



A Study on Adsorption of Cd(II) from Aqueous Solution Using Fly Ash

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Abstract: In this study, fly ash has been used to remove cadmium(II) ion from waste water by batch mode experiments. Different parameters such as initial concentration of metal ion, pH, temperature and particle size have been investigated to study the removal characteristics. Data obtained have been used to discuss the kinetics of adsorption using Lagergren's pseudo first order and pseudo second order kinetic equation. Equilibrium data have been discussed using Langmuir adsorption isotherm and Freundlich adsorption isotherm. Spontaneity and feasibility of the process have been evaluated using thermodynamic parameters such as change in free energy ΔG , change in enthalpy ΔH , change in entropy ΔS . Activation energy and sticking probability have been calculated and discussed.

Key words: Fly ash, adsorption, cadmium(II) ion, Langmuir isotherm, Freundlich isotherm, Lagergren first-order equation, pseudo-second-order equation.

I. Introduction

Cadmium is produced mainly as a byproduct from mining, smelting and refining sulfidic ores of zinc, lead and copper. Rocks mined to produce phosphate fertilizers contain varying amounts of cadmium. It is used in batteries, electroplating, nuclear fission, picture tubes of television, photocopier drums, paint pigments etc. In due course these are dumped in river or soil, thereby causing pollution to water and soil. This ultimately affects the environment and the living organisms. It causes pneumonitis, pulmonary edema and death.

There are a number of methods [1-3] to remove heavy metals from aqueous system. One of them is adsorption method which is effective, economical and easy to handle. A large number of substances have been used as adsorbent to remove heavy metals from aqueous system.

Fly ash is a waste product produced from a thermal power plant by burning of coal. Many studies have shown that it may be used as an adsorbent. Various parameters such as temperature, pH, particle size, contact time and initial metal ion concentration have been investigated to characterise fly ash as an adsorbent. Different isotherms, rate equations and thermodynamics of adsorption have been discussed.

II. Material and Methods

The fly ash used in this study was of JSPL, a coal burning power plant of Raigarh (C.G). To characterize it, SEM, FTIR and XRF analysis were obtained from SAIF – IIT Bombay. It was washed and dried at 105°C and sieved. Stock solution of Cd(II) was prepared from A.R quality Cd(NO₃)₂.

25 mL of aqueous solution of desired concentration of Cd(II) was taken in different glass bottles and in each bottle 1.0 g of fly ash of desired size was added. The pH of the solution was adjusted using 0.1M HCl and 0.1 M NaOH as required. It was then agitated by keeping it in shaking machine at desired temperature. After pre-determined time interval, the bottles were taken out, centrifused, filtered and the solution was analysed for concentration of remaining metal ion by Systronic Spectrophotometer 118. Different parameters were pH: 2.0, 4.0, 6.5, and 8.0, temperature: 303K, 313K and 323K, particle size: 45 μ , 75 μ , 150 μ , initial metal ion concentration: 100, 150, 200 and 250 mgL⁻¹ for rate study and 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 mgL⁻¹ for equilibrium study.

Following mass balance equations [4] to determine the amount of Cd(II) ions adsorbed in milligram per gram (q_e) and for percentage removal were used:

$$q_e = V (C_i - C_e) / m$$

$$\text{Removal \%} = 100 (C_i - C_e) / C_i$$

where C_i and C_e are Cd(II) ion concentration in mgL⁻¹ before and after adsorption respectively, V is the volume of adsorbate in litre, and m is the weight of the adsorbent in grams.

III. Results and Discussion

Characterisation of fly ash

Different fly ash contain the same basic chemical elements but in different proportions. The chemical composition (wt %) of present fly ash sample obtained from XRF studies are: SiO₂(43.17%), Al₂O₃(13.25%), Fe₂O₃(41.20%), CaO(1.09%), MgO(0.73%), TiO₂(1.26%).

Above results show that SiO_2 and Al_2O_3 contents make up about 56.42 % of fly ash. Fe_2O_3 and CaO contents compose about 42.29 %. This fly ash can be classified as class F [5] as CaO content is less than 10% and SiO_2 , Al_2O_3 and Fe_2O_3 content is greater than 70% .

