

Article

Removal of Cadmium from Aqueous Solutions Using Adsorption Technique: Kinetics and Equilibrium

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Abstract: Heavy metals are well recognized as potential health hazards as they can neither be degraded nor biologically detoxified. This experimental study aims to investigate the possible use of Libyan local soil (Ashkida soil), mined in the Southern Province of Libya as a low cost adsorbent for the removal of cadmium ions from aqueous solution. In this work, the effects of various parameters such as adsorbent dosage, initial cadmium concentration, agitation rate, contact time and solution pH value on the adsorption efficiency were investigated through batch experiments at room temperature. The results indicated that the optimum conditions for cadmium removal from aqueous solutions were 60 min, 10 g/l and 500 rpm as a contact time, adsorption dose and agitation rate, respectively, and natural pH value. The results were fitted to the Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherms. Satisfactory agreement between experimental data and the model-predicted values was expressed by the correlation coefficient (R^2) and the total mean error ($E\%$). The Freundlich model represented the sorption process better than others. The calculated monolayer adsorption capacity (q_{max}) was 31.25 mg/g. A comparison of kinetic models applied to the adsorption of cadmium ions on the adsorbent was evaluated for the simple first order, the pseudo first order and second order kinetic models. Kinetic parameters, rate constant, equilibrium sorption capacities and related correlation coefficients for each kinetic model were calculated and discussed. Results showed that the pseudo second order kinetic model was found to correlate the experimental data well. A linear relationship between the equilibrium rate constant of pseudo second order model and the system temperature suggests that the

adsorption process is controlled by an endothermic reaction. However, an efficient cadmium ions removal can be achieved at ambient temperature.

Keywords: cadmium; soil; adsorption; equilibrium; kinetics; removal.

1. Introduction

Cadmium is an important toxic material, as it does not undergo biodegradation. It is introduced into natural waters by a variety of industrial wastewaters including those discharged from textile, leather tanning, electroplating, and metal finishing industries. It is accumulation in human body at high levels, which can cause serious health problems, and ultimately become lethal.

A number of techniques for treating contaminated effluents have been developed over the years. The most important of these techniques include chemical precipitation, filtration, ion exchange, reverse osmosis and membrane systems. However, all these techniques have their inherent advantages and limitations in application. In recent years, adsorption has proven to be an effective method to remove dissolved metal ions from liquid wastes. Removal of heavy metals from industrial wastes using several adsorbents is an increasing interest in the scientific community. However, in order to minimize processing costs, several recent investigations have focused on the use of low cost adsorbents such as by-product lignin (Mohan and Chander, 2006), limestone (Aziz et al., 2008), agricultural wastes (Al-Othman et al., 2011; Odoemelam et al., 2011), dried activated sludge (Khosravan and Lashkari, 2011) and clay materials (Boparai et al., 2011; Harvey and Chantawong, 2001; Menntasti et al., 2003; Sajidu et al., 2006). Adsorbents, mainly clay minerals, are readily available and offer cost effective alternatives to conventional treatment of wastewater. Activated carbon is regarded as the most effective heavy metals adsorbent. Due to its high cost, low cost alternative adsorbents have attracted the attention of several investigators. As an abundant and low cost material, a Libyan soil is put to test as an adsorbent of cadmium.

The objective of this work is to investigate the removal of cadmium ions from aqueous solutions using Ashkida soil from Southern Libya. The effects of various parameters affecting adsorption are investigated and data are tested against a number of adsorption isotherms. Kinetic experiments with different cadmium concentrations at different temperatures are also performed. The activation energy involved in the adsorption process is determined from the best kinetic model constants.

2. Materials and Methods

2.1. Adsorbent (Ashkida soil)

Ashkida soil is brown in color and obtained from Ashkida region, which is located in Wadi Alshati in southwest Libya approximately at 27°33'16"N and 14°26'40"E. The surface area of the soil based on N_2 adsorption measurements is 28.7 m^2/g . The adsorption process is performed using soil

samples of particle sizes $\leq 300 \mu\text{m}$. The composition of the Ashkida soil used in this investigation is measured by X-ray fluorescence (Table 1).

