Kinetic study of copper and cadmium removal by soil-calcium alginate composite

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The investigation of possible use of soil-calcium alginate composite in the removal of Cu^{2+} and Cd^{2+} ions from aqueous solutions without and with NaCl was studied. Batch adsorption experiments were performed in order to evaluate the removal efficiency of the prepared composite. The parameters studied include contact time at three temperatures (30,45&55°c), the contact time necessary to attain equilibrium was found to be two hours. The effect of wetness or dryness of composite on the removal of Cu^{2+} ions and the effect of drying temperatures (30, 50&70°c) on the removal of Cd^{2+} ions were examined. In the batch kinetic study, the order of the reaction, the half-life, the rate constant for intraparticle diffusion and the pore diffusion coefficient were determined for both Cu^{2+} and Cd^{2+}.

تم دراسة إمكانية استخدام متراكب من التربة المصرية الجيرية و آلجينات الكالسيوم فى امتزاز بعض أيونات العناصر الثقيلة وهى النحاس و الكادميوم من المحاليل المائية وذلك فى وجود أو غياب ملح كلوريد الصوديوم.تم تقييم كفاءة عملية الامتزاز فى ثلاث درجات حرارة مختلفة وتم تحديد الوقت اللازم لحدوث الاتزان. كما تم دراسة تأثير وجود المتراكب فى صورة جافة أو مبتلة على عملية الامتزاز كما تم دراسة حركية عمليه الامتزاز لتحديد الخطوة المتحكمه فى عملية الامتزاز ثم رتبة التفاعل الحادث وكذلك تم تحديد ثابت التفاعل وفترة نصف العمر للتفاعل ومعدل الانتشار الثابت داخل الجزيئات وثابت الانتشار المسامى .و أظهرت النتائج أن المتراكب له كفاءة عالية لامتزاز عنصري النحاس والكادميوم.

Keywords: Calcium alginate, Soil, Adsorption, Heavy metals, Kinetics

1. Introduction

Heavy metals are nowadays among the most important pollutants in source and treated water, and are becoming a severe public health problem. Heavy metals removal from aqueous solutions has been commonly carried out by several processes; chemical precipitation, solvent extraction, ion-exchange, reverse osmosis or adsorption [1]. Among these processes, the adsorption with the selection of a suitable adsorbent could be an effective technique for the removal of heavy metals from wastewater. The suggested adsorbents are activated carbon, alumina, silica, ferric oxide, fly ash, and bentonite, which generally have high metal adsorption capacity, but they are expensive and most of them are difficult to be separated from the wastewater after use [2-10].

Soil has received particular attention as an economical adsorbent for removing heavy metals from wastewater due to its abundance and easy availability but it still difficult to be separated from the wastewater [11].

In order to over come the handling problem, Organic binding polymers for the granulation of soil have a number of advantages such as simplicity of preparation procedure and excellent physicochemical properties [12]. Alginic acid is a biopolymer having carboxyl groups capable of forming complexes with divalent cations such as Ca^{2+} and Ba^{2+}. Recently the gel forming property of this polymer has led to its extensive use in biomedicine and biotechnology industry to immobilize or encapsulate enzymes, subclleur organelles and living cells [13-14]. Thus the prominent immobilizing ability of alginic acid and alginates seems to be effective for the granulation of soil, and this new granulation method has a number of advantages such as simplicity for preparation, high content of active component (soil), high porosity, easy to be separated from the wastewater [12]. The objective of this study is to immobilize the soil

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into the porous matrices of alginate gel polymer in order to employ the granulated composite for the successive separation.

The present paper deal with the preparation procedure of soil alginate composite, to investigate the removal percentage of copper or cadmium ions at three different temperatures (30, 45 and 55°C). The kinetic study for the removal Cu^{2+} using wet and dry beads at 50°C as an adsorbent, and the kinetic study for the removal of Cd^{2+} using dry beads only at three different temperatures (30°C, 50°C & 70°C) as an adsorbent. The order of the reaction and the half-time, the rate constant for intraparticle diffusion, and pore diffusion coefficient were determined.

2. Material and methods

2.1. Soil

Calcareous soil samples were collected from the north western coast of Egypt. The soil samples were sieved to 45 micrometer size and dried at 110°C, pH :8.2 measured 1:2.5 soil: water suspension using *pH-meter* (Denver Instrument Co., U.S.A.) and % $CaCo_3$ 55.3 [15].

2.2. Granulation procedure of soil-calcium alginate composite (adsorbent)

Sodium alginate (NaALG) with a high viscosity (2% solution= 14000cP) was supplied from (Sigma-Aldrich company).

