Adsorption of Cd (II) metal ion on treated and untreated Bentonite clay from wastewater

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Abstract

In the present study, Bentonite has been used as adsorbent to remove Cd(II) ions from wastewater. The effect of different parameters such as initial Cd(II) ion concentration, temperature, pH have been studied. For kinetic study, Lagergren first order and pseudo second order equation have been used. For equilibrium study, Langmuir and Freundlich equation has been discussed. Thermodynamic parameters such as entropy change, enthalpy change, and Gibbs free energy change have been calculated and discussed.

Key words: - Cd(II) metal ion, Lagergren first-order equation, pseudo-second-order equation, Langmuir isotherm, Freundlich equation, Bentonite clay.

Introduction

Cadmium is used as an anticorrosive, electroplated onto steel. Cadmium sulphide and selenide are commonly used as pigments in plastics. Its compounds are used in electric batteries, electronic component and nuclear reactors. From these industries, the effluents going to the nearby river pollute water and cause severe health problems. A number of methods such as ion-exchange, reverse osmosis, membrane filtration etc. have been reported to remove the metals from polluted water. However, either these methods are costly or having insufficiency of technique. Among various methods, adsorption method is one of the easiest, safest and most cost effective methods because it is widely used in effluent treatment processes. A large number of substances have been studied as adsorbent. In the present study, Bentonite, a wastewater by-product of aluminium industry has been used as adsorbent.

Material and Methods

Bentonite clay and other chemicals were supplied by Loba Chemie. As analytical grade reagents and deionised water was used. The metal ions studied were Cd^{2+}. A.R. quality $Cd(NO_3)_2$ was used to prepare the stock solution in deionised water. Batch mode experiments were carried out for the study by shaking 1.0 g of Bentonite clay with 25 ml aqueous solution of Cd(II) of given concentration in different glass bottles. After pre-determined time interval, the solution was centrifuged and filtered and the solution was analyzed for concentration of Cd(II) ion by Atomic Adsorption Spectroscopy. Various parameters were contact time (20, 40, 60, 80, 100, and 120 min.), pH (2.0, 4.0, 6.5 and 8.0) and temperature (303K, 313K and 323K). Initial Cd(II) concentration used were 250,500,750,1000,1250,1500,1750,2000,2250 and 2500 mgL^{-1} for the equilibrium study and for rate study it was 250, 1000,1500, 2000 and 2500 mgL^{-1}.

Results and Discussion

Characterisation of Bentonite clay

Bentonite clay obtained from different sources contain the same basic chemical elements but in different proportions. Chemical composition of the present Bentonite clay obtained from XRF studies are: SiO_2 (47.73%) Al_2O_3(14.08%), Fe_20_3(4.03%), CaO(1.01%), Na_2O(1.60), MgO(2.06%), TiO_2 (1.00%) K_2O(1.60) and P_2O_5(1.05).

Effect of initial Cd(II) ion concentration and Contact time

The relationship between amount adsorbed (mgg^{-1}) and time (min.) at different initial concentration has been shown in figure 1. It is evident from the graph that the amount adsorbed increases with time till equilibrium is reached. The time of equilibrium is independent of initial concentration. Initially the rate of adsorption is fast which might be due to the presence of more number of active sites on the surface of Bentonite clay. As the process of adsorption goes on, the number of active sites decreases and so the rate of adsorption also decreases.

