorbed molecules, and that the adsorption energy is distributed homogeneously over the entire coverage surface[25]. The Langmuir isotherm is represented as:

$$q_e = \frac{(K_L\ b\ C_e)}{1+b\ C_e} \quad \text{............(3)}$$

where q_e (mg/g) and C_e (mg/L) are the amount adsorbed ampicillin per unit weight of adsorbent and unadsorbed ampicillin concentration in solution at equilibrium respectively. The K_L(L/g) and b_L (L/mg) are the Langmuir isotherm constants[26].

The Langmuir constants K_L and b_L are evaluated through linearization of equation (4):

$$\frac{C_e}{q_e} = \frac{C_e}{K_L} + \frac{1}{b\ K_L} \quad \text{...... (4)}$$

The adsorption data were analyzed according to the linear form of the Langmuir isotherm. The values of the Langmuir constants K_L and b_L with correlation coefficient are listed in Table (1) for ampicillin –magnesium oxide adsorption system and the Langmuir isotherm is plotted in Fig. (6).

To determine whether the adsorption process is favorable or unfavorable for Langmuir type adsorption process, this can be expressed in terms of a dimensional constant called separation factor R_L(also called equilibrium parameter) which is defined by the following equation:

$$R_L = \frac{1}{1+b\ C_o} \quad \text{.........(5)}$$

where C_o (mg/L) is the initial concentration and b_2 (L/mg) is the Langmuir constant related to the energy adsorption. The value of R_l indicates that the shape of that the isotherm for $0<R_L<1$, $R_L>1$, $R_L=1$ or $R_L=0$ is favorable, unfavorable, linear or irreversible, respectively. The calculated value of 0.169 indicated that adsorption is favorable for ampicillin.

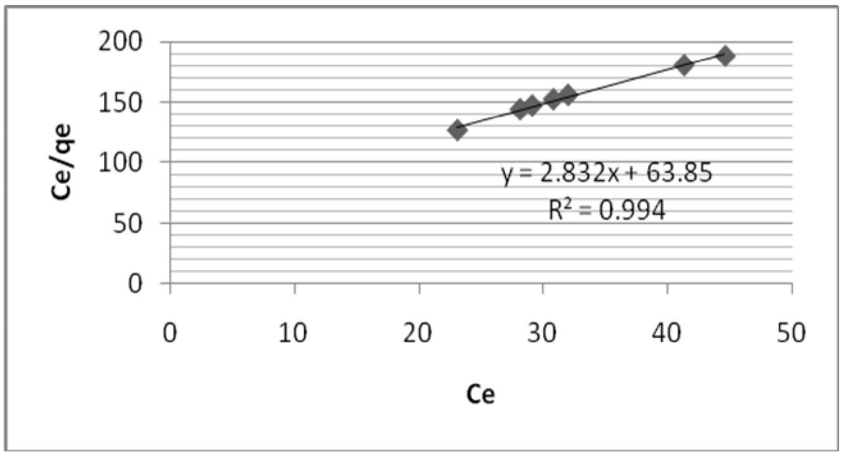

Fig. 6: Langmuir adsorption isotherm plot of ampicillin on magnesium oxide

6-Freundlich adsorption model isotherm:

Freundlich isotherm is an empirical equation employed to describe a heterogeneous adsorption surface and active site with different energy [26] and is expressed by the following equation:

$$q_e = K_f C_e^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(6)}$$

where K_F ($mgl^{-1}/nL/ng^{-1}$) is the Freundlich constant related to the bonding energy and n (g/L) is the heterogenity factor. A linear form of the Freundlish isotherm can be obtained by taking logarithms of equation (7):

$$\text{Log}(q_e) = \text{Log}(K_f) + \frac{1}{n}\text{Log}(C_e) \quad \ldots\ldots \text{(7)}$$

The validity of Freundlich model to fit the experimental data from the adsorption of ampicillin by magnesium oxide was examined. For this case the plot of log (C_e) versus log (q_e) was employed to generate the intercept value k_f and the slope n. The values of Freundlich constants together with the correlation coefficient are presented in Table (1) and the theoretical Freundlich equation is shown in Fig. (7).

