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Removal of Zinc(II) from Aqueous Solution Using Fly Ash

Saroj Kumar[1*], Mishra A.K.[1], Upadhyay M.[2], D Singh[1], M Mishra[1] and Sujata Kumar[3]
[1]Department of Chemistry, K.Govt. Arts and Sc. College, Raigarh, CG, INDIA
[2]Department of Chemistry, Dr. C.V.Raman University, Bilaspur, CG, INDIA
[3]Department of Chemistry, Kirodimal Institute of Technology, Raigarh, CG, INDIA

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Abstract

The removal characteristics of fly ash has been evaluated to remove Zn(II) from aqueous solution under different conditions. Batch experiments have been carried out for this purpose. Kinetics of adsorption have been discussed using Lagergren first order equation, pseudo second order equation and intraparticle diffusion models. Langmuir and Freundlich adsorption isotherms have been used to discuss the data. Different thermodynamic parameters such as change in Gibbs free energy ΔG, change in enthalpy ΔH and change in entropy ΔS have been calculated to discuss the spontaneity of the process. Various experimental conditions are : initial Zn(II) ion concentration, temperature, pH and particle size.

Keywords: Fly ash, adsorption, zinc (II) ion, Langmuir isotherm, pseudo-second-order equation, Intraparticle diffusion model, Freundlich isotherm.

Introduction

Zinc and its alloys are mostly used in galvanization, diecasting, plastic, paints and cosmetic industries.The effluents of these industries pollute soil and water. It causes liver damage and other health problems.

Out of various methods to remove heavy metals from aqueous system, adsorption method is effective and economical. Studies have shown that there are number of substances which can be used as adsorbent1-6.

In the present study, the removal characteristics of fly ash, an industrial waste of thermal power plant, have been evaluated as a low cost adsorbent. Effects of four different parameters – initial Zn(II) ion concentration, temperature, pH and particle size on adsorption have been investigated. Kinetics of adsorption, different isotherms and thermodynamics of adsorption have been discussed.

Material and Methods

The fly ash used in this study was of JSPL, a thermal power plant at Raigarh (C.G).To characterise it, XRF, FTIR and SEM image were obtained. A.R quality $Zn(NO_3)_2$ has been used to prepare stock solution of Zn(II) ion.

1.0 g of fly ash of desired size was added to 25 mL of the aqueous solution of Zn(II) of known concentration at fixed pH. Shaking machine was used to shake it at desired temperature. After pre-determined time interval,it was centrifused and filtered. The remaining concentration of Zn(II) ion was determined by spectrophotometer. Different initial Zn(II) ion concentration for rate study was 100,150,200 and 250 mgL^{-1}. At 303K,313K and 323K studies were performed. Various pH values were 2.0, 4.0, 6.5 and 8.0. Particle sizes were 45µ, 75µ and 150µ. For equilibrium studies 25, 50, 75, 100, 125, 150, 175, 200 and 250 mgL^{-1} of Zn(II) were used.

Following equation[7] has been used to determine the adsorbed amount of Zn(II) in mgg^{-1} .

$$q_e = V (C_i – C_e) /m$$

Where 'C_i' represents Zn(II) ion concentration in mg/L , 'C_e' represents the concentration of Zn(II) ion after adsorption in mg/L , 'V' is the volume of Zn(II) ion in solution in 'L' and 'm' is the mass of fly ash in'g'. Removal (%) of Zn(II) ion was determined using equation[7] mentioned below:

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

Results and Discussion

Characterisation of fly ash: XRF studies of fly ash sample shows the composition as given in table-1