Table 1. Results of the Chemical Composition of Ashkida Soil*

Compound	Wt%	Std. Err.	Compound	Wt%	Std. Err.
Fe_2O_3	68.69	0.23	MnO	0.34	0.017
SiO_2	8.56	0.14	TiO_2	0.305	0.015
Al_2O_3	6.79	0.13	Na_2O	0.177	0.011
CaO	5.97	0.12	K_2O	0.151	0.008
P_2O_5	2.27	0.07	SrO	0.109	0.005
SO_3	0.901	0.045	V_2O_5	0.0915	0.0046
MgO	0.481	0.024	Loss on ignition = 5.00 and D/S = 0.10 Cellulose		

* Average values for four different batch samples.

2.2. Chemicals and Metal Concentrations Analysis

A 10000 mg/l standard stock solution is prepared by dissolving the required amount of $Cd(NO_3)_2$ into 1 l of deionized water. A flame atomic absorption spectrometer (Varian SpectrAA-50) is used to determine the concentrations of Cd(II) in the solutions using air/acetylene flame at an analytical wavelength of 249.2 nm. The analysis of each sample is automatically carried out in triplicate and the mean is computed.

2.3. Optimum Conditions

The optimum time is obtained by adding 0.5 g of adsorbent to 100 ml of aqueous solution with 500 ppm of Cd(II) in 250 ml plastic bottles and shaken for 0 min, 5 min, 10 min, 30 min, 1 h, 2 h, 3 h, 6 h and 24 h at room temperature using an agitation speed of 200 rpm. All samples are filtered by glass wool, and the filtrate is collected to determine the Cd(II) concentration.

Adsorption experiments are conducted under a constant initial Cd(II) concentration of 500 mg/l. The solution pH is varied within 2-11 levels by adding of 0.1 N hydrochloric acid or 0.1 N sodium hydroxide solution. The duration of adsorption is 1 h and the agitation rate is kept constant at 200 rpm. The pH measurements are achieved by pH meter (Model: HI 8417, HANNA Instrument).

In order to assess the effect of agitation on metal removal efficiency, experiments are conducted under various agitation rates, 0, 50, 100, 200, 500, 1000, 1500 and 2000 rpm at 25 °C for 1 h using an adsorption dose of 0.5 g/100 ml, an initial Cd(II) concentration of 500 mg/l and solution pH 7.

The adsorbent doses effect on removal of Cd(II) ions is investigated under constant conditions (25 °C, 1 h equilibrium time, 200 rpm agitation rate, pH 7 and initial concentration 500 mg/l) with adsorbent doses of 0.1, 0.3, 0.5, 0.8, 1.0, 1.5 and 2 g for 100 ml aqueous solutions.

2.4. Adsorption Isotherms

A comparison of the adsorption models Freundlich, Langmuir, Dubinin-Radushkevich and Temkin to find the most representative one is based on the batch adsorption results. The batch adsorption experiments are carried out by using 0.5 g doses of adsorbent added to 100 ml of Cd(II) solutions in 250 ml plastic bottles with initial concentrations within 50-1000 mg/l of Cd(II), agitated at 200 rpm, 25 °C and pH 7 for an optimum time duration of 1 h.

2.5. Adsorption Kinetics

In order to examine the controlling mechanism of adsorption process such as mass transfer and the chemical reaction, the experimental data are assessed by simple first order, pseudo first order and pseudo second order kinetic models.

2.6. Thermodynamic Parameters

Batch runs of Cd(II) adsorption on Ashkida soil is performed at 25, 40, 55, 70 and 85 °C to determine activation energy using Arrhenius equation:

$$k = A_o \exp\left(\frac{-E_a}{RT}\right) \quad (\text{Eq. 1})$$

where A_o is the temperature independent factor, k is the second-order rate constant and R is the gas constant (8.314 J/mol/K). The activation energy, E_a , can be determined from the slope of $\ln(k)$ versus $1/T$ plot.