The adsorption isotherms of ampicillinon magnesium oxide are shown in Figs. (6) and (7). The calculated values of constants in Langmuir and Freundlish equations and the regression coefficient (R^2) are given in the Table (1). Both models were found to be suitable for describing the adsorption of ampicillin by magnesium oxide.

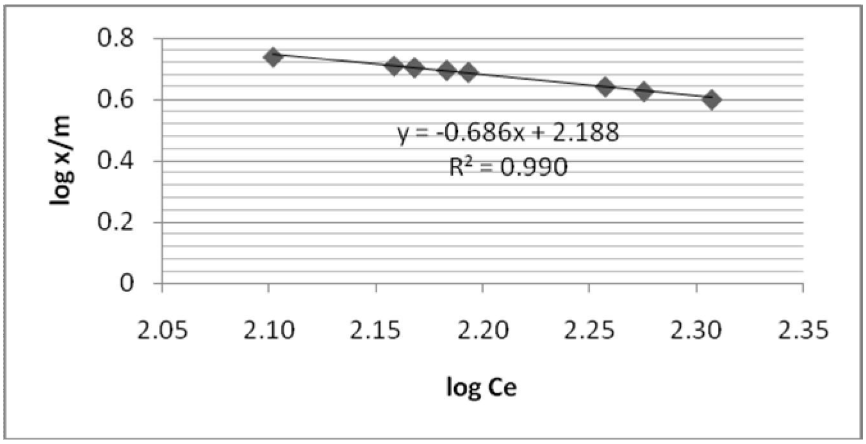

Fig. 7: Freundlich adsorption isotherm plot of ampicillin on magnesium oxide

Table 1 : Parameters of Langmuir and Freundlish isotherm models fitted on experimental data of adsorption of ampicillin on magnesium oxide

Langmuir isotherm			Freundlich isotherm		
b (L/g)	K_L(L/mg)	R^2	1/n	K_f (1/g)	R^2
0.0195	2.95	0.9504	1.486	194.98	0.9902

7-Kinetic model:

The adsorption kinetics of ampicillin-antacid may be described by pseudo first order and second order kinetic models. The pseudo first order Lagergren is based on adsorption capacity and considers that the rate of occupation of adsorption sites is proportional the number of unoccupied sites[27]. This model generally expressed as follows:

$$\frac{dq}{dt} = K_1 (q_e - q) \quad \ldots\ (8)$$

where K_1 is the rate constant of a first order adsorption.

After integration and applying boundary conditions=0, to t=t and q=0 to $q=q_{eq}$ the integrated form of equation (8) becomes:

$$Log(q_e - q) = Log(q_e) - \frac{K_1}{2.303} t \quad \ldots\ (9)$$

A straight line of log $(q_e\text{-}q)$ versus t suggests the applicability of this kinetic model, in order to fit equation (9) to the experimental data. The equilibrium adsorption capacity, q_e must be known to obtain a real equilibrium adsorption capacity, q_e by extrapolating the experimental data.

The value of K_1 was calculated from Fig. (8) of the plot of log $(q_e\text{-}q)$ versus t for different ampicillin concentrations. The experimental q_e value did not agree with the calculated ones obtained from linear plots and the correlation coefficient is lesser. This shows that the adsorption of ampicillin on magnesium oxide is not a first order, but it is best fit to the second order kinetic model.