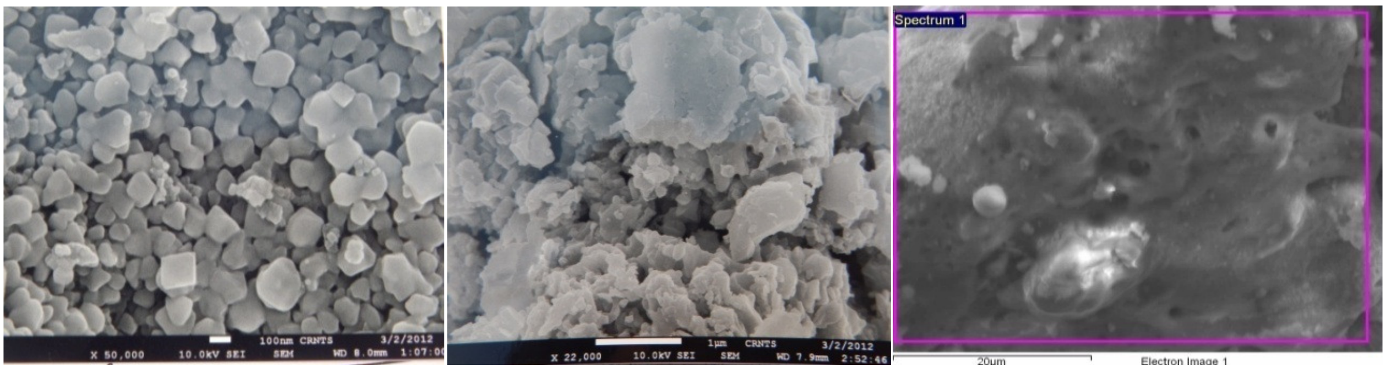
Table-1
Chemical composition of fly ash

Constituent	wt (%)
SiO_2	43.170
Al_2O_3	13.248
Fe_2O_3	41.198
CaO	1.090
MgO	0.727
TiO_2	1.262

It may be seen that SiO_2 and Al_2O_3 constitute about 56.42% of fly ash and Fe_2O_3 and CaO constitute about 42.29 %. As CaO content is less than 10% and SiO_2, Al_2O_3 and Fe_2O_3 is greater than 70% so the fly ash used in this study may be classified as class F[8].

Figure-1 presents the SEM image of fly ash which shows that particles of small size (45µ) are mainly spherical whereas the big size (150µ) particles are porous in nature and irregular in shape. Figure- 1(c) is the SEM image of fly ash(45µ) after adsorption.

The FTIR spectra of fly ash before and after adsorption is shown in figure-2. The main broad band at 1084.88 cm^{-1} in the fly ash before adsorption, corresponds to asymmetric stretching vibrations of Si-O-Si and Al-O-Si becomes sharper and shifts toward lower frequency 1061.97 cm^{-1} as a result of the formation of new reaction products[9].



