ADSORPTION OF CADMIUM METAL ION (Cd^{2+}) FROM ITS AQUEOUS SOLUTION BY ALUMINIUM OXIDE AND KAOLIN : A KINETIC AND EQUILIBRIUM STUDY

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ABSTRACT

In this work, the effects of various experimental parameters on kinetics and equilibrium adsorption of cadmium metal ion (Cd^{2+}) from its aqueous solution on aluminium oxide (Al$_2$O$_3$) and kaolin have been investigated using laboratory batch adsorption experiments. It has been found that amount of adsorption of cadmium metal ion increases with initial metal ion concentration, contact time, solution pH, amount and type of adsorbents respectively Kinetics data are best described by pseudo-second order model for both the systems. The experimental equilibrium data are fitted to the Freundlich and Langmuir isotherms and find out suitability of both adsorption isotherm.

Key Words : Cadmium adsorption, Isotherm, Aluminium oxide, Kaolin adsorbent

NOMENCLATURE

1. C_0 = Initial cadmium metal ion (Cd^{2+}) concentration, ppm (mg/L)
2. C_t = Metal ion (Cd^{2+}) concentration at time t, ppm (mg/L)
3. C_e = Equilibrium metal ion concentration, ppm (mg/L)
4. q_t = Amount of metal ion (Cd^{2+}) adsorbed, mg/g
5. q_e = Amount of metal ion adsorbed at equilibrium, mg/g
6. K_1 = Pseu-1st-order rate constant, min^{-1}
7. K_2 = Pseudo-second-order rate constant, g/mg-min
8. V = Volume of reaction mixture, ml
9. M = Amount of adsorbent, aluminium oxide, g

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INTRODUCTION

Now a days heavy metal ions such as cadmium, zinc, copper, lead, nickel etc are the most important pollutants in source and treated water and are becoming a severe public health problem. Cadmium (Cd^{2+}) is released into natural water from the electroplating industry, cadmium-nickel batteries, phosphate fertilizers, pesticides, mining, pigments, and alloy

Industries and sewage sludge[1-3]. Because of high toxicity and mobility in soil, the case of cadmium is of great importance. The permissible limit of cadmium metal ion in waste water is 2 mg/L[4]. Conventional methods such as precipitation, ion exchange, filtration, reverse osmosis, solvent extraction and adsorption on activated carbon are used for the removal of heavy metals from its aqueous solution[1]. Among these processes, the adsorption with the selection of a suitable adsorbent can be an effective technique for the removal of heavy metal ions from waste waters[1,5]. Aluminium oxide and clay minerals such as kaolin are the most widespread minerals of the earth crust which are known to be a good adsorbent of various metal ions, inorganic anions and organic ligands[1]. In general most solid phases in natural water contain aluminum oxide. Aluminium oxide due to its high surface area and pH depended surface charge and mechanical strength has found several applications such as adsorbent and catalyst[1]. On the other hand, kaolin is the most abundant phyllosilicate minerals in highly weathered soils. It is a 1:1 aluminosilicate comprising a tetrahedral silica sheet bonded to an octahedral sheet. The tetrahedral sheet carries a small permanent negative charge and the octahedral sheet has a pH-depended variable charge. Readers are encouraged to read review article by Bhattacharyya and Gupta[6] on Cd^{2+} metal ion and other metal ion adsorption on clay minerals and on oxides as

well. Adsorption of inorganic/organics at solid/liquid interface is governed by many factors such as contact time, initial metal ion concentration, solution pH, ionic strength and temperature respectively[7-8].

In this work laboratory batch kinetic and equilibrium isotherm studies are conducted to determine the adsorption capacity, kinetic rate constant and isotherm constants respectively. It has been found that amount of adsorbed cadmium metal ion increases with initial metal ion concentration, contact time, solution pH and with adsorbent doses respectively for both aluminum oxide and kaolin adsorbent.. The adsorption kinetics is found to follow a pseudo-second-order kinetic model for both the systems. Rate constants at different initial concentration as well as at different solution pH and adsorbent dosages have also been estimated. Finally adsorption characteristics are compared between kaolin and aluminium oxide adsorbent respectively.