Figure-1 is the SEM image of fly ash. It is clear that finer fly ash particles (45μ) are primarily spherical whereas the coarser particles (150μ) are mainly composed of irregular and porous structure. Figure-1(c) is the SEM image of fly ash(45μ) after adsorption.

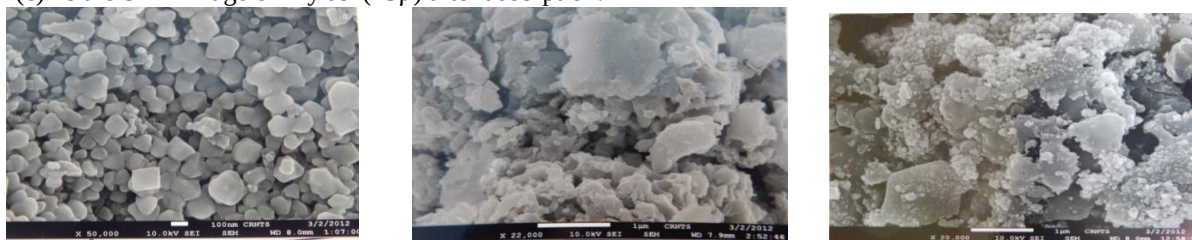


Figure 1. (a) Before adsorption (45μ) (b) Before adsorption (150μ) (c) After adsorption

The FTIR spectra of fly ash before and after adsorption is shown in figure-2. It shows a broad band around 3500 cm^{-1} , which is attributed to surface -OH group of silanol groups (-Si-OH) and adsorbed water molecules on the surface. A peak around 1622.19 cm^{-1} is attributed to bending mode (δ O-H) of water molecule [5].

