Study Mechanisms and Kinetics of removal Cadmium Ions from Aqueous soultions on Bentonite surface

دراسة ميكانيكية وحركية ازالة ايونات الكادميوم الثنائي من محاليلها المائية على سطح البنتونايت

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Abstract :

In this paper a study was carried out to estimate the ability of Bentonite clay as a new adsorbent surface for removal and adsorption of Cadmium ion from aqueous solutions . The effect of contact time was evaluted and found that the removal process of Cadmium Ion by Bentoniite surafce was reached complete equilibrium at 60 min .The maximum removal or adsorption of Cadmium ion by Bentonite adsorbent were found 87.2% at 40 min . The kinetic results were well fitted to lagergren pseudo – second order models . This behavior was discussed depending on the chemical structure of Cadmium ion and Bentonite surface area. The intraparticle difusion model was also used to studied the kinetics and mechanisms of Cadmium Ion removal . Results model plays a significant role in the adsorption mechanism

Keyword : adsorption , Cadmium ion removal .

الخلاصة :

يتضمن البحث دراسة فعالية سطح طين البنتونايت كسطح ماز جديد لازالة و امتزاز ايونات الكادميوم من المحاليل المائية . تم دراسة تاثير زمن التماس لعملية ازالة ايون الكادميوم بواسطة سطح البنتونايت حيث وجد ان عملية الامتزاز تصل الى حالة التوازن عند الزمن 60 دقيقة . وجد ان كمية الامتزاز العظمى لايون الكادميوم هي 87.2% عند زمن مقداره 40 دقيقة . اظهرت نتائج حركية الامتزاز بان عملية الامتزاز تتبع موديل لاجرجرين للمرتبة الثانية- الكاذبة . وقد نوقش هذا السلوك على ضوء التركيب الكيميائي لايون الكادميوم و مساحة سطح البنتونايت . كذلك تم دراسة ميكانيكية ازالة ايون الكادميوم بالاعتماد على موديل الانتشار الضمني وقد بينت النتائج ان الانتشار الضمني للدقائق يلعب دورا رئيسيا في عملية الامتزاز .

Introduction :

Wastwater and industrial wastwater consist of amany contaminats including dyes , acids , bases , dissolved solids , toxic compound , phenoles and heavy metals . One of the most important toxic heavy metals cadmium ion that setting the biological treatment process with in the treatment plant .

Also the high concentration of Cd(II) are toxic to some micro organisms and cause inhibition of their catalytic capilities and metabolism of lipids [1] . In addition , cause the hybertention for human.[2]

They , therefore we need to be removed cadmium ion before the Industrial wastwater can be charged.[3]

Adsorption method is a widely used for the treatment of industrial wastwaters containing dyes , heavy metals and other organic and inorganic impurities[4-6].

The advantages of adsorption are its simplicity of operation , low costs compared to other separation method and absence of sludge formation . Adsorption method including physical and chemical adsorption and ion exchange process . In adsorption method ions (adsorbates) contained in a liquid phase diffuse to the surface of a solid phase clays (adsorbent)[7] , where they are chemically bound to the surface or held there by intermolecular forces . The most common method used for Cd(II) , removal from industral wastewater are natural materials have also been investigated as potential industrial adsorption media [8-10] , activated carbons[11 , 12] and also using clay as adsrbant surface for removal Cd(II) from wastewater [13 , 14].

Experimental part :

Instrument used :

1.Atomic Absorption spectrophotometer – 5000 , perkin – Elmer , U. S. A.
2.Shaker EB75 .
3.Centrifuge tubes . Hettich EBA35 .
4.Sartorius Balance Lab. L420 B .

Materials used :

1.preparation of adsorbent material :

Bentonite clay was obtained from (The General company for Geological survey and mining) in Baghdad . The clay was washed with excessive amounts of distilled water , dried at 130 C^o for 12 hours.

2.Preparation of adsorbate material :

0.0027 gm of $Cd(NO_3)_2 . 4H_2O$ dissolved in 100 ml of distilled water in a volumetric flark of 100 ml in order to prepared a solution of 10 $\mu g.ml^{-1}$ of Cd(II) . solution of different concentration
(0.05 – 5 $\mu g.ml^{-1}$) were prepared by serial dilution .

Results and Discussion :

Determinetion of calibration curve :

Absorbance of solutions in the range of 0.05-5 $\mu g.ml^{-1}$ were measured using atomic absorption spectrophotometer – 5000 , perkin– Elmer U. S. A. And plotted against the concentration values . In order to produce the calibration curve at shown in fig. 1.