MATERIAL AND METHODS

All chemicals used were of analytical grade. Stock standard solution of Cd^{2+} has been prepared by dissolving the appropriate amount of its nitrate in deionizer water, acidified with small amount of nitric acid. This stock solution was then diluted to specified concentrations. The pH of the system was adjusted using reagent grade NaOH and HNO_3 respectively. Aluminium oxide, Al_2O_3 (sauter mean diameter = 3µm) and kaolin (sauter mean diameter is 30 3µm) was obtained from local Chemical R & M, Malaysia and was used as such after drying at a temperature of 70 ^{0}C in a temperature controlled oven. Cadmium nitrate was obtained from Mark. All plastic sample bottles and glassware were cleaned, then rinsed with deionized water and dried at 60 ^{0}C in a temperature controlled oven. All measurements were conducted at the room temperature (28 ± 2, ^{0}C).

The concentration of Cd^{2+} was measured using double beam flame atomic absorption spectrophotometer. Sizes of particles were measured by Malvern Master Sizer. The pH was measured by Orion pH meter.

ADSORPTION EXPERIMENTS

Effect of pH on metal ion adsorption

The effect of pH on the amount of cadmium metal ion removal was analyzed over the pH range of 2.68, 6.70 and 9.50 respectively. In this study 50 ml of metal ion solution of 30 ppm (mg/L) was agitated with 30 mg of adsorbent using rotary shaker at 80 rpm and 30 $^{\circ}$C in a series of 100 ml plastic bottles as per method by Sen et al[8]. A period of 3 hours was found to be more than sufficient to attain equilibrium. Speed was such that it maintains the contents completely mixed and the adsorbents were suspended throughout the bottle. The samples were then collected in different time intervals throughout equilibrium time period and filtered each time through a what man glass micro filter (0.2 μm) and the left out concentrations in the filtrate solution was analyzed using flame atomic absorption spectrophotometer with air-acetylene flame. Cadmium hollow cathode lamp was used. The spectral slit width and the working wavelength were 0.7 and 228.8 nm respectively. The quantity of adsorbed metal ion on aluminium oxide and kaolin was calculated as the difference between initial concentration and concentration at any time, t. Each experiments were repeated in twice to check the reproducibility. Measurements are, in general, reproducible within ± 10 %.

Effect of adsorbent dose on metal ion adsorption

The effect of adsorbent mass on the amount of metal ion adsorbed was obtained by contacting 50 mL of metal ion solution of initial concentration of 30 ppm (mg / L) with different weight amounts of 10 mg and 30 mg of aluminium oxide and kaolin separately using rotary shaker at 30 $^{\circ}$C for 3 hours at a constant speed of 80 rpm and solution pH of 6.65. At each time intervals, the samples were then filtered and the filtrates solution was analyzed as mentioned in earlier section.

Kinetics of metal ion adsorption

The kinetics of metal ion adsorption was carried out at two different initial metal ion concentrations at a fixed pH on adsorbent as per earlier experimental procedure. The only difference was that samples were collected and analyzed at regular intervals during adsorption process.

Adsorption equilibrium

For equilibrium isotherm experiments, metal ions of different concentrations were taken in batches of 50 ml solutions in a series of 100 ml plastic bottles. The adsorption equilibrium studies carried out separately for each adsorbents. Measured weight of adsorbent was added to each bottle and samples were shaken in a contant temperature rotary shaker for a period of 3 hours. After equilibrium, each sample was analyzed for left out equilibrium Cd^{2+} as per mentioned in earlier section.

RESULTS AND DISCUSSION

Effect of pH on metal ion adsorption

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The effect of pH on the amount of metal ion adsorbed q_t (mg / g) which is not shown here. The term q_t has been calculated from the mass balance equation which is given by

$$q_t = \frac{(C_0 - C_t)V}{m}$$

Where C_0 (ppm or mg / L) and C_t (ppm or mg / L) are the concentration in the solution at time t = 0 and at time t, V is the volume of solution (L) and m is the amount of adsorbent (g) added. It has been found that

amount of Cd^{2+} metal ion adsorbed increases with time as well as with increase in pH or alkalinity for both $Cd-Al_2O_3$ system and Cd-kaolin system but more adsorption takes place in case of Cd-kaolin system Such increase in adsorption can be attributed to the favorable change in surface charge and to the extent of hydrolysis of the adsorbing metal ion change with varying pH. As the surface charge of aluminium oxide become more negative with increasing pH, the surface attracts bivalent metal cations for adsorption[1]. Furthermore, the proportion of hydrated ions increases with pH and these may be more strongly adsorbed than unhydrated ions. Therefore, both the effects are synergistically enhancing the amount of adsorption at higher pH. Whereas in case of kaolin, adsorption takes place through permanently negative charge ion exchange as well as specific ion adsorption through variable charge octahedral site.