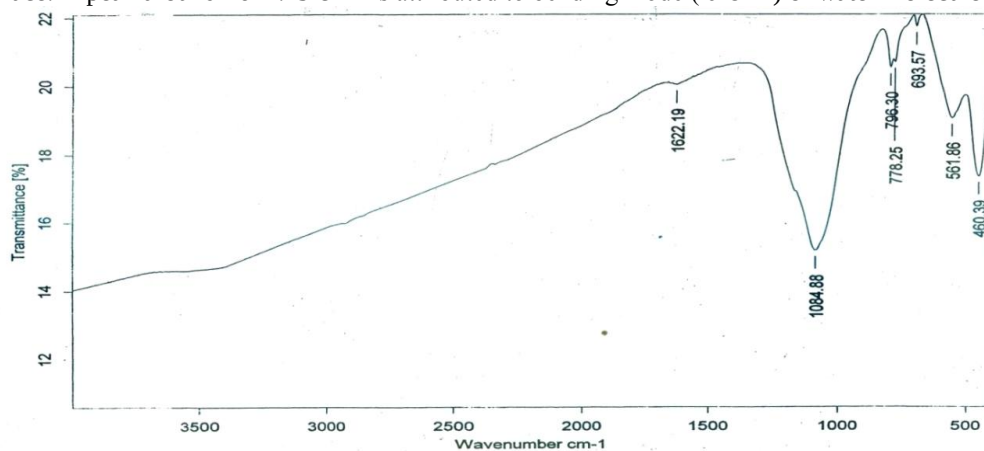


Figure 2. (a) FTIR Before adsorption

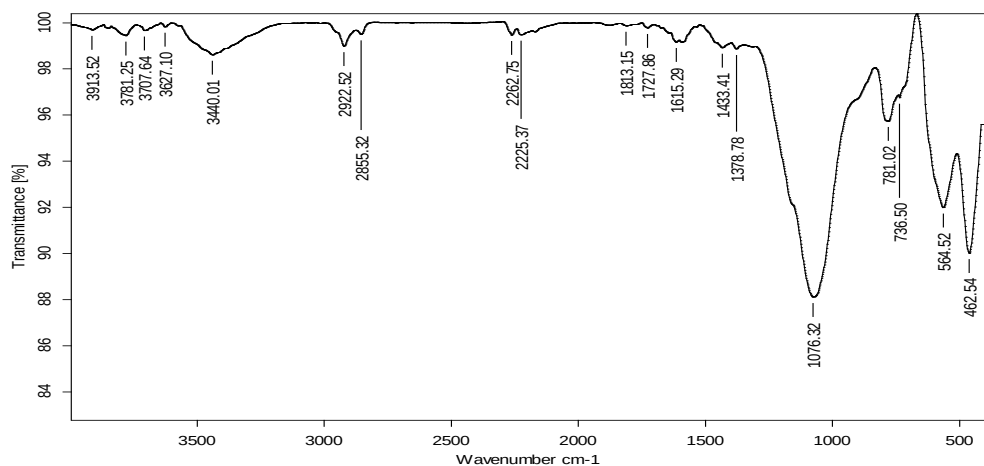


Figure 2. (b) FTIR After adsorption

The main broad band at 1084.88 cm^{-1} in the fly ash before adsorption, corresponding to asymmetric stretching vibrations of Si-O-Si and Al-O-Si becomes sharper and shifts toward lower frequency 1076.32 cm^{-1} as a result of the formation of new reaction products. The bands located at 796.30 cm^{-1} and 460.39 cm^{-1} are ascribed to bending vibrations of Si-O-Si and O-Si-O bonds, implying the presence of quartz. The bands located at 693.57 cm^{-1} and 561.86 cm^{-1} indicate the presence of mullite [6]. After adsorption appearing of new bands and shifting of old bands indicate that adsorption has taken place.

Effect of initial Cd(II) ion concentration

Percentage removal of Cd(II) ion versus initial metal ion concentration has been plotted in Figure-3. It is evident that percentage removal of Cd(II) ion decreases from 72.4% at 100 mgL^{-1} to 60.96% at 250 mgL^{-1} . Figure-4 represents relationship between q_e versus initial metal ion concentration. It is evident that q_e increases from 1.81 mgg^{-1} at 100 mgL^{-1} to 3.81 mgg^{-1} at 250 mgL^{-1} . The reason that percentage removal decreases with increase in

metal ion concentration might be due to the fact that adsorbents possess a limited number of active sites which becomes saturated at certain concentration. However, actual amount adsorbed (q_e) increases with initial metal ion concentration. The reason might be the fact that higher concentration provides necessary driving force to overcome the mass transfer resistance of Cd(II) ion between the aqueous phase and solid phase [7].

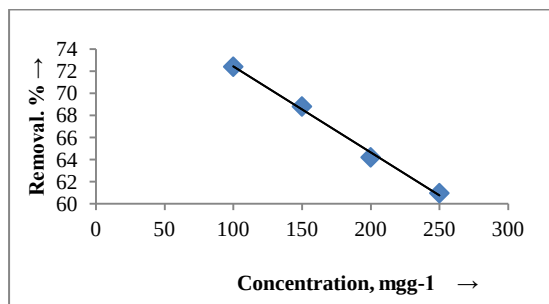


Figure-3. Effect of initial conc. on Cd(II) adsorption

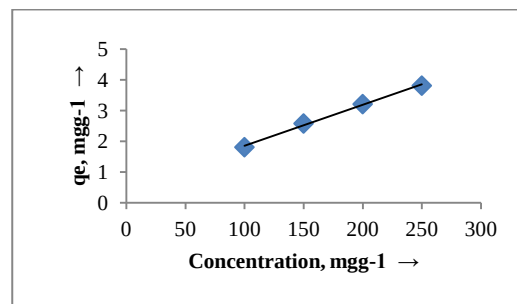


Figure-4. Effect of initial conc. on Cd(II) adsorption

Effect of contact time

Figure-5 represents the relationship between amount adsorbed and contact time. The amount adsorbed increases with time. Initially, the adsorption rate is fast which slows down till equilibrium. Initial high rate of adsorption may be attributed to the presence of more number of active sites which decreases slowly due to adsorption and so rate of adsorption also decreases [8-9].