The preparation procedure for soil–calcium alginate composite (soil-CaALG) was carried out as follow:

A viscous NaALG weighted amount solution was dissolved in distilled water to form 1.25 wt% solutions; the soil was added to the alginate to form a mixture of 2.5:1 soil-alginate with good mixing by vigorous stirring. Here the mixing ratio was defined as mass (g) of soil to the mass (*g*) of NaALG. The formed mixture was added drop wise by prestetic pump at flow rate 0.5 ml/1 with tube 2.79mm internal diameter to 3% $CaCl_2$ with stirring at room temperature to form spherical shape after overnight standing. They were separated from calcium chloride solution, washed with

distilled water, dried at 50°c and finally stored in sealed vessel

2.3. Adsorbate solution

Stock solution (1000 mg l^{-1})of Cu^{2+} or Cd^{2+} was prepared by dissolving the desired quantity of $CuSO_4.5H_2O$ or $CdCl_2$ anhydrous (AR grade) in distilled water. In addition the desired quantity of $CuSO_4.5H_2O$ or $CdCl_2$ anhydrous (AR grade) in 0.05 M NaCl.

2.4. Kinetic studies

Adsorption kinetic studies for heavy metal ions were carried out by batch process with the aid of the PMC Hot Plate/Stirrer model 502 (Brunstead International Co., U.S.A.). 50 ml solution of 100 mg/l Cu^{2+} was added to 25 g wet composite or 2.8 g dry composite (dried at 50 °C) in a conical flask and the mixture was stirred at 250 rpm at three different temperatures (30, 45 and 55 °C) for a certain time. The solution is then separated from the adsorbent and the residual heavy metal concentration in solution was determined by "Atomic Absorption Spectrophotometer (Birken Elmer model GBC 902) (AAS).

For *Cd^{2+}* ions **:** 50 ml solution of 100 mg/l Cd^{2+} ions was added to 2.8 g dry composite dried at (30, 50 and 70 °C) in a conical flask and the mixture was stirred at 250 rpm at three different temperatures (30, 45 and 55°C) for a certain time. The solution is then separated from the adsorbent and the residual heavy metal ion concentration in solution was determined by AAS.

3. Results and discussion

3.1. Effect of time and electrolyte on the % removal

Figs. (1 and 2) represent the effect of time and electrolyte at three different temperature (30, 45 and 55°c) on the copper and cadmium ions removal from suspension. The plot reveals that the rate of copper or cadmium removal is higher at the beginning.

This could be due to the larger active surface area of the soil calcium alginate composite being available at the beginning of

the process. As the surface adsorption sites become limited, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [16]. Also the effect of form (wet or dry) of adsorbent on % removal of Cu^{2+} ions are shown in fig. (1 and 3), at the beginning, the percentage removal of copper by using the wet soil calcium alginate composite was higher than that using dry one at the same time and temperature. This is easy to explain since the dry beads need first to swell to enable the metal cations from reaching to the soil part of the composite which coated with the alginate and this consumes time. Indeed, the needed swelling here is not so high, so we still kept the advantages of constant flow rates of the effluent and avoiding the pressure drop problems. The presence of electrolyte decrease the adsorption of Cu^{2+} an Cd^{2+} in all cases studied due to the competition between Na^+ ion with Cu^{2+} or Cd^{2+} for adsorption sites[17-18]. Increasing the contact time between the adsorbent and the heavy metal ion solution increased the removal % at the same temperature.

3.2. Adsorption equilibrium time

Kinetic experiments were carried out to assess the desired time taken for equilibrium and the results are presented in figs. (1 and 2) for Cu^{2+} and Cd^{2+} with and without electrolyte. It is clear from the figures that significant removals of copper ions occurred with 30 min
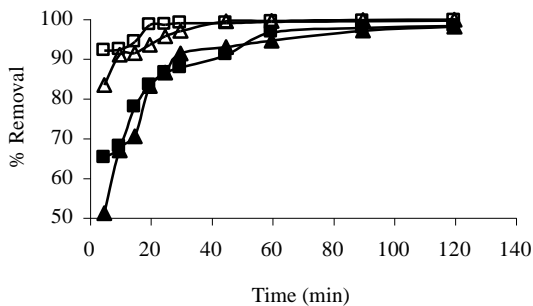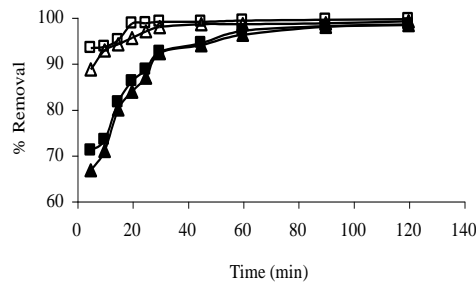

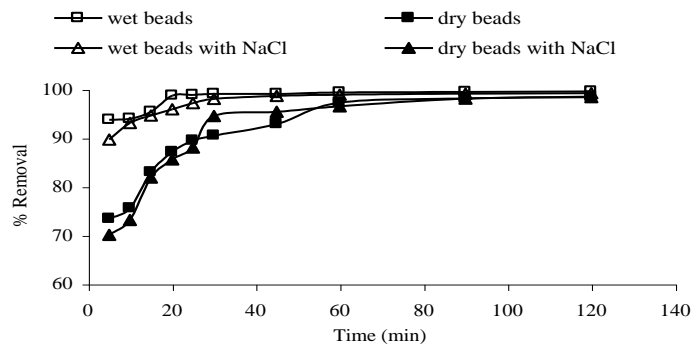Fig. 1-a. Cu^{2+} Removal at 30°C

Fig. 1-b. Cu^{2+} Removal at 45°C.