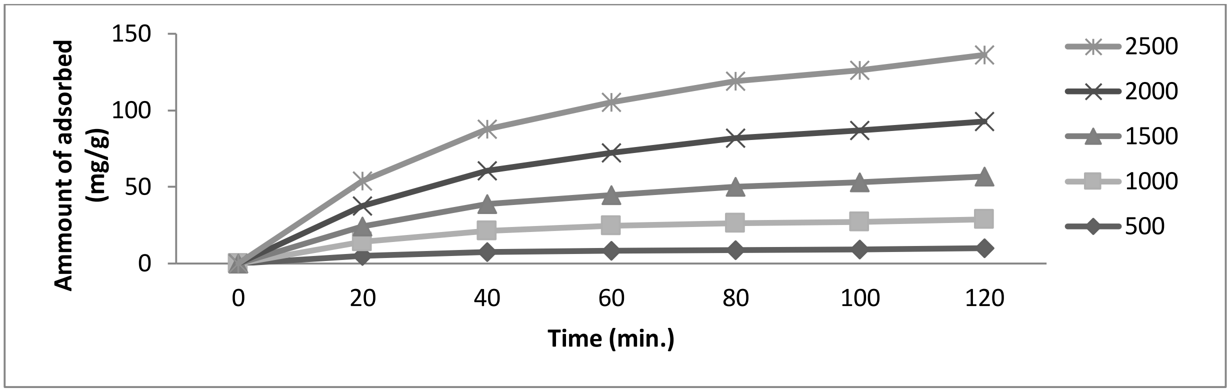

Fig. 1- Effect of initial Cd(II) ion concentration and Contact time

Effect of pH

The pH of the medium has pronounced effect on the adsorption. From figure-2 it is evident that the amount of Cd(II) adsorbed on Bentonite clay increased from 6.16 mgg^{-1}(49.28 %) to 30.73 mgg^{-1} (86.24 %) by increasing pH of solution from 2.0 to 10.0

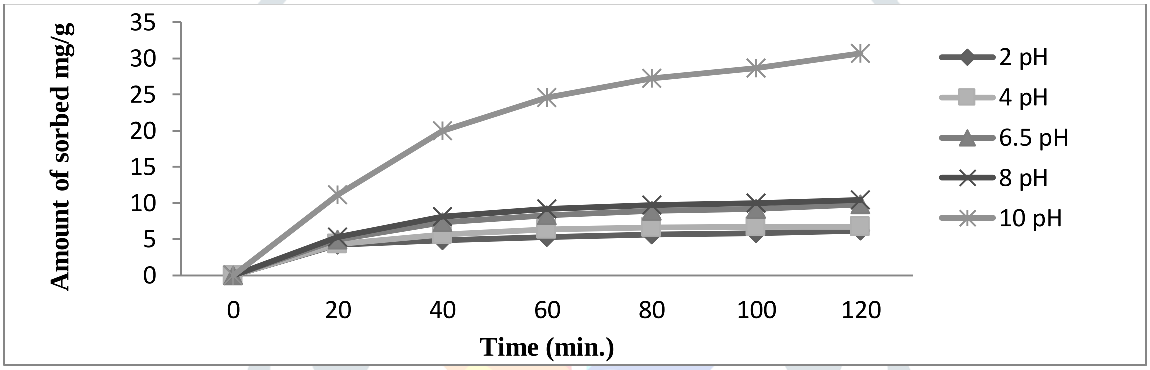

Fig 2 - Effect of pH on the adsorption of Cd(II) on Bentonite clay

Effect of temperature

The relationship between q_e (mgg^{-1}) and time (min.) at different temperatures has been presented in figure 3. It is evident that adsorption of Cd(II) ion on Bentonite clay increases from 9.76 mgg^{-1} (78.08 %) to 11.64 mgg^{-1} (93.12%) by increasing temperature from 303K to 323K indicating the process to be endothermic.