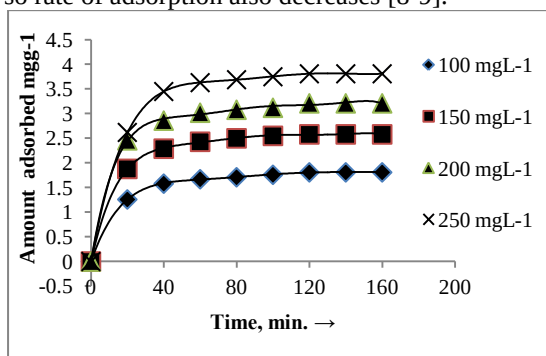


Figure-5. Effect of contact time on adsorption of Cd(II) ion

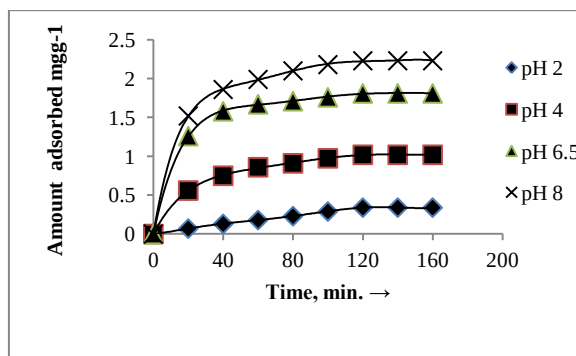


Figure-6. Effect of pH on adsorption of Cd(II) ion

Effect of pH

Figure-6 represents the relationship between amount adsorbed and pH. It is evident that the amount of Cd(II) ion adsorbed increases from 0.34mgg^{-1} (13.6%) to 2.23mgg^{-1} (89.2%) by increasing pH from 2.0 to 8.0. It has been shown that [10] fly ash particles are positively charged at low pH and negatively charged at high pH. As the metal ion possess positive charge so it is attracted more towards adsorbent surface at higher pH due to electrostatic force of attraction.

Effect of temperature

Figure-7 shows the relationship between amount adsorbed and temperature. It is evident that adsorption of metal ion increases from 1.81mgg^{-1} (72.4%) to 2.02mgg^{-1} (80.8%) by increasing temperature from 303K to 323K indicating the process to be endothermic. The rate constant of adsorption are 4.8×10^{-2} , 5.3×10^{-2} and 5.7×10^{-2} at 303K, 313K and 323K respectively supporting the endothermic nature of adsorption. The higher uptake of metal ion at higher temperature might be due to the fact that as temperature increases, mobility of ions increases and pore size of the adsorbent also increases which facilitates more adsorption.

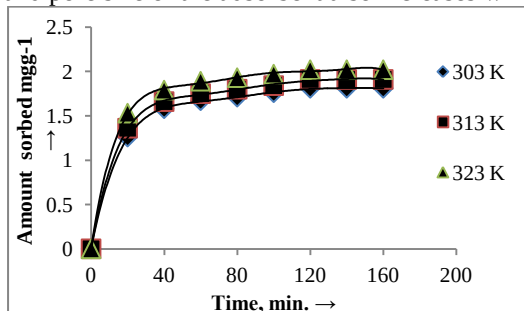


Figure-7. Effect of temperature on adsorption of Cd(II) ion

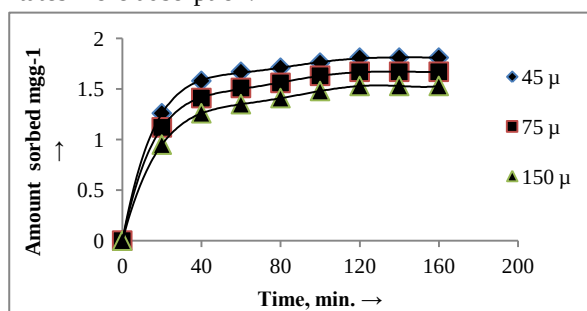


Figure-8. Effect of particle size on adsorption of Cd(II) ion

Effect of particle size

Figure-8 represents the relationship between amount adsorbed versus particle size. It is evident that amount adsorbed increases from 1.53 mgg^{-1} (61.2%) to 1.81 mgg^{-1} (72.4%) by decreasing the particle size from 150μ to 45μ . As particle size decreases, surface area increases. As a result the number of active sites increases thereby increasing the amount of adsorption.