(a) **(b)** **(c)**

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

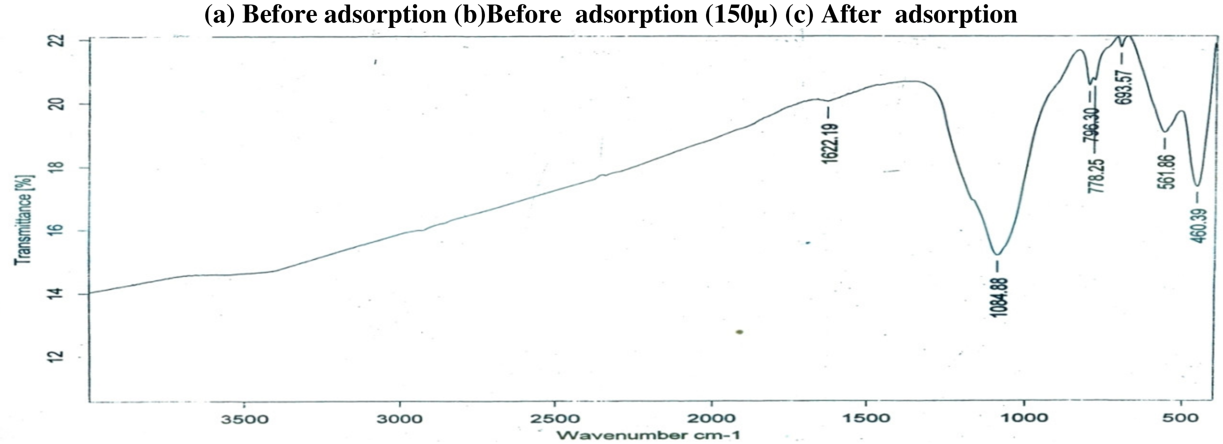


Figure-2
(a) FTIR Before adsorption

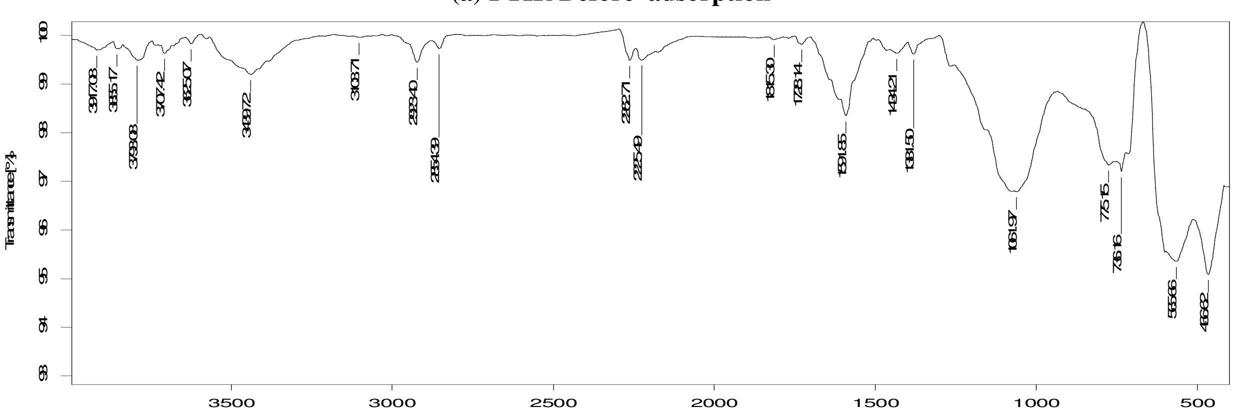


Figure-2
(b) FTIR After adsorption

Effect of initial Zn(II) ion concentration: The relationship between C_i and % removal has been represented in figure-3 . It is evident that the % removal decreases from 76.4% at 100 mgL^{-1} to 64.61% at 250 mgL^{-1}. It means as C_i increases the percentage removal decreases.. The reason might be the possibility of saturation of active sites present in the adsorbent at certain concentration[10]. It may also be seen that when the initial concentration of Zn(II) is 100mgL^{-1} , the adsorbed amount at equilibria, q_e , is 1.91 mgg^{-1} whereas at initial concentration of 250 mgL^{-1} it is 4.04 mgg^{-1}. This means that actual amount adsorbed increases with concentration.The reason might be that higher concentration of sorbate provides required driving force so as to exceed the mass transfer resistance of Zn(II) ion of the two phases i.e. the liquid and solid phase. Besides, due to high concentration of Zn(II), interaction of Zn(II) with fly ash surface increases resulting more adsorption[10].

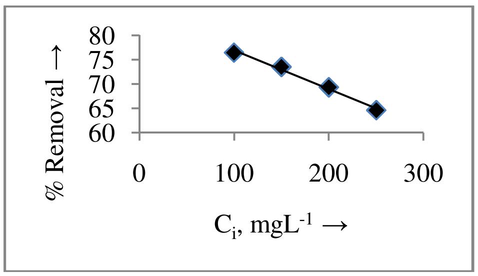


Figure-3
Plot of C_i*vs* % removal

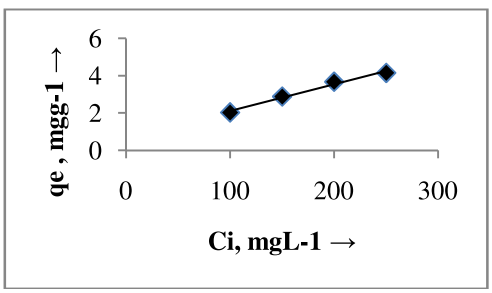


Figure-4
Plot of q_e*vs* C_i

Effect of contact time: Amount adsorbed(mgg^{-1})*vs* time(min.) has been shown in figure-5. It is evident that amount adsorbed increases till saturation. It has been found that initially rate of adsorption is fast and slows down till saturation. The reason might be that before adsorption, fly ash surface possess a large number of active sites. So, the initial rate of adsorption is high. But as adsorption goes on, the number of active sites get reduced and consequently the rate of adsorption also slows down[11-12].

Effect of pH: Adsorption of Zn(II) ion on fly ash is much influenced by pH of the medium. Amount adsorbed *vs* pH has been shown in figure-6. It is evident that amount adsorbed increases with increase in pH . It increases from 1.62 mgg^{-1}(64.8%) to 2.36mgg^{-1}(94.4%) by increasing pH of solution from 2.0 to 8.0.