2.7. Statistical Analysis

The data are analyzed with a parametric two-way analysis of variance (ANOVA) to test the significant differences between treatments ($p = 0.05$). The goodness of fit between the experimental data and predicted values is expressed by the correlation coefficient R^2 (values close or equal 1). Just because R^2 is close to one, this does not mean that the fit is necessarily good (Chapra and Canale, 1998). Therefore, the conformity between the experimental data and the model predicted values is expressed by the total mean error ($E\%$) (Okasha and Ibrahim, 2010; Press et al., 1989):

$$E \% = \frac{\sum_{i=1}^n |q_{e(\text{exp.})} - q_{e(\text{Calc.})}|}{\sum_{i=1}^n q_{e(\text{exp.})}} \quad (\text{Eq.2})$$

3. Results and Discussion

3.1. Optimum Conditions

3.1.1 Effect of Contact Time

The effect of contact time on adsorption of Cd(II) onto Ashkida soil is shown in Fig. 1. The plot reveals that the adsorption process is relatively fast, whereas the percentage of Cd(II) removal reaches

equilibrium in 60 min of contact time. The Cd(II) removal efficiency at 60 min is 89.6%. It is evident that there is no benefit further agitation beyond 60 min (statistically no significant difference between data from 1 to 24 h). Therefore, an equilibrium time of 60 min can be regarded as an optimum contact time. Reaching equilibrium in a short time duration is an indication that the adsorption sites are well exposed, and bonding of the Cd(II) ions to active sites occurs preferably on the solid surface, with no significant ion diffusion towards the inside of the particle (Blazquez et al., 2005; Pehlivan et al., 2006).

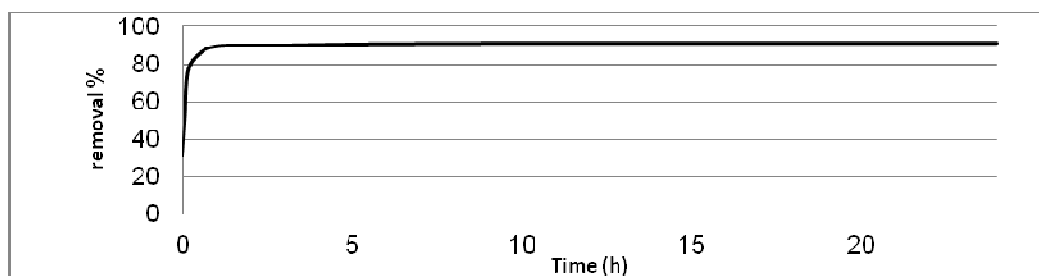


Figure 1. Effect of Time on Cadmium Removal by Ashkida Soil

3.1.2. Effect of pH

The pH of the aqueous solution is an important variable, as it controls the adsorption of the metal at the clay-water interfaces. Hence, the influence of pH on the adsorption of Cd(II) ions onto Ashkida soil is investigated in the pH range of 2-11. It can be observed from the results (Fig. 2) that the adsorption of ions increases with an increase in pH of the solution. However, an efficient removal corresponds to a natural pH or slightly basic pH. The major components of adsorbent (Ashkida soil) are clays and iron oxides which are known to possess negative surface charges in solution. As pH changes, surface charge also changes, and the sorption of charged species are affected (attraction between positively charged Cd(II) ions and negatively charged clay surface). It is conceivable that at low pH values, where there is an excess of H^+ ions in the solutions, a competition exists between the positively charged hydrogen ions and the metal ions for the available adsorption sites on the negatively charged adsorbent surface. On one hand as the pH increases and the balance between H^+ and OH^- are rather equal, more of the positively charged metal ions in solution are adsorbed onto the negative adsorbent surface and thus the percentage removal of the metal ions increases. On the other hand, precipitation of metal hydroxides may also occur as the pH in solution increases that results in a corresponding decrease in the amount of metal ions adsorbed.

Apparently as in Fig. 2, the removal percentage increases as the pH level increases. The sorption of Cd(II) ions is primarily affected by the surface charge on the adsorbents, which in turn is influenced by the pH of the solution. The low metal adsorption at low pH can be explained by the competitive sorption between proton and Cd(II) ions. As the solution pH increases, the number of negatively charged sites increases, which result in further sorption of Cd(II) ions. The change in H^+ and OH^- ions in the solution cause the surface functional groups on adsorbent minerals to protonate or deprotonate by adsorption of H^+ or OH^- ions. Above the pH value of 6.0, metal ions can be

precipitated with OH^- ions, and precipitation plays an important role in controlling Cd(II) concentrations.