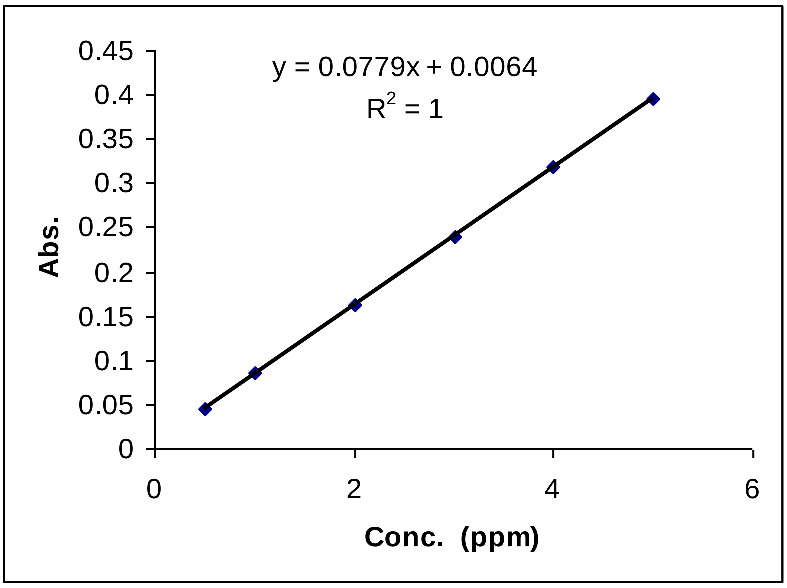

Fig. 1. Calibration curve for the determination of Cadmium ion .

Calculate the quantity adsorbed :

The quantity of cadmium adsorbed was calculated according to the following equation

$$\% \text{ adsorption} = \frac{X}{W} = \frac{V(C_o - C_e)}{W} * 100 \text{ ....(1)}$$

Where X = the quantity adsorbed of Cd(II) ion (mg)
W = weight of adsorbent (g) .
Co = initial concentration of Cd(II) ion (mg/L)
C_e = final concentration of Cd(II) ion (mg/L)
V = volume of solution (L)
% = adsorption percentage

Kinetic studies :

The effect of contact time was determined by adding 0.5 gm of adsorbent (Bentoniteclay) into 25 ml Cd(II) ion solution , with intial concentraion of 0.5 µg.ml^{-1}under shaking . The temperature of solution was room temperature . After different time shaking intervals , the solutions were centrifuged and volume of 5 ml supernatant were taken to measurements of absorbance by using atomic absorption spectrophotometer in order to determine cadmium metal using calibration curve as show in Fig (1) .To evalute the effectiveness of an adsorbate , The adsorption of Cd(II) ion on Bentonite surface was studied as a function of contact time , and the results are show in Fig (2) , and (3).

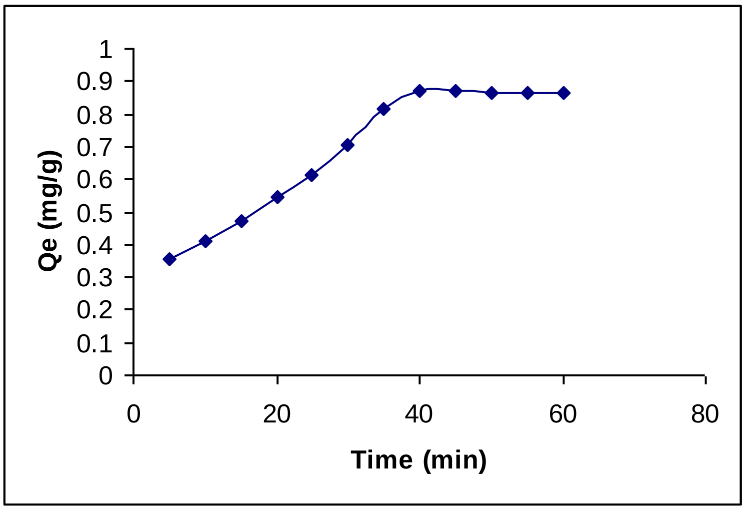

Fig . 2. Removal kinetic of Cadmium ion on Bentonite surface .