Fig. 1-c. Cu^{2+} Removal at 55°C.

Fig. 1. Effect of time on the % removal of Cu^{2+} ions from solution with wet and dry soil –calcium alginate composite at different temperatures with and without 0.05 M NaCl.(50 ml of 100 mg/l Cu^{2+} solution, 2.8 g dry composite or 25 g wet composite, 250 rpm and pH 8.2).
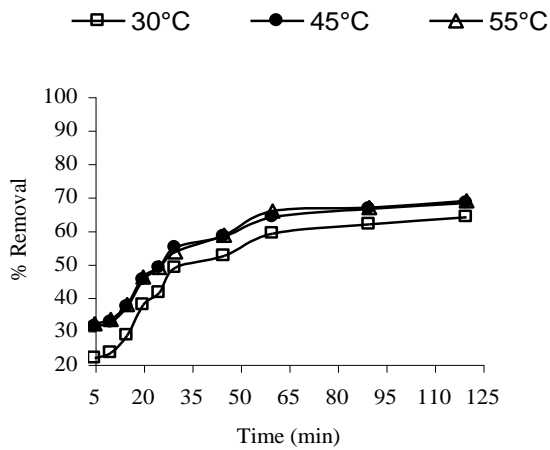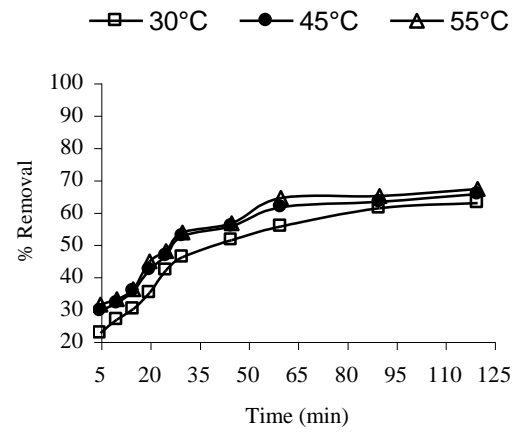
Fig. 2-a.1. beads dried at 30°C.

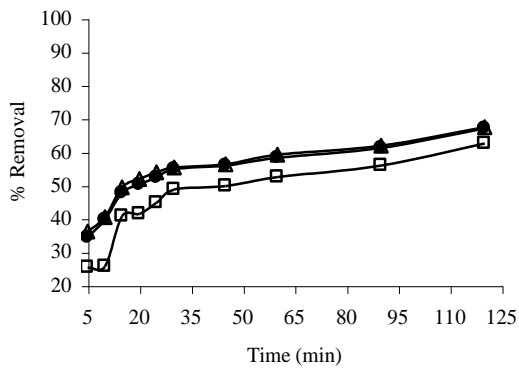Fig. 2-b.1 beads dried at 30°C with 0.05 NaCl.
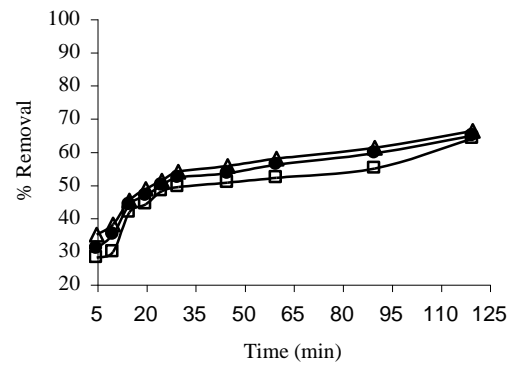