Adsorption Isotherm

The linear form of the Langmuir [11] isotherm is given by the following equation

$$C_e/q_e = 1/\phi \cdot b + C_e/\phi$$

where C_e (mgL^{-1}) is equilibrium concentration of Cd(II) and ϕ and b are Langmuir constants. ϕ is related to adsorption capacity and b is related to adsorption energy. Figure-9 represents the relationship between C_e/q_e versus C_e which is linear suggesting that Langmuir isotherms is applicable. Slope and intercept of the straight line gives the value of ϕ and b respectively and are given in Table- 1. The result shows that the values of ϕ and b increases on increasing the temperature.

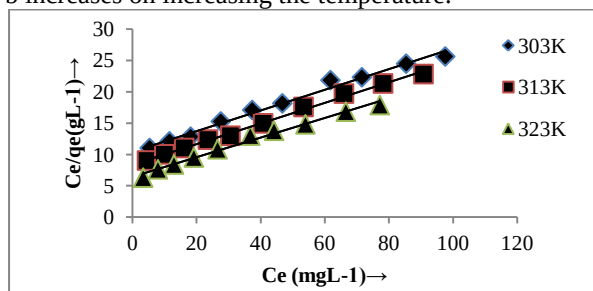


Figure-9. Langmuir isotherm for the adsorption of Cd(II) ion

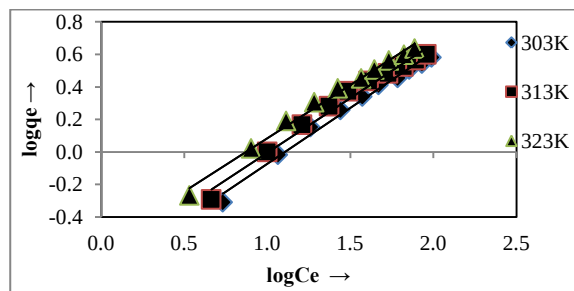


Figure-10. Freundlich isotherm for adsorption of Cd(II) ion

Table- 1. Adsorption isotherm constants for adsorption of Cd(II) on fly ash

Langmuir Isotherm Results				Freundlich Isotherm Results		
Temp.(K)	Correlation coefficient, R^2	ϕ	b	Correlation coefficient, R^2	K_f	n
303	0.987	6.06	0.016	0.988	0.175	1.46
313	0.996	6.09	0.019	0.982	0.213	1.49
323	0.987	6.41	0.024	0.991	0.222	1.53

A dimensionless separation factor (R_L) gives important information about the nature of adsorption and is defined as [12]

$$R_L = 1/(1+b \cdot C_i)$$

where C_i is the initial concentration in mgL^{-1} and b is Langmuir constant (L/mg) related to adsorption energy. The adsorption process is favourable if $0 < R_L < 1$ and unfavourable if $R_L > 1$. Besides $b > 0$ indicates the favourable adsorption process [13]. The calculated values of b and R_L is given in Table-1 and 2 respectively. As $b > 0$ and $0 < R_L < 1$, it suggests that the process is favourable.

Table- 2. Dimensionless separation factor (R_L)

-----	R_L		
C_i (mgL^{-1})	303 K	313 K	323 K
25	0.716	0.670	0.623
50	0.557	0.504	0.452
75	0.456	0.404	0.355
100	0.386	0.337	0.292
125	0.335	0.289	0.248
150	0.295	0.253	0.216
175	0.264	0.225	0.191
200	0.239	0.202	0.171
225	0.218	0.184	0.155
250	0.201	0.169	0.142

The Freundlich equation [11] has also been employed which is represented as :

$$\log q_e = \log K_f + 1/n \log C_e$$

where q_e is the amount of Cd(II) ion adsorbed (mgg^{-1}), C_e is the equilibrium concentration of Cd(II) ion in solution (mgL^{-1}) and K_f and n are constants for the adsorption capacity and intensity of adsorption respectively.