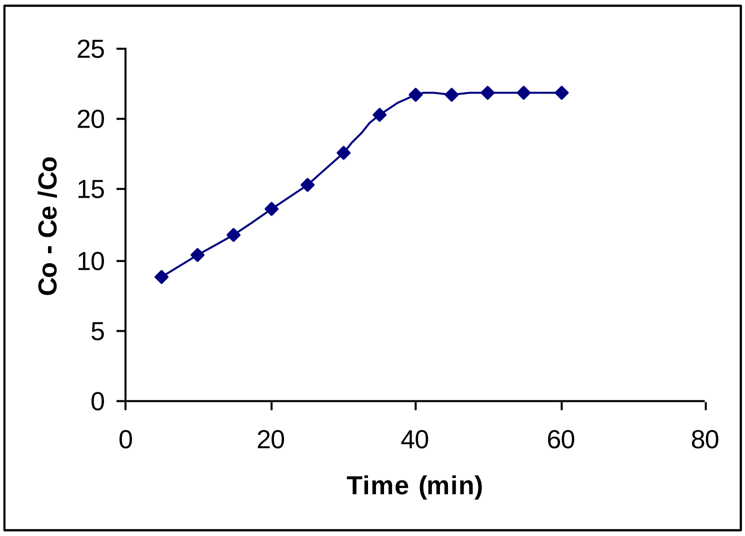

Fig . 3. Effect of contact time of Cadmium ion Adsorption .

The adsorption rate of Cd(II) ion on to Bentonite surface are observed to be very fast with in the first few minutes and gradually decrease and become almost constant after a 35 min .The value of adsorption quantity versus t during the initial hour of contact shows avery fast increase in adsorption quantity of cadmium ions with time , intially followed by agradual plateau at quasi equilibrium situations . The initial uptake is attributed to surface adsorption . When the cadmium ion adsorption at the exterior surface reached the saturation level , the cadmium begins to enter the pores of Bentonite surface and adsorbed by the interior surface of the adsorbent particles . The interior surface seems to be very active and have avery high affinity toward cadmium ions . Hence , a high cadmium ion uptake by Bentonite surface is observed . As the surface saturates with cadmium ions , the adsorption rate decreases due to an increase in the diffusion resistance . This means that the pore diffusion is the rate controlling step during cadmium ions adsorption [15] .The effect of contact time on the removal of cadmium ions by Bentonite is show in Fig . 4 .

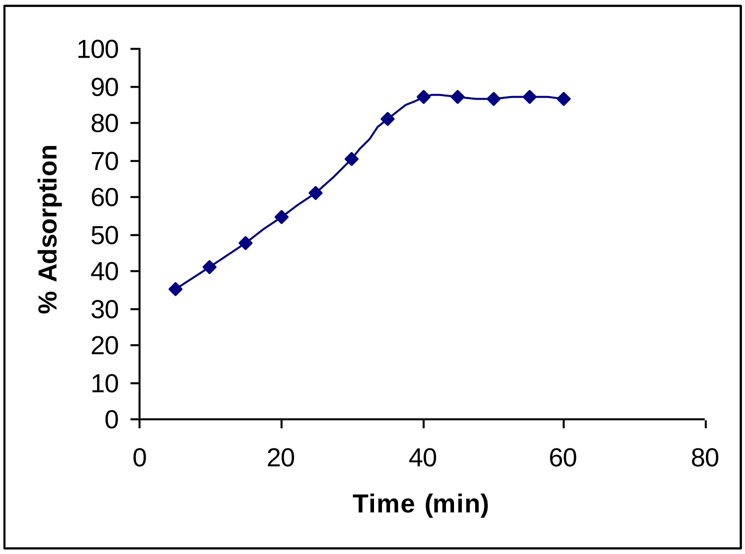

Fig . 4. Effect of contact time on the Adsorption percent of Cadmium ion by Bentonite surface

This figure showed that a rapid adsorption of cadmium ions in the first 30 min , and there afteer , the adsorption rate decrease gradually . Nearly 87.2% removed from an agueos solution with in 40 min numerous kinetic models have been proposed to explane the mechanism by which pollutants are adsorbed . The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent , as well as on the mass transport process . The rate constant of cadmium Ions removal from the solution by Bentonite surface were determined using first order and second order equations.

The first order rate equation was used to fit the expermental results . The integral form of the model is :[16]

$\ln (qe - qt) = \ln qe - K_1 t$ ....(2)

where qe(mg/g) = the equilibrium sorption capacity

qt (mg/g) = the amount of cadmium Ions adsorbed at time t (min) .

K_1 = the equilibrium first order constant .