Fig. 2-a.2. beads dried at 50°C.
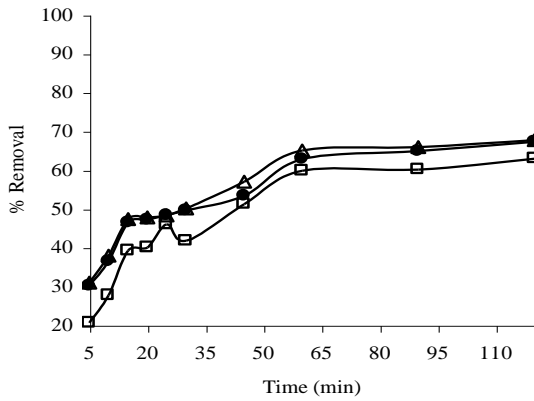

Fig. 2-b.2. beads dried at 50°C with 0.05 NaCl.
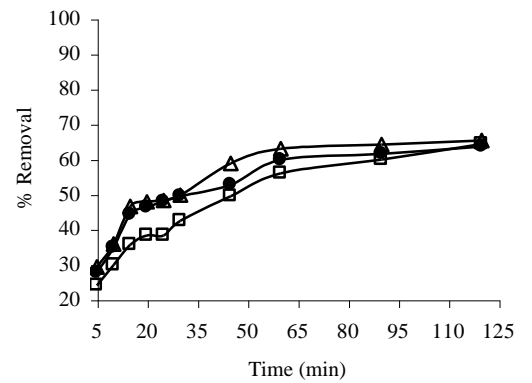

Fig. 2-a.3. beads dried at 70°C.

Fig. 2-b.3. beads dried at 70°C with 0.05 NaCL.

Fig. 2. Effect of time and temperature on the % removal of Cd^{2+} ions with and without 0.05M NaCl using soil-calcium alginate composite dried at different temperatures.(50 ml of 100 mg/l Cd^{+2} solution, 2.8 g composite, 250 rpm and pH 8.2).

and 45 min for cadmium ions from the stirring time and no appreciable changes in terms of removal were noticed after 2 hours. In all subsequent experiments showed that such equilibrium time was reached within 2 hr, which was considered as sufficient time for both of Cu^{2+} and Cd^{2+} ions removed by composite [19].

This could be due to the larger active surface area of the soil calcium alginate composite being available at the beginning of the process. As the surface adsorption sites become limited, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [16]. Also the effect of form (wet or dry) of adsorbent on % removal of Cu^{2+} ions are shown in fig. (1 and 3), at the beginning ,the percentage removal of copper by using the wet soil calcium alginate composite was higher than that using dry one at the same time and temperature. This is easy to explain since the dry beads need first to swell to enable the metal cations from reaching to the soil part of the composite which coated with the alginate and this consumes time. Indeed, the needed swelling here is not so high, so we still kept the advantages of constant flow rates of the effluent and avoiding the pressure drop problems. The presence of electrolyte decrease the adsorption of Cu^{2+} and Cd^{2+} in all cases studied due to the competition between Na^+ ion with Cu^{2+} or Cd^{2+} for adsorption sites[17-18]. Increasing the contact time between the adsorbent and the heavy metal ion solution increased the removal % at the same temperature.

3.2. Adsorption equilibrium time

Kinetic experiments were carried out to assess the desired time taken for equilibrium and the results are presented in figs. (1 and 2) for Cu^{2+} and Cd^{2+} with and without electrolyte. It is clear from the figures that significant removals of copper ions occurred with 30 min and 45 min for cadmium ions from the stirring time and no appreciable changes in terms of removal were noticed after 2 hours. In all subsequent experiments showed that such equilibrium time was reached within 2 hr,

which was considered as sufficient time for both of Cu^{2+} and Cd^{2+} ions removed by composite [19].

The adsorption of both metals on the soil-calcium alginate composite in this study can be considered as a fast process. This may be due to the high lime content. The lime content of the soil polymer composite seems to be an important parameter that would govern the use of soil polymer composite as an adsorbent, neutralizing agent for acidic wastewater and for the immobilization of heavy metals in a solid matrix, as lime plays an important role in the reaction leading to the formation of a solid matrix [4, 5, 19]. Furthermore, it is expected for the alginate to have a role in the removal of heavy metals since it has carboxylic groups in its structure [20]. The fact that the soil-alginate composite beads cross-linked overnight in calcium chloride cross-linker solution eliminate this possibility since most of the carboxylic groups have been incorporated in binding with calcium ions leading to cross-linking of the beads. Exchanging of calcium cations with copper or cadmium is not possible to be happen since it needs an acidic pH range from 1.5 to 5.0. The pH of the soil in these composites is 8.2 which is not in favor with the exchange process [20].