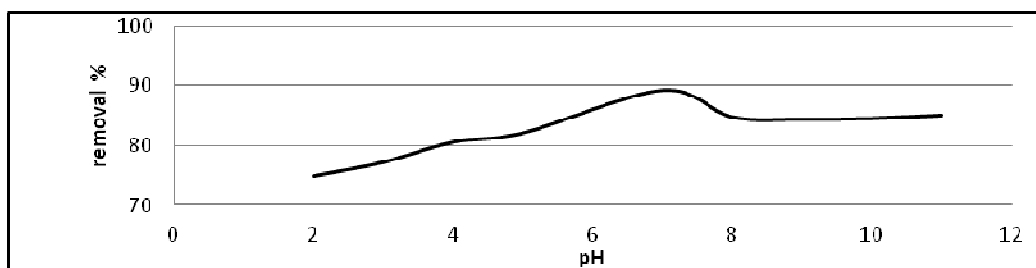


Figure 2. Effect of pH on Cadmium Removal by Ashkida Soil

3.1.3. Effect of the Amount of Adsorbent

The relationship between the amount of Ashkida soil and Cd(II) removal from the aqueous solution is illustrated in Fig. 3. Increased amount of soil, up to 1.0 g, increases the percentage removal of cadmium. This is an expected result as the amount of adsorbent increases, the number of adsorbent particles surrounded by metal ions increases. Therefore, these particles can accommodate more ions onto their surfaces (Gong et al., 2005). Despite the significant removal percentage of Cd(II) as the adsorbent doses increased from 1.0 to 2.0 g, statistical analysis shows that there are no significant differences between 1.0 and 1.5 g and between 1.5 and 2.0 g of adsorbent dose. Therefore one gram dose of adsorbent can be regarded as an efficient amount to perform the investigation.

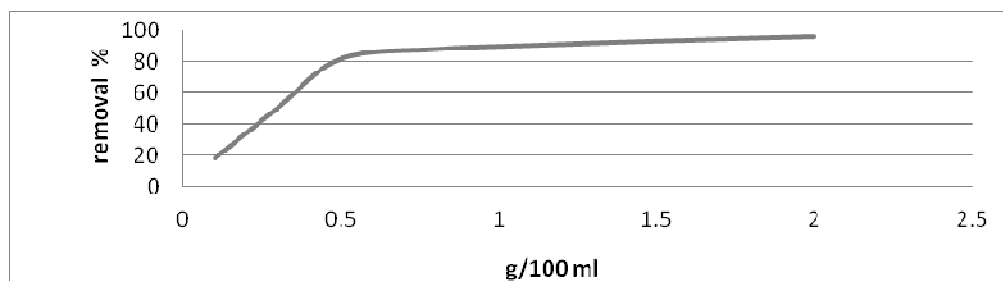


Figure 3. Effect of Adsorption Dose on Cadmium Removal by Ashkida Soil

3.1.4. Effect of Agitation

The effects of agitation rate on cadmium removal from aqueous solutions are illustrated in Fig. 4. The removal of cadmium ions increases as the agitation rate increases from 50 to 500 rpm. Increasing agitation rate decreases the boundary layer resistance to mass transfer surrounding particles. A statistical test shows that there is a significant difference between the percentage of heavy metal removal as agitation rate from 50 to 500 rpm and no significant difference between the percentages of

Cd(II) removal from as agitation rate is increased from 500 to 1500 rpm. Therefore, the optimum agitation rate corresponds to the highest of 89.27% is 500 rpm.

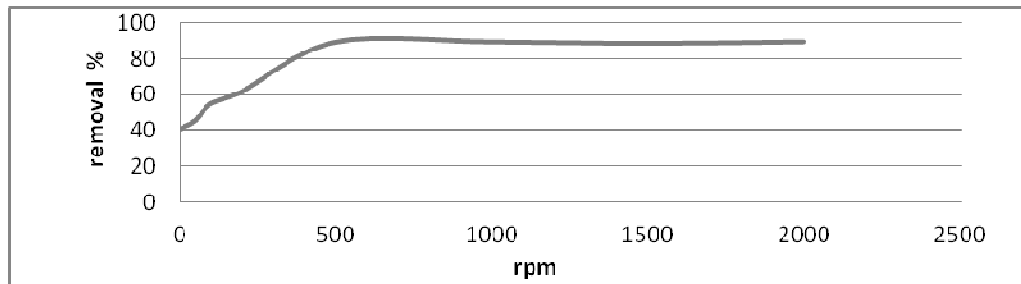


Figure 4. Effect of Agitation Rate on Cadmium Removal by Ashkida Soil

3.2. Equilibrium Studies

Three isotherms, Freundlich, Langmuir and Temkin show that adsorption of cadmium rises sharply at the initial stage for two C_e values (Fig. 5), an indication of presence of plenty radial sites. It can be observed that adsorption corresponding to equilibrium concentrations above 20 mg/l is reduced dramatically due to lesser available active site at the end of the adsorption process. However, Dubinin-Radushkevich is excluded as it does not fit with the experimental data.