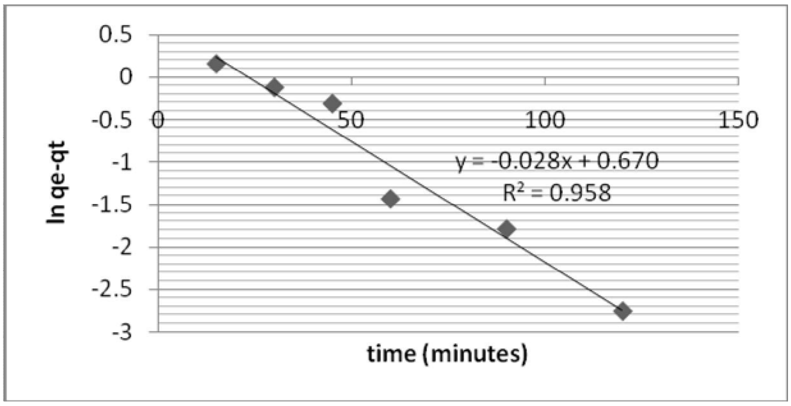

Fig 8: The pseudo-first order kinetic of ampicillin on magnesium oxide

The pseudo-second order equation is also based on the adsorption capacity of the solid phase and it's expressed as:

$$\frac{dq}{dt} = K_2 (q_e - q)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

The integrated form of equation (11) becomes:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad \ldots\ldots\ldots\ldots\ldots (11)$$

If second-order kinetic is applicable, the plot of t/q against t should give a linear relation from which q_e and K_2 can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand and the equilibrium adsorption concentration q_e can be calculated from equation (11). Values of K_2 and q_e were calculated from the slope and intercept of Fig. (9).

The linear plots show a good agreement between experimental and calculated q_e values mentioned in Table (2). The correlation coefficient for the second order shows a high value, indicating that the adsorption of ampicillin onto magnesium oxide follows a second order model.

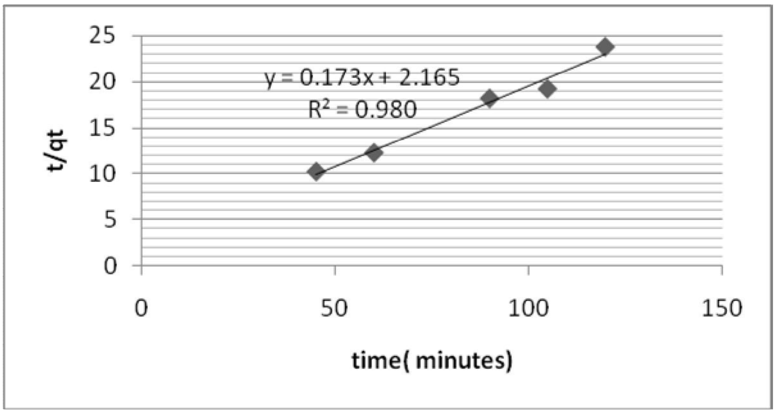

Fig. 9: Pseudo-second order plot for kinetic of ampicillin on magnesium oxide

Table 2: Comparison of the first and second order adsorption rate constants and experimental q_e values

Pseudo-first order kinetic model			pseudo-second order kinetic model			
K_1 (1/min)	q_e (cal) (mg/g)	R^2	K_2 (g/mg.min)	q_e (cal) (mg/g)	R^2	q_e(exp) (mg/g)
0.028	1.786	0.9586	0.0123	5.694	0.9806	5.16

Because the two simplified kinetic models including pseudo-first order and pseudo-second order equations are not sufficient to identify the adsorption mechanisms, the intra-particle diffusion model is used to elucidate the adsorption mechanism in this work. According to Weber and Morris for most adsorption process[28,29], the uptake is proportional to $t^{0.5}$ rather to contact time which can be represented as follows:

$$q_t = K_d t^{0.5} + C \quad \text{....... (12)}$$

where q_t is the amount adsorbed at time t and $t^{0.5}$ is the square root of time and K_d (milligram per gram minute $^{0.5}$) is the rate constant of intra-particle diffusion determined from the linear plot of q_t versus $t^{0.5}$ and C is related to the boundary layer thickness.

If the intra-particle diffusion is involved in the adsorption process, then the plot of the square root of time versus uptake would result in a linear relationship and the particle diffusion would be the controlling step, if this line passes through the origin.