3.3. Effect of changing the solution temperature

Figs. 3 and 4 showed that, as the temperature of adsorption increased, Cd^{2+} removal increased which means that, adsorption favored at higher temperatures. For instance at 55°C, the maximum removal is reached faster than at 30°C under the same experimental conditions, which means an endothermic process tookplace. Higher rate of beads swelling could be the explaination of such behavior since the swelling increased as the temperature increased (the internal energy of the system increased) and hence facilate the diffusion of the cations solution to reach the pores inside the soil part of the composite. On the other hand, by increasing temperature of the solution, the kinetic energy of the system increased and consequently the rate of Cd^{2+} removal will increased.
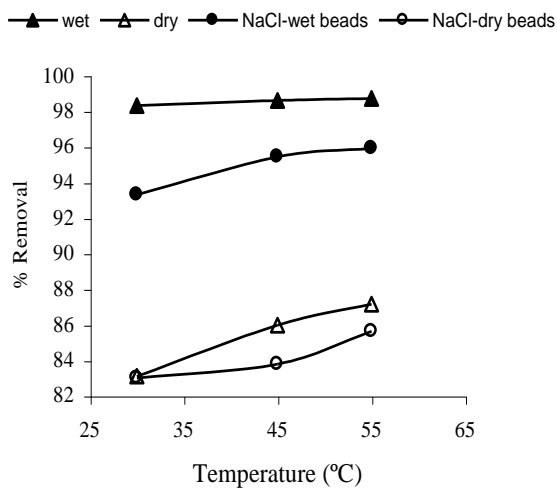
Fig.3. Effect of temperature on % removal of Cu^{2+} ions using dry or wet soil-calcium alginate composite with and without 0.05M NaCL. (50ml of 100mg/l solution, 2.8g dry composite or 25 g wet composite , 250 rpm, pH 8.2, time 20 min.).
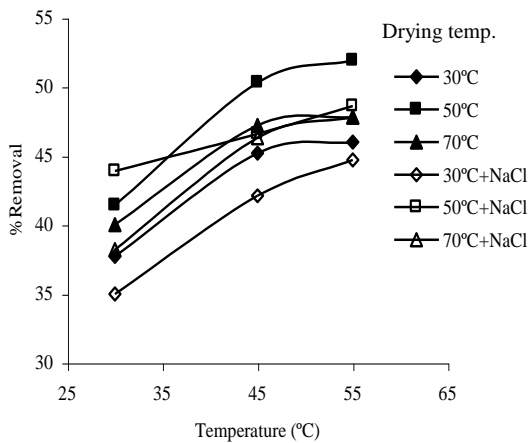

Fig. 4. Effect of temperature on % removal of Cd^{2+} ions at different drying temperatures for soil-calcium alginate composite with and without 0.05M NaCL. (50ml of 100mg/l solution, 2.8g dry composite , 250 rpm, pH 8.2, time 20 min.).

Studying the effect of the drying temperature of the composite beads on cadmium ions removal is presented in fig. 4. An interseting behavior has been observed,where the removal increased as the drying temperature increased and reached its maximum value at 50°C, then decreased at 70°C but still higher than that of 30°C. This phenomenon might be due to influence of drying temperature on the

drying rate and hence on the porossity of the resultant dry beads which is optimum at 50°C. Further increase in the drying tempera-ture, 70°C leads to higher rate of drying and more compact structure.

3.4. Adsorption dynamics

The two important aspects for parameter evaluation of the adsorption study are the ki-netic and the equilibria of adsorption. The adsorption of heavy metals from liquid phase to solid phase can be considered as a reversible reaction with an equilibrium being established between two phases [21].

3.4.1. Reaction rate

In a kinetic study of Cu^{2+} or Cd^{2+} adsorption on soil calcium alginate composite at different temperatures without and with electrolyte was investigated. A plot of (*log C*) against time (*t*) was applied up to 30 min for copper ions and 45 min for cadmium ions. The data gave straight lines, which indicated that the reaction was classified as first order [21]. In a first order reaction the rate is directly proportional to the concentration of the reacting substance. According to the first order eq. (1) the slope of the straight line is =-(K/2.303) and the intercept is (*log C_o*).

$$log\ C = -(K/2.303)\ t + log\ C_o. \tag{1}$$

Where, C_o is the initial concentration of heavy metal ion in solution (mg/L), C is residual concentration of heavy metal ion in solution after time '*t*' (mg/L), t is time (min) and K is the rate constant (min^{-1}).

From the slope of the straight lines obtained, the rate constants were calculated and tabulated in tables 1-4.

The K values indicated a preferential adsorption of Cu^{2+} on the soil calcium alginate composite as compared to Cd^{2+}.

3.4.2. Half- life (half- time)

For the first order reactions, it is commonly to use not only the rate constant (*K*) for the reaction but also the related quantity, the half-life or half-time. The half-time is the time taken by the reaction to reduce the initial concentration to half its

value i.e. ($C= \frac{1}{2} C_0$). The half time for Cu^{2+} and Cd^{2+} without and with electrolyte at different temperatures and different conditions of adsorbent surfaces is calculated according to the following eq. (2) and are tabulated in tables (1-4).

$$t_{1/2} = 0.693/K \qquad . \qquad (2)$$

the half – time of Cd^{2+} is much longer than that of Cu^{2+}, this could be attributed to the relation between the ionic radii and the pore size of adsorbent. The ionic radius of copper is smaller than that of cadmium therefore they are easily to be adsorbed by adsorbent.