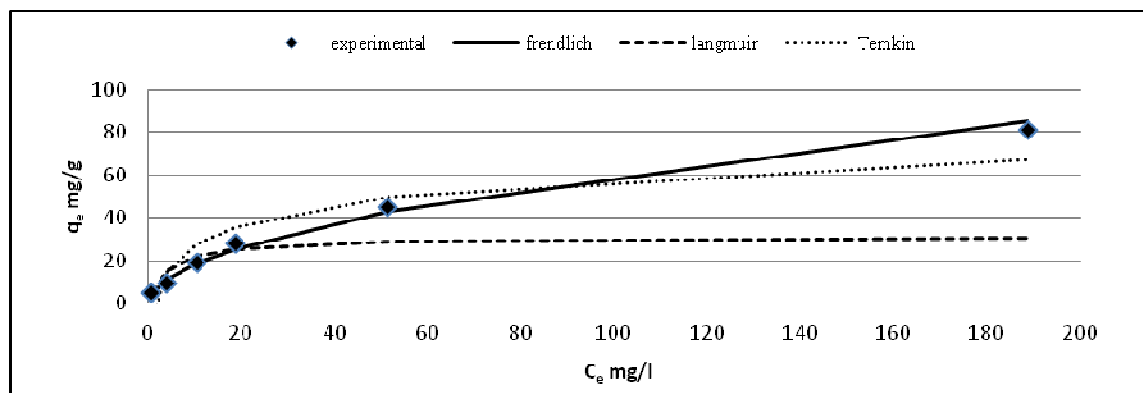


Figure 5. Equilibrium Isotherms of Cadmium on Ashkida Soil.

3.1.1. The Langmuir Isotherm

Langmuir isotherm has found successfully application in many real sorption processes and is expressed as:

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

Where q_e (mg/g) and C_e (mg/l) are the amount of adsorbed Cd(II) per unit weight of adsorbent and unadsorbed Cd(II) concentration in solution at equilibrium, respectively. The constant K_L is the Langmuir equilibrium constant and the K_L/a_L gives the theoretical monolayer solution capacity, q_{max} . Therefore, a plot of C_e/q_e versus C_e gives a straight line of slope a_L/K_L and intercepts $1/K_L$. The values of the Langmuir constants a_L , K_L and q_{max} with the correlation coefficient are listed in Table 2 and the Langmuir isotherm is plotted in Fig. 5 together with the experimental data points. The mean total error ($E\%$) between this model with the experimental data is 5.68 %. We note that the monolayer saturation capacity (q_{max}) is 31.25 mg/g. The total mean error is higher than Freundlich isotherm value.

Table 2. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Constants

Langmuir				Temkin			
K_L (l/g)	q_{max} (mg/g)	R^2	$E\%$	B	A (l/g)	R^2	$E\%$
0.236	31.25	0.915	5.68	0.738	181.9	0.864	22.52
Freundlich				Dubinin-Radushkevich			
K_F	n	R^2	$E\%$	q_m (mg/g)	B (mg ² /J ²)	R^2	$E\%$
5.383	1.898	0.991	0.14	363.1	98.73	0.545	--

3.1.2. Freundlich Isotherm

The Freundlich isotherm equation is given as:

$$q_e = K_F C_e^{1/n} \quad (\text{Eq. 4})$$

Where K_F is Freundlich constant and n is Freundlich exponent. K_F and n can be determined from the linear plot of $\log q_e$ versus $\log C_e$. The values of the Freundlich constant together with the correlation coefficient are presented in Table 2 and the theoretical Freundlich equation is shown in Fig. 5. The mean total error, $E\%$, of 0.41% is much lower than those corresponding to the other two models. It is evident from Fig. 5 that Freundlich equation represents the best fit of the experimental data.