Value of K_1 were obtained from the slope of the plot of ln (qe – qt) Vs . t Fig. 5. The adsorption kinetic parameters .From Fig. 5. are indicated in Tab . 1 .

Table(1) The removal kinetic parameters for Cadmium ion on Bentonite surface

Pseudo – first order			Pseudo – second order			
K_1 (min^{-1})	qe (mg/g)	R^2	K_2 (g.mg^{-1}.min^{-1})	qe (mg/g)	R^2	h
0.0449	**1.219**	**0.9426**	**0.1652**	**0.9386**	**0.9921**	**0.1456**

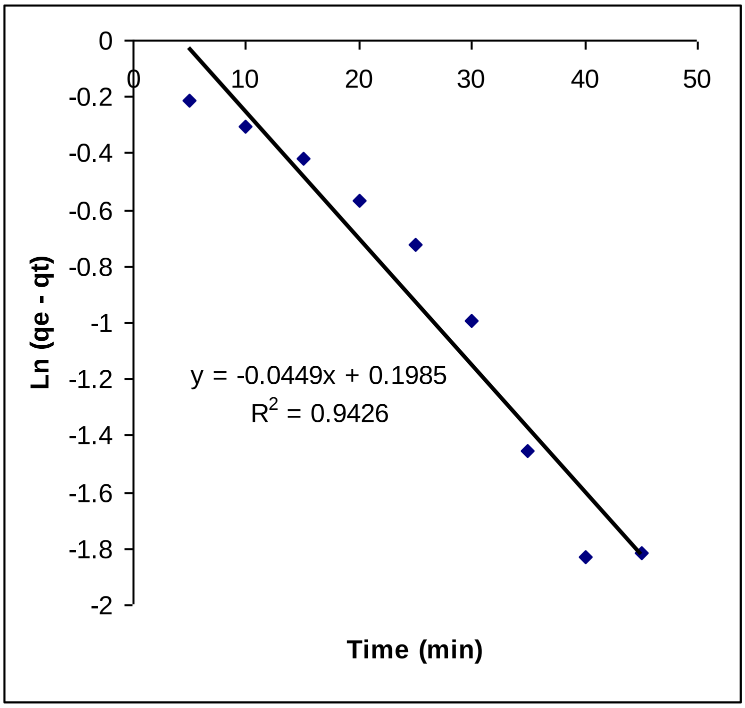

Fig . 5. The first order kinetic model for the Cadmium ion removal by Bentonite surface

The adsorption values were also analyzed in terms of second ordermechanism [16, 17] . The linearized – intergral form of this model is :

$$\frac{t}{q_t} = \frac{1}{K2q_e^2} + \frac{1}{q_e} t \text{ ....(3)}$$

where K_2 = the rate constant of second order adsorption .
if the initial adsorption rate is $h = K_2 q_e^2$ then equation (3) becomes :

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \text{ ....(4)}$$

By plotting t/q_t versus t yielding fig . 6 . , a q_e obtained from the slope . and h , K_2 could be obtained from the value of the intercept of the straight line . The adsorption Kinetic parameters from Fig . 6 . are indicated in Tab . 1 .

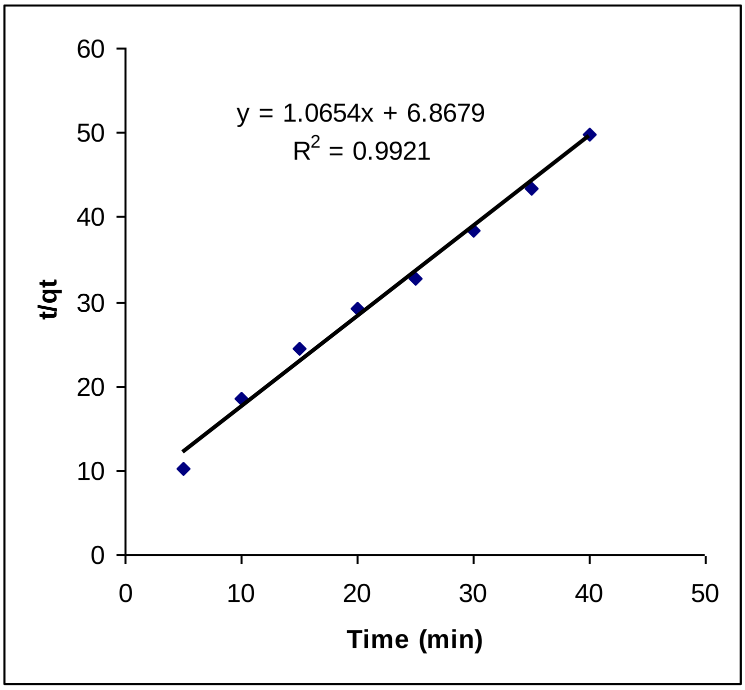

Fig . 6. The second order kinetic model for the Cadmium ion removal by Bentonite surface

The linearity of these plots indicates the applicability of the two models . However , the correlation coefficients , R^2 , show that the pseudo – second order model fites the experimental data slightly better than the pseudo-first order model .