The half – time of both Cd^{2+} and Cu^{2+} with and without electrolyte decreased, as adsorption temperature increased. The result revealed that by using dry composite as adsorbent the half – time of Cu^{2+} with and without electrolyte was longer than that of wet composite. The half – time of Cd^{2+} with electrolyte was much longer than that of Cd^{2+} without electrolyte for the adsorbent drying at 30, 50 and 70 ℃. The half – time of Cd^{2+} with and without electrolyte increased as the drying temperature of composite increased.

3.4.3. Intraparticle diffusion

It is necessary to study the kinetics of adsorption in batch systems in order to determine the rate-limiting step in the adsorption process. The overall adsorption process is assumed to occur by the following three steps [22]:
1. Mass-transfer of adsorbate (Cu^{2+} or Cd^{2+}) from the bulk solution to the particle surface (external mass transfer);
2. Adsorption of an interior site;
3. Intraparticle diffusion of adsorbate (Cu^{2+} or Cd^{2+}) via either a pore diffusion, or a homogeneous solid-phase diffusion.

During the establishment of the rate-limiting step, step (2) is assumed to be rapid and hence not considered in any kinetic analysis. Consequently, the two possible rate-limiting steps considered are external mass transfer and intraparticle diffusion. The effect of intraparticle diffusion on adsorption can be assessed by a plot q_t versus square root of time($t^{0.5}$) where, q_t is solid-phase concentration (mg g^{-1}) at time t (min). Several investigators

have been reported good linearization of adsorption data for a porous adsorbent by plotting q_t versus $t^{0.5}$ [23].

The plot of q_t versus $t^{0.5}$ has a characteristic shape the initial curved portion due to external-mass transport effects, followed by the effect of intraparticle diffusion (linear portion). This is followed by a decreased rate of diffusion, which is observed as a curved portion, leading eventually to an equilibrium plateau.

The slope of the linear portion (K_{ad}) has dimensions of mass of solute adsorbed per unit mass of adsorbent per square root of time (mg Cu^{2+} / g adsorbent.min$^{0.5}$). These units are not the usual dimensions for a rate constant of a typical chemical reaction. Several investigators have been described this slope as a "relative rate constant" [24]. This approach is conceptually incorrect. A better approach is to characterize the slope of q_t versus $t^{0.5}$ plot as a "macropore rate parameter" [23]. Plots of q_t vs. $t^{1/2}$ are shown in figs. 5 and 6 for both Cu^{2+} and Cd^{2+} with and without electrolyte at different temperatures, K_{ad} values were calculated and tabulated (table 1- 4).

The pore diffusion coefficient, D, at different temperatures was determined by using the following equation [5, 23].

$$t_{1/2} = 0.03 r_o^2 / D \ , \qquad (3)$$

where, $t_{1/2}$ (min) is the time for the adsorption of half amount of heavy metals, r_o (cm) is the radius of adsorbent {r_o for dry adsorbent = 0.1 cm & r_o for wet adsorbent = 0.2cm}. The values of D have been calculated and are tabulated in tables 1-4, its valued were found in the order of 10^{-6} and 10^{-7} cm^2 s^{-1} indicating that the rate-controlling step is mainly intraparticle diffusion [5, 25].

4. Conclusions

From this study it was concluded that, the reaction rate of Cu^{2+} and Cd^{2+} adsorption increased as temperature increased, which means that an endothermic process tookplace, adsorption process was chemisorption, followed first order kinetics, and the half time of cadmium adsorption was much longer than

that of copper adsorption. The kinetic studies indicated that equilibrium of Cu^{2+} and Cd^{2+} adsorption on the composite was reached in two hours of contact between composite and the solution. The mechanism of Cu^{2+} or Cd^{2+} adsorption onto adsorbent is complex involv-ing an initial rapid rate for Cu^{2+} or Cd^{2+} removal due to external mass-transfer (~5min) followed by intraparticle diffusion which appears to be the rate-controlling step in the most of the system (5-100min).

Table 1
Adsorption kinetic parameters at different temperatures for Cu^{2+} without electrolyte

Surface	Dry composite				Wet composite			
Temp (°c)	$K(min^{-1})$	$T_{0.5}$ (min)	K_{ad}(mg ions / g adsorbent.min$^{0.5}$)	D' (cm²s⁻¹)	$K(min^{-1})$	$T_{0.5}$ (min)	K_{ad} (mg ions /g adsorbent.min$^{0.5}$)	D' (cm²s⁻¹)
30	0.0621	11.16	0.186	4.48*10⁻⁷	0.1291	5.37	0.067	3.72*10⁻⁶
45	0.0672	10.31	0.18	4.85*10⁻⁷	0.133	5.21	0.055	3.84*10⁻⁶
55	0.0685	10.12	0.151	4.94*10⁻⁷	0.1359	5.1	0.05	3.92*10⁻⁶