Figure-10 represents the plot of $\log q_e$ versus $\log C_e$ and values of K_f , n and R^2 (correlation coefficient) values have been obtained and given in Table-1.

It is evident from comparing R^2 values obtained from Langmuir plots and Freundlich plots that the experimental data fits better in Langmuir equation.

The Lagergren first order kinetic model

The Lagergren first order rate equation [14] is represented as :

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

where q_e and q_t are the amounts of Cd(II) adsorbed (mg g^{-1}) at equilibrium and at time t , respectively. k_1 is the Lagergren rate constant (min^{-1}). Figure-11 represents the plot of $\log(q_e - q_t)$ versus t . Slope and intercept of the straight lines obtained give the values of q_e and k_1 respectively. These values have been given in Table- 3.

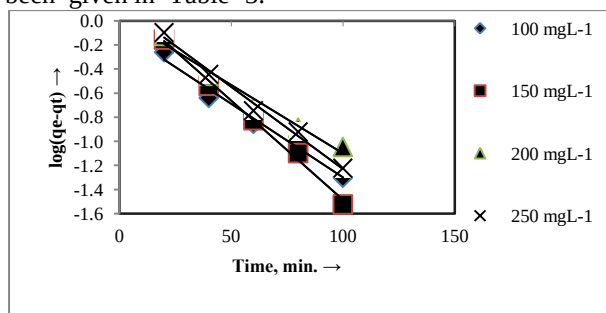


Figure- 11. Lagergren first-order kinetic plot

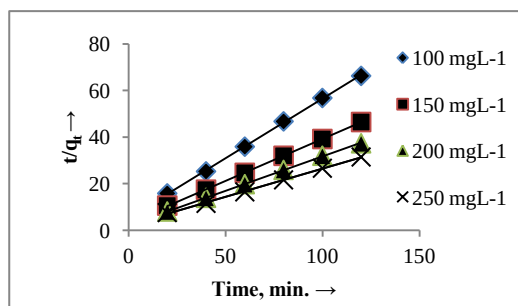


Figure- 12. Pseudo-second-order kinetic plot

The pseudo-second-order kinetic model

Pseudo-second-order kinetic model [15] is represented as :

$$t/q_t = 1/K_2 q_e^2 + t/q_t$$

where K_2 is the rate constant of second order adsorption (g/mg/min.). Figure-12 represents plot of t/q_t versus t . From the slope of the graph K_2 and q_e have been calculated and have been given in Table- 3.

Table- 3. Kinetic parameters for adsorption of Cd(II) ion on Fly ash

Conc mg L^{-1}	Lagergren first order				Pseudo- second- order		
	k_1 min^{-1}	q_{exp} mg g^{-1}	q_{cal} mg g^{-1}	R^2	k_2 g/mg/min	q_{cal} mg g^{-1}	R^2
100	2.76×10^{-2}	1.81	1.19	0.977	4.8×10^{-2}	1.96	0.999
150	3.68×10^{-2}	2.58	1.45	0.993	3.9×10^{-2}	2.79	0.999
200	2.53×10^{-2}	3.21	1.08	0.972	2.9×10^{-2}	3.86	0.999
250	2.99×10^{-2}	3.81	1.35	0.989	2.5×10^{-2}	4.13	0.998

It is evident from Table-3 that as R^2 values are higher in the case of pseudo-second-order kinetic model than Lagergren pseudo-first-order kinetic model, so the kinetic data fit better in pseudo-second-order kinetic model. Moreover, $q_e(\text{cal})$ values agree better with the experimental data in the case of pseudo-second-order kinetic model.