3.1.3. Temkin Isotherm

The linear form of Temkin isotherm is represented by Eq.5:

$$q_e = \frac{RT}{b} \ln(A) + \frac{RT}{b} \ln(C_e) \quad (\text{Eq. 5})$$

A plot of q_e versus $\ln C_e$ enables one to determine the Temkin constants A and B (Table 2) and the corresponding theoretical plot of this isotherm is shown in Fig. 5. The correlation coefficient is also listed in Table 2. The mean total error, $E\%$, of 22.52 % associated with this model is higher than the Langmuir's and Freundlich's.

3.1.4. Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich equation has the following form:

$$q_e = q_m e^{-\beta \varepsilon^2} \quad (\text{Eq. 6})$$

Where q_m is the Dubinin-Radushkevich monolayer capacity (mg/g), β is a constant related to sorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = \frac{RT}{M} \ln \left(1 + \frac{I}{C_e} \right) \quad (\text{Eq. 7})$$

Where R is the gas constant (8.314 J/mol/K), T is the absolute temperature and M is the molecular weight of adsorbate.

The constants, q_m and β obtained for Dubinin–Radushkevich isotherm model are showed in Table 2. The correlation coefficient of 0.545 indicates that the Dubinin–Radushkevich isotherm model is inappropriate for the equilibrium experimental data as the maximum adsorption capacity, q_m , is unrealistic.

3.3. Kinetic Studies

In order to examine the mechanism of adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the adsorption rate. A number of models such as homogeneous surface diffusion and heterogeneous diffusion models have been extensively applied in batch experiments to describe the transport of adsorbate inside the adsorbent particles (Wu et al., 2009). The conformity between experimental data and the model predicted values is expressed by the correlation coefficient, R^2 . A relatively higher R^2 value implies that the tested model describes the kinetics of Cd(II) adsorption better.

3.3.1. Simple First Order Model

The sorption kinetics may be described by a simple first order equation (Boparai et al., 2011; Eligwe et al., 1999). The change in bulk concentration of the system can be described using the following linear form:

$$\log C_t = \frac{k_1}{2.303} t + \log C_o \quad (\text{Eq. 8})$$

Where C_t and C_o are the concentration of Cd(II) at time $t=t$ and $t=1$ in mg/l , respectively, and k_1 is the first order rate constant (l/min).

The experimental results show that $\log C_t$ versus t (Fig. 6) for different initial concentrations of Cd(II) deviates considerably from the theoretical data. A comparison of the results and the correlation coefficient is shown in Table 3, which indicates the failure in expressing this adsorption process by the simple first order kinetics. It is proposed that simple kinetic models such as first order rate equation are not applicable to the adsorption system with solid surfaces, which are rarely homogeneous like Ashkida soil, as the effect of transport phenomena and chemical reactions are often experimentally inseparable (Boparai et al., 2011; Sparks, 1989).

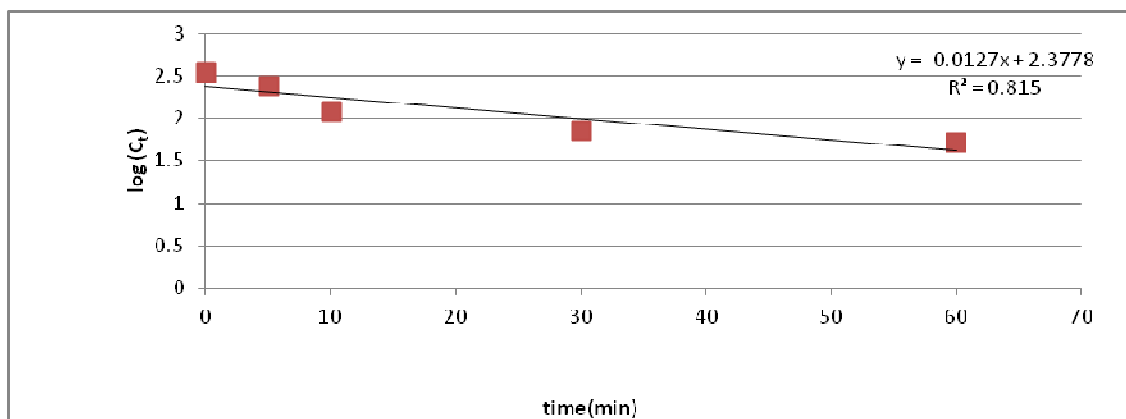


Figure 6. A simple First Order Adsorption Kinetics of Cd(II) on Ashkida Soil

3.3.2. Pseudo First-Order Model

The sorption kinetics may also be described by a pseudo first order equation (Boparai et al., 2011; Ho and McKay, 1999; Wu et al., 2009; Zhau et al., 2011). Integration of the linear form of the differential equation and using the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ is yields:

$$\log (q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (\text{Eq. 9})$$

Where q_e and q_t are amounts of adsorbed cadmium in (mg/g) at equilibrium and at a time t , respectively, and k_1 is the equilibrium rate constant of pseudo first-order adsorption (1/min).

Fig.7 shows a plot of the linear form of pseudo first-order model at all concentrations studied. The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t are used to determine the pseudo first-order constant k_1 and equilibrium adsorption density q_e . The experimental data show a considerable deviation from the theoretical data. A comparison of the results and the correlation coefficients in Table 3 reveal that the correlation coefficients for the pseudo first order kinetic model obtained at all the solution concentrations are relatively low. And the theoretical q_e values calculated by the pseudo first-order kinetic model offer no reasonable values. This suggests that this adsorption system is not a pseudo first-order reaction.

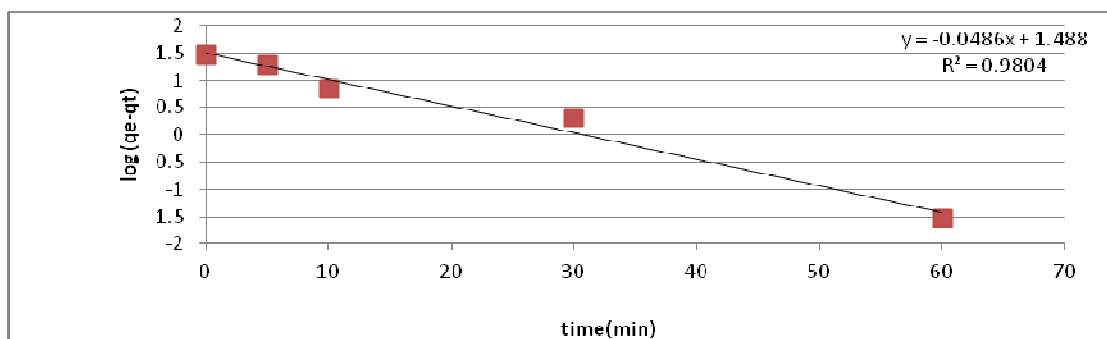


Figure 7. A Pseudo First-order Adsorption Kinetics of Cd (III) on Ashkida Soil.

3.3.3. Pseudo Second-order Model

The adsorption kinetics may also be described by a pseudo second-order equation (Boparai et al., 2011; Ho and McKay, 1999; Wu et al., 2009; Zhau et al., 2011). Applying the boundary conditions to the linear form of the integrated differential equation the model becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (\text{Eq. 10})$$

Where k_2 is the equilibrium rate constant of pseudo second-order adsorption ($g/mg/min$). The slopes and intercepts of plots t/q_t versus t (Fig. 8) are used to calculate the pseudo second-order rate constants k_2 and q_e . The result shows a good agreement between the experimental data and the pseudo second-order kinetic model for different initial Cd(II) concentrations. The computed results obtained from the pseudo second-order kinetic model are provided in Table 3. The correlation coefficient for pseudo second-order kinetic model is 0.986 and the calculated q_e value agrees very well with the experimental data.

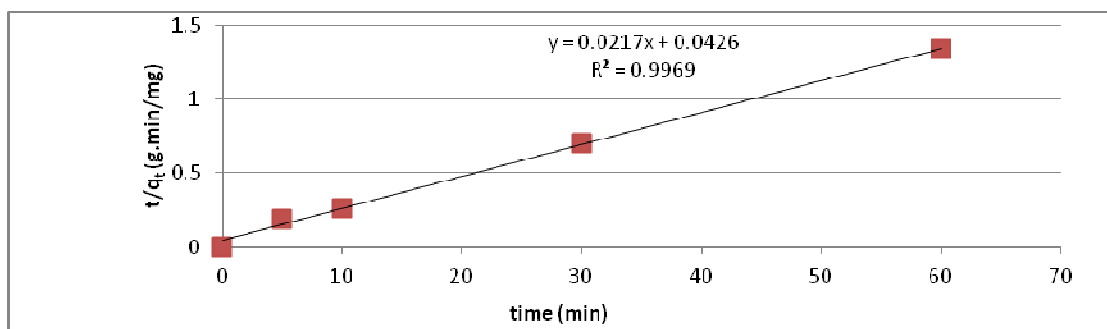


Figure 8. The Pseudo Second-order Adsorption Kinetics of Cd(II) on Ashkida Soil.