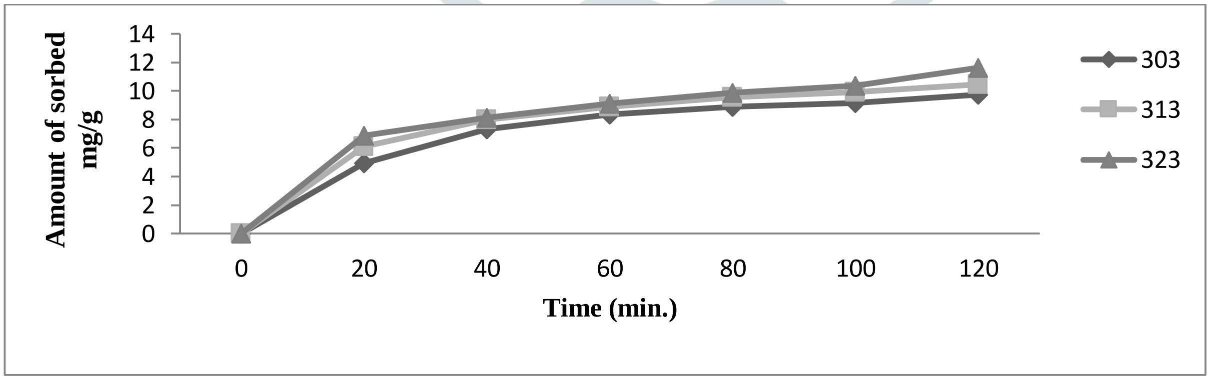

Fig. 3 - Effect of temperature on the adsorption of Cd(II) ion on Bentonite clay

Adsorption Isotherm

Langmuir adsorption isotherm assumes that monolayer adsorption takes place on a homogeneous surface without interaction between adsorbate and adsorbent particles. The linear form of Langmuir isotherm is given as

$$Ce/qe = 1/\varphi.b + Ce/\varphi$$

Where Ce (mgL^{-1}) is equilibrium concentration of Cd(II) and φ and b are Langmuir constants related to adsorption capacity and adsorption energy respectively.

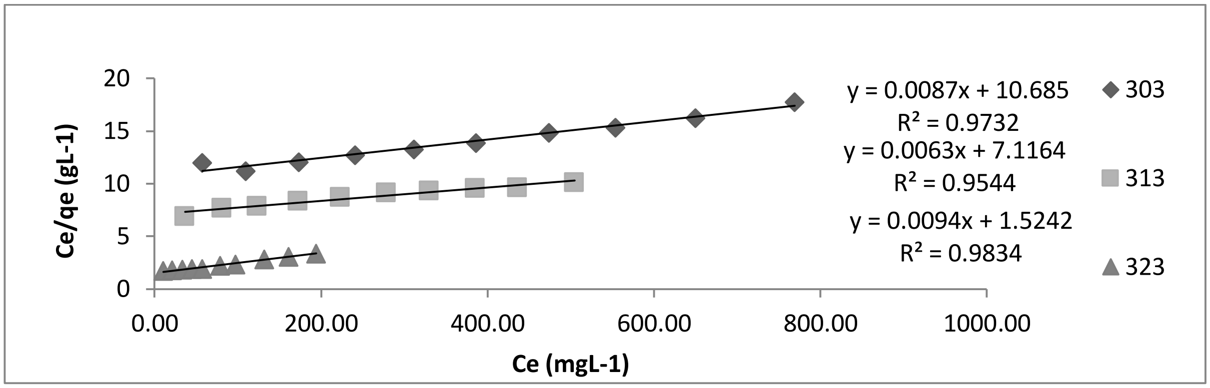

Fig. 4 – Langmuir isotherm for adsorption of Cd(II) ion on Bentonite clay

Table – 1 adsorption isotherm constants for adsorption of Cd(II)ion on Bentonite clay

Langmuir isotherm results			
Tem. K	Correlation coefficient R^2	φ	b
303	0.973	125.00	0.000749
313	0.954	166.67	0.000843
323	0.983	111.11	0.005906

Kinetics of Adsorption

The Lagergren first order and pseudo-second-order have used to discuss the adsorption kinetics.

The Lagergren first order rate equation is represented as:

$$\log (q_e - q_t) = \log q_e - k_1.t/2.303$$

Pseudo second order rate equation is represented as:

$$t/q_t = 1/k_2.q_e^2 + t/q_t$$

Where qe and qt are the amounts of Cd(II) adsorbed (mgg^{-1}) at equilibrium and at time t, respectively. k_1 is the Lagergren rate constant (min^{-1}). k_2 (g/mg/min.) is the rate constant of second order adsorption. Plots for both Lagergren first order and pseudo second order equation has been shown in figure -5 and 6 respectively.

Different adsorption parameters for both models have been presented in table -2 and 3. Values of qe(cal) and k_1 and k_2 at different initial concentrations have been calculated from the slope and intercept respectively. These values have been given in table-2 and 3.