Table 2
Adsorption kinetic parameters at different temperatures for Cu^{2+} with electrolyte

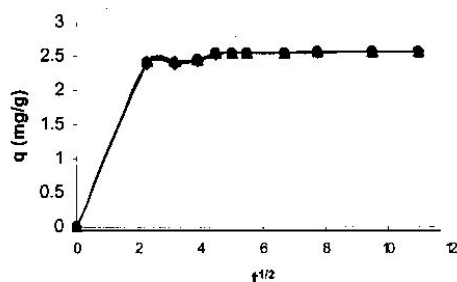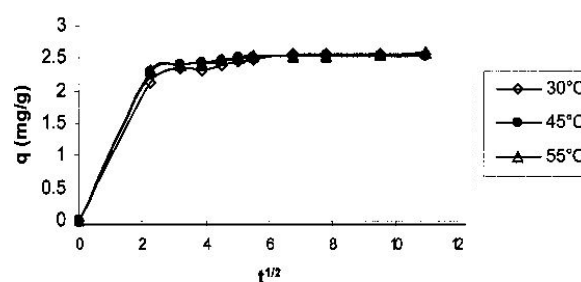| Surface	Dry composite				Wet composite			
Temp (°c)	$K(min^{-1})$	$T_{0.5}$ (min)	K_{ad}(mg ions /g adsorbent.min$^{0.5}$)	D' (cm²s⁻¹)	$K(min^{-1})$	$T_{0.5}$ (min)	K_{ad}(mg ions / g adsorbent. min$^{0.5}$)	D' (cm²s⁻¹)
30	0.0745	9.3	0.318	5.38*10⁻⁷	0.094	7.34	0.1	2.7*10⁻⁶
45	0.0719	9.64	0.205	5.19*10⁻⁷	0.104	6.68	0.072	2.99*10⁻⁶
55	0.08	8.67	0.195	5.77*10⁻⁷	0.11	6.29	0.065	5.77*10⁻⁶

Fig. 5a: Wet beads without NaCl
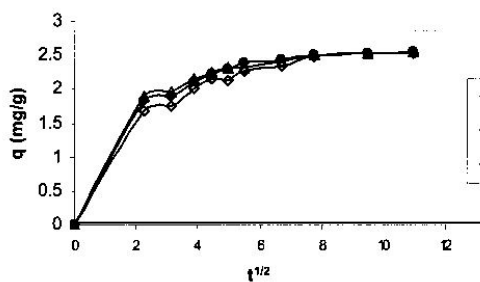

Fig. 5c: Wet beads with NaCl
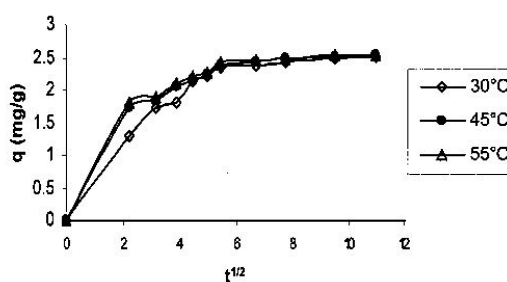

Fig. 5b: Dry beads without NaCl

Fig. 5d: Dry beads with NaCl

Fig. 5. Intraparticle diffusion for Cu^{2+} adsorbed amount with and without electrolyte (50ml of 100mg/l solution, 75 rpm, pH 8.2).
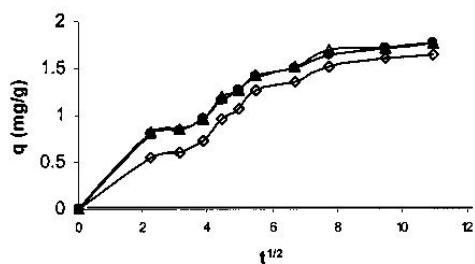
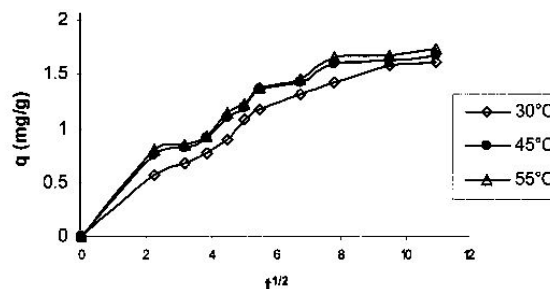Fig. 6.a: drying at 30°C without 0.05 M NaCl