Table 3. Comparison of the Simple First Order, Pseudo First and Second Order Adsorption Values

$q_e \text{ exp.}$ (mg/g)	Simple 1st order		Pseudo 1 st order			Pseudo 2 nd order		
	k_1 (1/min)	R^2	k_1 (1/min)	$q_e \text{ cal.}$ (mg/g)	R^2	k_2 (g/mg.min)	$q_e \text{ cal.}$ (mg/g)	R^2
44.85	0.02764	0.815	9.046	30.76	0.980	0.0105	47.62	0.996

3.3.4. Activation Energy

The values of the pseudo second-order constant k_2 at different temperatures are deployed to estimate the activation energy of Cd(II) adsorption onto Ashkida soil by the Arrhenius equation as follows:

$$\ln k_2 = \ln A_o - E_a / RT \quad (\text{Eq. 11})$$

Where: A_o is the Arrhenius factor and R is the gas constant.

A straight line is obtained by plotting $\ln(k_2)$ constants against the reciprocal of the absolute temperature (Fig. 9) and the calculated value of activation energy is 10.77 kJ/mol . This relatively low activation energy indicates that the adsorption of Cd(II) on the adsorbent surface is rapid, and the adsorption is endothermic physisorption (Boparai et al., 2011).

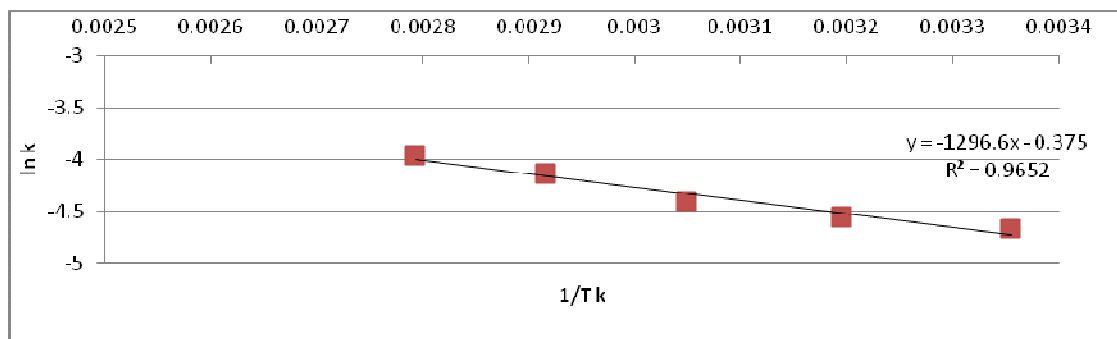


Figure 9. Arrhenius Diagram of Cd(II) Adsorbed on Ashkida Soil.

4. Conclusions

This study successfully concludes that Cd(II) can be adsorbed from aqueous solutions in significant amounts by Ashkida soil. In batch adsorption studies, removal of the metal ions increases with the increase in contact time, amount of Ashkida soil and pH value. The optimum conditions for Cd(II) removal are 60 min contact time, and pH 7 at 25 °C. The increase in initial metal ion concentration increased the amount of metal uptake per unit weight of the soil (mg/g). The equilibrium data have been analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Freundlich isotherm provides the best correlation and the lowest total error for sorption of cadmium onto Ashkida soil. The adsorption capacity of cadmium is 31.25 mg/g. The pseudo second-order kinetic model tends to agree very well with the dynamical behavior for the adsorption onto Ashkida soil for different initial concentrations over the whole range studied. The rate constant increases linearly with an increase in temperature, an indication of endothermic processes are involved. The Arrhenius' plot of the rate constants yields a small value of activation energy indicating that cadmium ions are easily adsorbed on the Ashkida soil. Therefore, removal at temperatures above ambient is rather cost ineffective.

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