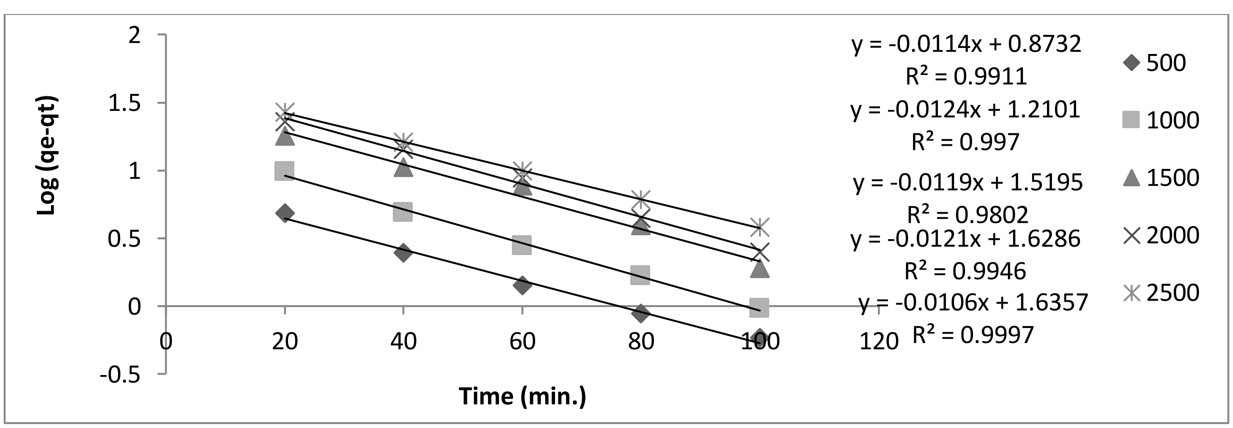

Fig. - 5 Lagergren first order for adsorption of Cd(II) ion on Bentonite clay

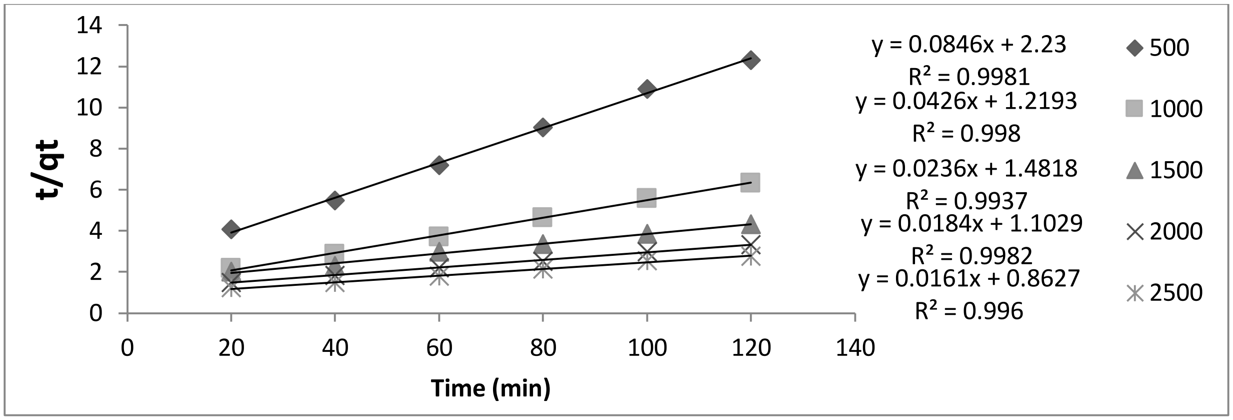

Fig. - 6 pseudo-second-order for adsorption of Cd(II) ion on Bentonite clay

It is evident from table-2 and 3 that R^2 values are higher in the case of pseudo second order equation than in the case of first order equation. It may be concluded therefore that kinetic data fit better in pseudo second order equation. It can be seen from the table that k_2 decreases with increase in concentration. It might be due to the possibility of low competition for active sites at lower concentration of metal ions at higher concentration of metal ions. The competition for the surface active sites increases which decreases the rate. Other investigators have found the same result.