Thermodynamic treatment of the adsorption process

Thermodynamic parameters indicates the spontaneity and feasibility of the process. Thermodynamic parameters such as free energy, enthalpy and entropy changes can be estimated from the following equations [16].

$$\begin{aligned} K_c &= C_s / C_e \\ \Delta G &= -RT \ln K_c \\ \log K_c &= \Delta S / 2.303 R - \Delta H / 2.303 RT \end{aligned}$$

where C_e is the equilibrium concentration in solution in mg L^{-1} , C_s is the equilibrium concentration on adsorbent in mg L^{-1} and K_c is the equilibrium constant. The Gibbs free energy change (ΔG) was calculated from the above equation. Slope and intercept of the plot between $\log K_c$ versus $1/T$ (not shown) gives the values of ΔH and ΔS . All these values are listed in Table- 4.

Using modified Arrhenius type equation [17] related to surface coverage (θ), the values of activation energy (E_a) and sticking probability (S^*) have been calculated from the experimental data.

$$\theta = (1 - C_e / C_i)$$

$$S^* = (1 - \theta)e^{-E_a/RT}$$

The sticking probability, S^* , is a function of the adsorbate/adsorbent system under consideration and depends on the temperature of the system. It must satisfy the condition $0 < S^* < 1$. The values of E_a and S^* has been calculated from slope and intercept of the plot of $\ln(1-\theta)$ versus $1/T$ (not shown) respectively and have been shown in Table-4.

Table-4. Thermodynamic parameters for adsorption of Cd(II) ion on fly ash

Temp. K	ΔG , kJ/mol	ΔH , kJ/mol	ΔS , J/mol	E_a , kJ/mol	S^* , J K mol ⁻¹
303	-2.429	19.204	71.304	14.74	8.03×10^{-04}
313	-3.057				
323	-3.859				

Negative values of ΔG values indicate that the process is spontaneous. It is also evident from Table-4 that as temperature increases, negative values of ΔG increases which indicates the endothermic nature of the process. Endothermic nature of adsorption is further supported by positive ΔH value. The positive value of ΔS shows the affinity of the adsorbent for the Cd(II) ions. The value of E_a has been found to be 14.74 kJ mol⁻¹ for the adsorption. Positive value of E_a also support the endothermic nature of the adsorption process. Since $S^* \ll 1$, it indicates that the probability to stick on surface of fly ash is very high [18].

Mechanism:

Speciation [19] of Cd(II) with varying pH has been shown in figure-14.

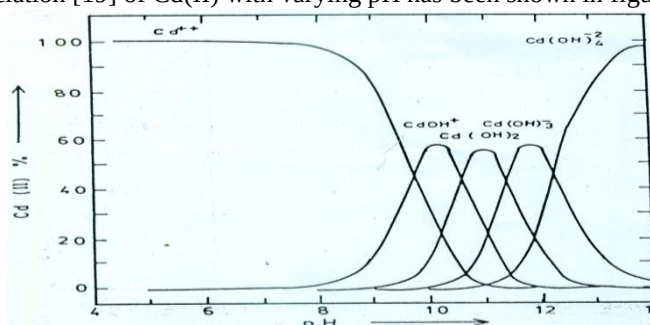
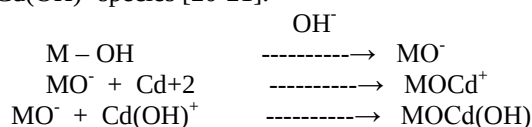


Figure-14. Speciation of Cd(II) with varying pH

It is evident that at lower pH, cadmium is in the form of Cd^{+2} and at higher pH it is in the form of $Cd(OH)^+$. It is probable that in acidic medium positively charged surface of adsorbent does not favour the association of cationic adsorbate species. In alkaline medium negatively charged surface offers the suitable sites for the adsorption of Cd^{+2} and $Cd(OH)^+$ species [20-21].



IV. Conclusion

It is evident that initial Cd(II) ion concentration, contact time, pH, temperature and particle size have marked effect on adsorption. The equilibrium data are best explained by Langmuir adsorption isotherm. Kinetic data for adsorption follows second order rate equation. Thermodynamic parameters also favour the adsorption. It is expected that due to chemical composition, structure, more adsorption sites, cheap, availability in plenty etc. fly ash may prove to be an efficient adsorbent.

Acknowledgements

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