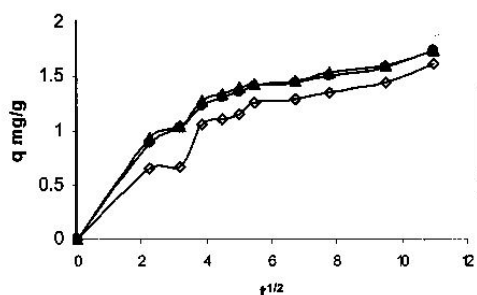Fig. 6.d: drying at 30°C with NaCl
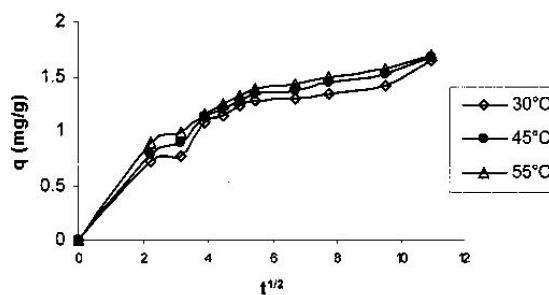

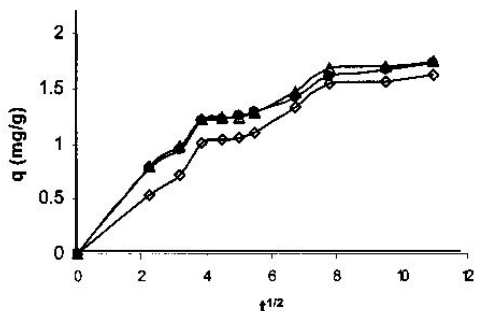Fig. 6.b: drying at 50°C without NaCl

Fig. 6.e: drying at 50°C with NaCl

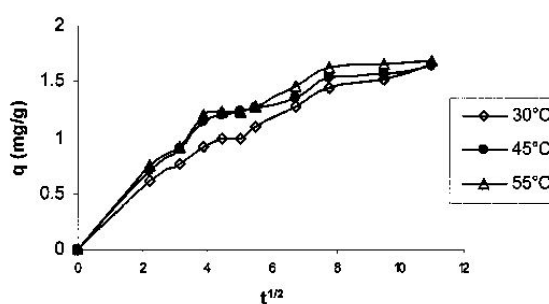Fig. 6.c: drying at 70°C without NaCl

Fig. 6.f: drying at 70°C with 0.05 M NaCl

Fig. 6. Intraparticle diffusion for Cd^{2+} adsorbed adsorbed amount with and without electrolyte
(50ml of 100mg/1 solution, 250 rpm, pH 8.2 g dry beads).

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Table 3
Adsorption kinetic parameters at different temperatures for Cd^{2+} without electrolyte

Surface Temp (ºc)	Dry composite at 30ºc				Dry composite at 50ºc				Dry composite at 70ºc			
	K (min^{-1})	$T_{0.5}$ (min)	K_{ad} (mg ions /g adsorbent. $min^{0.5}$)	D' (cm^2s^{-1})	K (min^{-1})	$T_{0.5}$ (min)	K_{ad} (min^{-1})	D' (cm^2s^{-1})	K (min^{-1})	$T_{0.5}$ (min)	K_{ad} (mg ions/g adsorbent. $min^{0.5}$)	D' (cm^2s^{-1})
30	0.0159	43.72	0.204	$1.14*10^{-7}$	0.0144	48.23	0.162	$1.04*10^{-7}$	0.0141	49.04	0.169	$1.02*10^{-7}$
45	0.018	38.54	0.179	$1.3*10^{-7}$	0.0158	44	0.131	$1.14*10^{-7}$	0.0159	45.89	0.14	$1.09*10^{-7}$
55	0.0176	39.4	0.177	$1.27*10^{-7}$	0.016	43.2	0.126	$1.16*10^{-7}$	0.1531	43.61	0.141	$1.15*10^{-7}$

Table 4

Adsorption kinetic parameters at different temperatures for Cd^{2+} with electrolyte NaCl

Surface Temp (ºc)	Dry composite at 30ºc				Dry composite at 50ºc				Dry composite at 70ºc			
	K (min^{-1})	$T_{0.5}$ (min)	K_{ad} (mg ions/ g adsorbent. $min^{0.5}$)	D' (cm^2s^{-1})	K (min^{-1})	$T_{0.5}$ (min)	K_{ad} (min^{-1})	D' (cm^2s^{-1})	K (min^{-1})	$T_{0.5}$ (min)	K_{ad} (mg ions/ g adsorbent. $min^{0.5}$)	D' (cm^2s^{-1})
30	0.01502	46.14	0.181	$1.08*10^{-7}$	0.0145	47.79	0.149	$1.05*10^{-7}$	0.0131	52.82	0.141	$9.47*10^{-8}$
45	0.01628	42.57	0.171	$1.17*10^{-7}$	0.015	46.26	0.142	$1.08*10^{-7}$	0.0149	46.64.	0.145	$1.07*10^{-7}$
55	0.01678	41.3	0.168	$1.21*10^{-7}$	0.0153	45.25	0.131	$1.1*10^{-7}$	0.0159	43.67	0.153	$1.14*10^{-7}$