Table 2- Lagergren first order kinetics parameters for adsorption of Cd(II) ion on Bentonite clay

	Lagergren first order			
Conc. mgL^{-1}	K_1 min^{-1}	q_{exp} mgg^{-1}	q_{cal} mgg^{-1}	R^2
500	$2.533X\ 10^{-2}$	9.76	7.464	0.991
1000	$2.764\ X\ 10^{-2}$	18.97	16.22	0.997
1500	$2.533X\ 10^{-2}$	27.83	33.04	0.980
2000	$2.764\ X\ 10^{-2}$	36.14	42.56	0.994
2500	$2.303\ X\ 10^{-2}$	43.26	43.15	0.999

Table 3- pseudo-second- order kinetics parameters for adsorption of Cd(II) ion on Bentonite clay

	pseudo-second- order kinetics			
Conc. mgL^{-1}	K_2 g/mg/min	q_{exp} mgg^{-1}	q_{cal} mgg^{-1}	R^2
500	$3.16\ X\ 10^{-3}$	9.76	11.90	0.998
1000	$1.45\ X\ 10^{-3}$	18.97	23.81	0.998
1500	$0.36\ X\ 10^{-3}$	27.83	43.48	0.993
2000	$0.29\ X\ 10^{-3}$	36.14	55.56	0.998
2500	$0.29\ X\ 10^{-3}$	43.26	62.50	0.996

Thermodynamic treatment of the adsorption process

The thermodynamic parameters such as free energy, enthalpy and entropy changes have been calculated using the following equations.

$$K_e = C_s/C_e$$

$$\Delta G = -\ RT\ In\ Kc$$

$$\log K_c = \Delta S/2.303\ R - \Delta H/2.303\ RT$$

Where C_e is the equilibrium concentration in solution in mgL^{-1} and C_s is the equilibrium concentration on the adsorbent in mgL^{-1} and K_c is the equilibrium constant. The Gibbs free energy, ΔG was calculated from the above equation. Slope and intercept of the straight line obtained from the plot between log K_c vs. 1/T gives the value of ΔH and ΔS respectively. These values have been given in table-4.

Table-4 Thermodynamic parameters for adsorption of Cd(II) on Bentonite clay

Temp. K	ΔG kJ/mol	ΔH kJ/mol	ΔS J/mol
303	-2.888	27.304	99.85
313	-4.076		
323	-4.877		

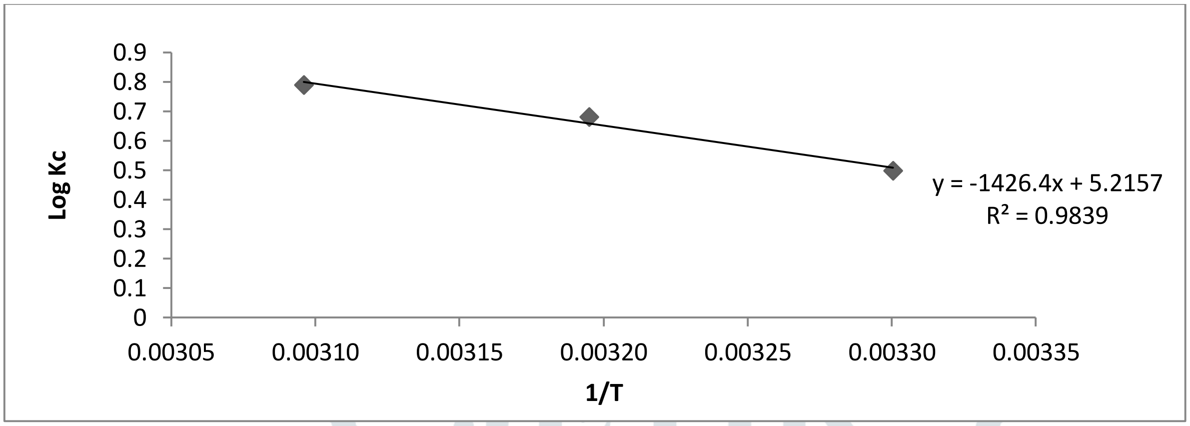

Fig.7 Thermodynamic treatment of the adsorption of Cd(II) on Bentonite clay

The negative value of free energy indicates the spontaneity of the process. Positive value of enthalpy shows the endothermic nature of adsorption. The positive value on entropy show the affinity of the adsorbent for the Cd(II) ions.

Conclusion

It is evident that initial Cd(II) ion concentration, contact time, pH and temperature have marked effect on adsorption. The equilibrium data are best explained by Langmuir adsorption isotherm. Kinetics of adsorption follows second order rate equation. Thermodynamic parameters also favour the adsorption. It is expected that Bentonite clay may be used as an efficient adsorbent under suitable conditions.

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