When the plot does not pass through the origin, this would indicate some degree of boundary layer control and reveal that the intra-particle diffusion is not the only rate-controlling step, but also other processes may control the rate of adsorption, all of which may be operating simultaneously.

It can be understood from Fig. (10) that the intra-particle diffusion is not the rate controlling step. Other processes may control the rate of adsorption of ampicillin on magnesium oxide. The linear portion of curve between of q_t versus $t^{0.5}$ does not pass through the origin and the correlation coefficient is 0.9486.

The intercept of the plot reflects the boundary layer effect. The larger the intercept as shown in the Fig. (10), the greater is the contribution of the surface sorption in the rate determining step. This also confirms that adsorption of ampicillin on magnesium oxide was a multistep process, involving adsorption on the external surface and diffusion into the interior.

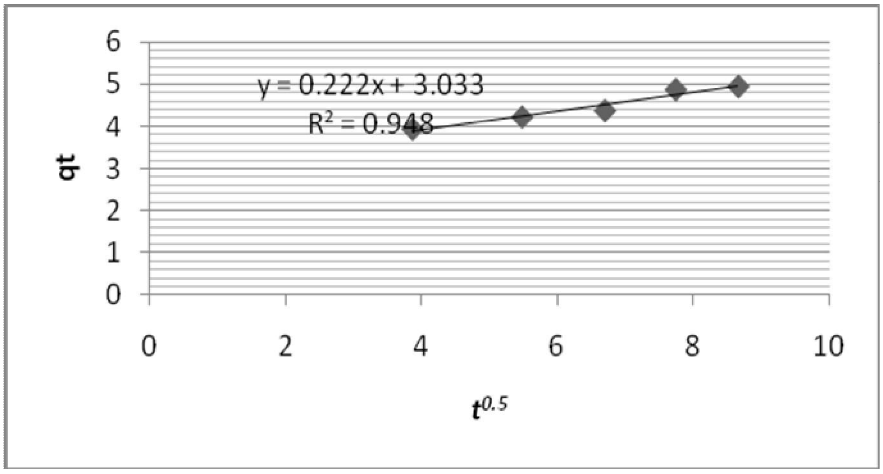

Fig 10: A plot of the intra-particle diffusion equation for adsorption of ampicillin on magnesium oxide

CONCLUSIONS:

In the following are the conclusion remarks on the above results:

1-The adsorption of ampicillin increased with increasing contact time and become almost constant after two hours.

2-The adsorbed amount of ampicillin decreased with increasing the pH.

3-The dimensionless separation factor showed that the magnesium oxide can effectively be used for removal of ampicillin from aqueous solution.

4-The experimental data correlated reasonably well with the Freundlich adsorption isotherm.

5-The adsorption process follows a second order model indicating that the rate limiting step may be a chemical adsorption or chemisorption involving valence forces through sharing or exchange of electrons between adsorbate and adsorbent.

6-The intra-particle diffusion equation revealed that adsorption of ampicillin on magnesium oxide was a multistep process.

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الأزالة الادمصاصية للأمبيسيليـن من الوسط المائي بواسطة أكسيد المغنسيوم

عبد الرحمن علوي بن يحيى

مركز دراسات وعلوم البيئة – جامعة عدن - اليمن

تم في هذا البحث دراسة تأثير العوامل المختلفة مثل: زمن الاحتكاك، جرعة أكسيد المغنسيوم، التركيز الأولى للأمبيسيلين ودرجة الحموضة على أدمصاص الأمبيسيلين باستخدام أكسيد المغنسيوم عند درجة حرارة الغرفة. وأظهرت النتائج أن الأزالة الادمصاصية تتبع نموذج معادلة فريندلش أكثر من نموذج لانجمير، كما تم دراسة حركية الادمصاص بواسطة معادلات الرتبة الأولى والرتبة الثانية ومعادلة الانتشار البيني للجسيمات، ومن النتائج وجد أن عملية الامصاص تتبع الرتبة الثانية و العملية ذات خطوات متعددة.