Kinetics of cadmium metal ion adsorption

Effect of Contact time and Effect of adsorbent type on Cd^{2+} adsorption

Fig. 1 represents a plot of the amount of cadmium metal ion adsorbed (mg/g) versus contact time for aluminium oxide and kaolin separatetely for a fixed initial metal ion concentration of 30 ppm. From this plot it is found that the amount of adsorption i.e. mg of adsorbate per gram of adsorbent increases with time and an equilibrium is reached within 40 minutes for both the systems. This kinetic experiments clearly indicates that adsorption of cadmium metal ion (Cd^{2+}) on aluminium oxide and also on kaolin is a two step processes similar to experiments by Sen et al[8]: a rapid adsorption of cadmium metal ion to the external surface is followed by possibly slow intraparticle diffusion in the interior of the adsorbent[1].
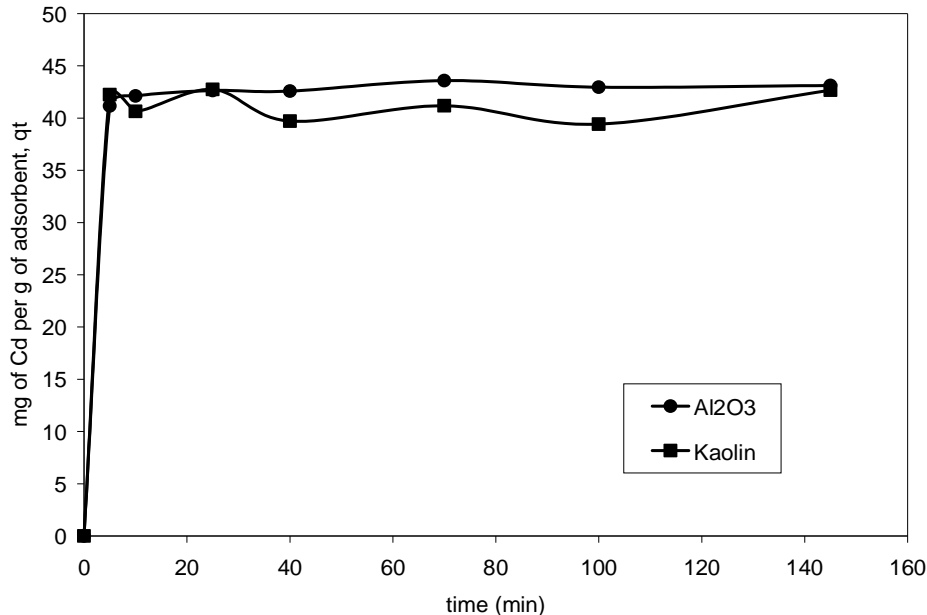

Fig. 1 : [●Initial Cd2± = 30ppm; Amount of Al_2O_3 added = 30mg; Initial pH 6.2; Temperature = 28.2°C; Shaker Speed = 188rpm

■Initial Cd2+ = 30ppm; Amount of Kaolin added = 30mg; Initial pH 6.2; Temperature = 28.2°C; Shaker Speed = 188rpm]

The **Fig. 1** also shows Al_2O_3 is a better adsorbent than kaolin because it has slightly higher adsorption capacity 43.29mg/g compared to kaolin, 41.84mg/g.

In order to investigate the mechanism of adsorption, particularly potential rate-controlling step, the transient behavior of the cadmium metal ion (Cd^{2+}) adsorption process was analyzed using the pseudo first order and pseudo second order which are explained as follows:

Lagergren pseudo-first order kinetics

The integral form of the Lagergren pseudo first order equation can be expressed as

$$\log \frac{q_e}{(q_e - q)} = -\frac{K_1 t}{2.303}$$

Thus the rate constant K_1 (min^{-1}) can be obtained from the plot of log $(q_e / q_e - q)$

Versus time t which is not shown here. Actually experimental data does not follow pseudo-first-order kinetics as the value of regression coefficient (R^2) is very poor for both Cd-aluminium oxide and Cd-kaolin systems.