This is normally attributed to enhanced association of the Cadmium cations with the negatively charged Bentonite surface . In aqueous medium , the exchangeable alkali and other metal cations on the surface and in the interlayer region of the clay undergo hydration creating a hydrophilic environment[18] .

If the movement of the solute from the bulk liquid film surrounding the adsorbent is ignored , the adsorption process for porous solids can be separated into three stages , viz , (1) mass transfer (boundary-layer diffusion) , (2) sorption of ions onto sites and (3) intraparticle diffusion . In many cases , three is a possiblity that intraparicle diffusion will be the rate-limiting step, which is normally determined using the equation proposed by weber and Morris[19] :

$q_t = k_p t^{1/2} + C$……………(5)

Where q_t (mg/g) is the amount adsorbed at time t , K_p is the intrapaticle rate constant (mg.min $^{-1/2}$.g^{-1}) and C is the intercept .

q_t was found to be linearly correlated with $t^{1/2}$. The k_p vaules were claulated using correlation analysis (Table (2) . The R^2 values are close to unity , indication the appropriateness of the application of this model . This reveals the occurrence of an intraparticlee diffusion process[19] . The intraparticle diffusion plots are presented in Figure (7) . It can also observed that the plots did not pass through the origin , this was indicative of some degree of boundary layer control (the larger the intercept , the greater the boundary-layer effect) and this further showed that the intraparticle diffusion was not the only rate – limiting step ,but other processes might control the rate of adsorption .

Table (2) The interparticular model for Cadmium ion Removal on Bentonite surface .

Pseudo – first order		
K_p (min^{-1})	intercept	R^2
0.7612	1.4061	0.9915

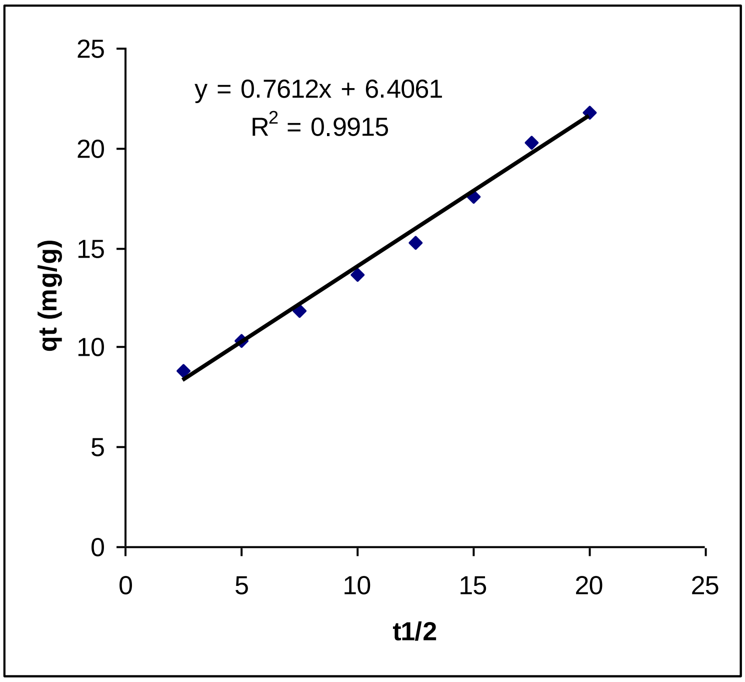

Fig . 7. The intraparticle diffusion model for the removal of Cadmium ion by Bentonite surface

The initial process , when a Cadmium ion is added to the clay suspension , is the adsorption of the molecules on the external surface of the particles . This increase significantly the local concentration , giving rise to the formation of ion aggregates . With time , the ion molecules can migrate to the interlamellar region in the disaggregation of the aggregates and restoring protonated monomers because of the higer acidity in this region , and so the adsorption proceeds through an ion pairing mechanism [20, 21] .

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