Pseudo-second-order model

The liberalized form is as[1]

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

A plot between t / q versus t gives the value of the constants K_2 (g / mg -min) and also q_e (mg / g) can be calculated.

The Constant K_2 is used to calculate the initial sorption rate h, at t→0, as follows

$$h = K_2 q_e^2$$

Thus the rate constant K_2, initial adsorption rate h and predicted q_e can be calculated from the plot of t / q versus time t using Eq. (3). Plots between t / q versus time t kinetic plots for cadmium adsorption on different adsorbents are shown in **Fig. 2.**
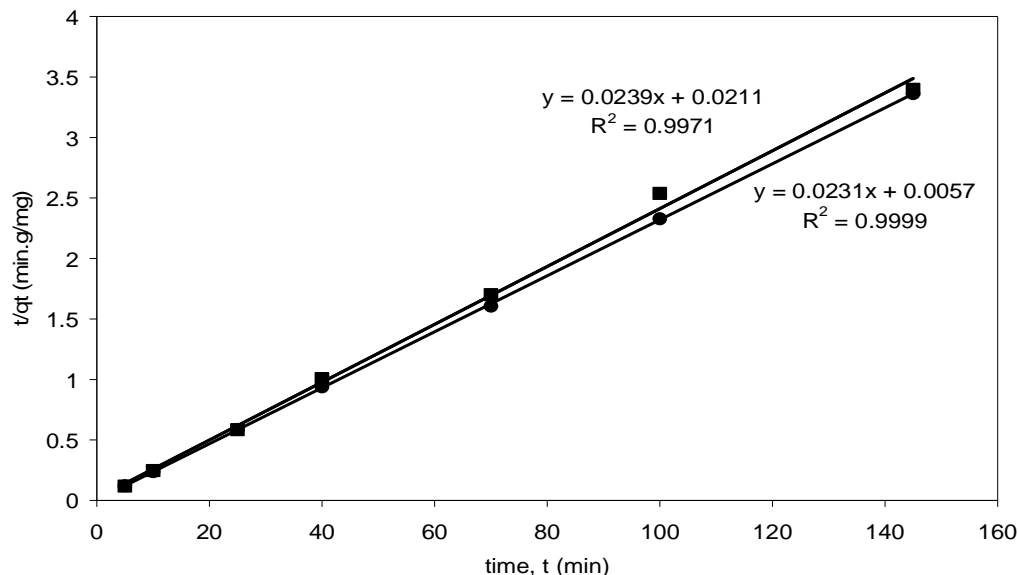

y = 0.0239x + 0.0211
R^2 = 0.9971

y = 0.0231x + 0.0057
R^2 = 0.9999

Fig. 2 : Pseudo-second-order model for Cd-aluminium oxide and Cd-kaolin system.
[●Initial Cd2+ = 30ppm; Amount of Al_2O_3 added = 30mg; Initial pH 6.2; Temperature = 28.2°C; Shaker Speed = 188rpm
■Initial Cd2+ = 30ppm; Amount of Kaolin added = 30mg; Initial pH 6.2; Temperature = 28.4°C; Shaker Speed = 188rpm]

The initial sorption rates is the $h = kq_e^2$. All parameters including the correlation coefficients, R^2, the pseudo-second-order rate constant, K_2 and equilibrium sorption capacity, q_e were calculated and tabulated in **Table 1.**

Table 1: Kinetic parameters for Cd^{2+} adsorption on aluminium oxide and kaolin respectively

System	k_2 (g/mg-min)	q_e (mg/g)	h(mg/g-min)	R^2
Cd-Al_2O_3	0.0936	43.29	175.4386	0.9999
Cd-kaolin	0.0271	41.84	47.3934	0.997

Higher correlation coefficients with respect to fitted pseudo 1st-order reaction model suggest that adsorption of cadmium metal ion on aluminium oxide and kaolin follows pseudo second-order kinetics. Also this suggests the assumption behind the pseudo-second-order model that the metal ion uptake process is due to chemisorptions. It has been found that the rate constant k_2 and initial sorption rate, h and adsorption capacity for aluminium oxide are greater than kaolin adsorbent.

The assumption behind the pseudo second order kinetic model was that the rate-limiting step might be chemisorptions involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate[1].

Adsorption equilibrium isotherm

The mechanism of adsorption and designing of an adsorption system can be explained from equilibrium isotherm model. Therefore the adsorption equilibrium data were fitted for Langmuir-2 and Frenundlich isotherms within the metal ion concentration range of 30-80 ppm respectively. Linear regression was frequently used to determine the most fitted isotherm.

The Freundlich adsorption isotherm can be expressed as[1]

$$\text{Ln } q_e = \ln K_f + 1/n \, (\ln C_e)$$

Where q_e is the amount of metal ion adsorbed at equilibrium time, C_e is equilibrium concentration of cadmium metal ion in solution. K_f and n are isotherm constants which indicates the capacity and the intensity of the adsorption respectively [1-5] and can be calculated from the intercept and slope between $\ln q_e$ and $\ln C_e$ which are shown in **Table 2** for both the systems. The Freundlich plots are not shown here.

Table 2: Freundlich parameters obtained from Freundlich plots. Initial Cd2+ = 30, 40, 50, 60, 70 and 80ppm; Amount of Kaolin and also Al2O3 added = 10mg; pH 6.40; Temperature = 27.5oC; Shaker speed = 188rpm

Adsorbent	Equation	Freundlich constants		
		K_F	1/n	R^2
Al_2O_3	y = 3.0924x - 1.3394	0.262	3.0924	0.9589
Kaolin	y = 3.517x - 2.1589	0.1155	3.517	0.9505

Also Langmuir-2 isotherm equation was tested for both the system with this same metal ion concentration range. The linearized form of Langmuir-2 can be written as[1]

$$1/q_e = (1/K_a q_m) 1/C_e + 1/q_m$$

The Langmuir constants, q_m (maximum adsorption capacity) and K_a (values for Langmuir-2) can be obtained from plots between $1/q_e$ versus $1/C_e$ which are shown in **Table-3** with fixed initial conditions. The plots are not shown here. The maximum

adsorption capacity of Cd^{2+}, q_m for both the systems are 89.28 mg/g and 78.74 mg/g respectively whereas constant related to the binding energy for the adsorption, K_a for both the systems are 0.08 . From **Table 2** and From **Table 3,** It has been found that regression coefficient for both the systems are high and cadmium adsorption on aluminium oxide and kaolin follows both Freundlich and Langmuir adsorption isotherm.

Table 3: Langmuir parameters. Initial Cd^{2+} = 30, 40, 50, 60, 70 and 80ppm; Amount of Kaolin and aluminium oxide added = 10mg; pH 6.40; Temperature = 27.5oC; Shaker speed = 188rpm

Adsorbent	Equation	Langmuir constants		
		q_m	K_a	R^2
Al_2O_3	y = 0.14x - 0.0112	89.2857	0.08	0.9832
Kaolin	y = 0.1496x - 0.0127	78.7402	0.08489	0.9877

CONCLUSION

Batch adsorption kinetic studies show that the adsorption of cadmium metal ion (Cd^{2+}) is strongly affected by initial solution pH, initial metal ion concentration, contact time and adsorbent types respectively. The amount of metal ion (Cd^{2+}) adsorption on aluminium oxide ($Al_2 O_3$) and on kaolin increases with contact time, initial metal ion concentration, solution pH, and adsorbent doses[1] respectively. It has also been found that the amount of adsorption i.e. mg of adsorbate per gram of adsorbent increases with increasing contact time at all initial metal ion concentrations and equilibrium is attained within 40 minutes at a fixed solution pH for both the Cd-Al_2O_3 and Cd-kaolin system. Basically, this kinetic experiments clearly indicate that adsorption of cadmium metal ion (Cd^{2+}) on aluminium oxide and on kaolin is a two steps process : a rapid

adsorption of cadmium metal ion to the external surface is followed by possible slow intraparticle diffusion in the interior of the adsorbent. Overall the cadmium adsorption process followed pseudo-second-order kinetics for both the systems. Freundlich and Langmuir both isotherms are reasonably fitted for both the systems within this metal ion concentration range. Al_2O_3 is a better adsorbent than kaolin. The adsorption capacity, qt for Al_2O_3 is higher than kaolin as well.

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