Studies have shown[13] that at low pH fly ash particles are positively charged and at high pH negative charge is dominant. When pH is increased, there is more electrostatic attraction between Zn^{2+} ion which is positively charged and negatively charged fly ash surface. In morealkaline medium both adsorption and precipitation take place.

Effect of temperature: Temperature influences much the process of adsorption. As temperature increases, adsorption increases. It increases from 1.91mgg^{-1}(76.4%) at 303K to 2.26mgg^{-1}(90.4%)at 323K. The rate constant of adsorption are $2.8x10^{-2}$ and $3.4x10^{-2}$ per min at 303K and 323K respectively which shows that the adsorption rate increases with temperature. It indicates that nature of adsorption is endothermic.

Effect of size of fly ash particle: Figure-8 shows the effect of particle size on adsorption. The amount adsorbed is 1.71mgg^{-1} (68.4%) for 150 μ and 1.91mgg^{-1} (76.4%)for particle size of 45μ. It is evident that as particle size of fly ash decreases, the amount of Zn(II) ion adsorbed increases. The reason might be that as size of particle decreases, its surface area increases. As a result the number of active sites increases, thereby, increasing the adsorption.

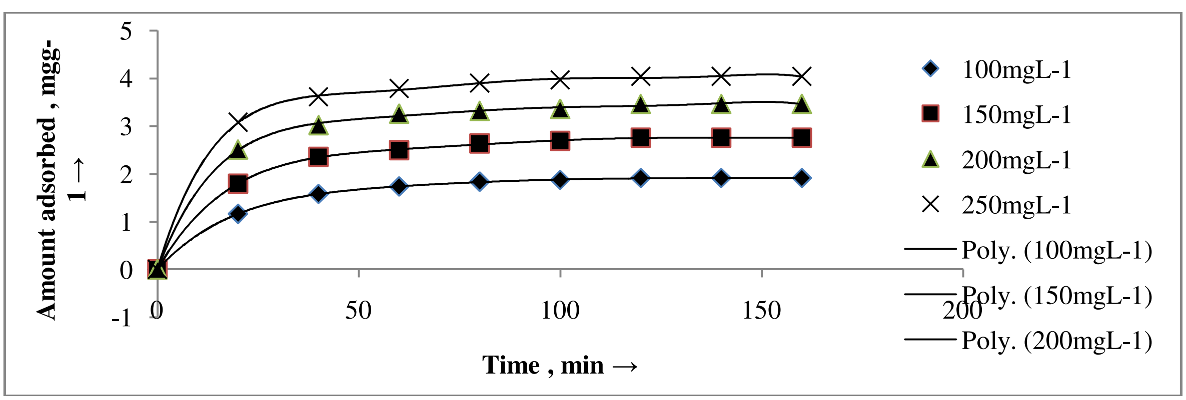


Figure-5
Effect of contact time on adsorption of Zn(II) ion on fly ash

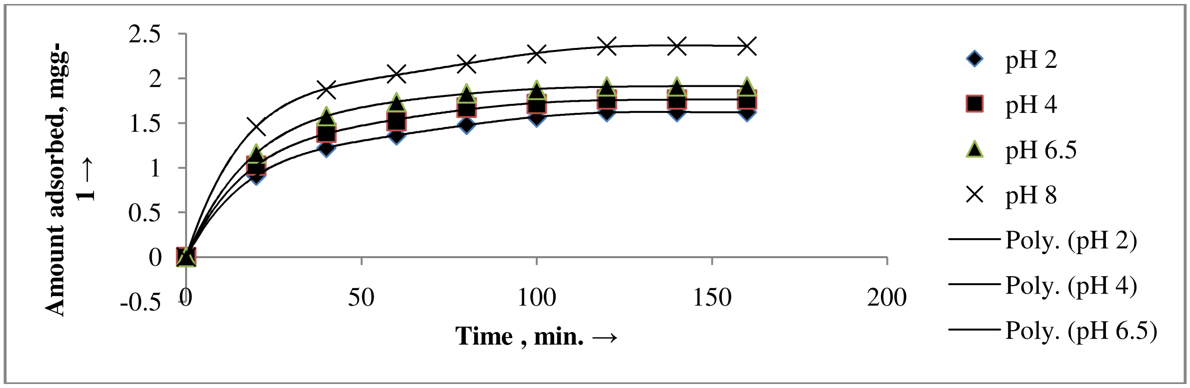


Figure-6
Effect of pH on adsorption of Zn(II) ion on fly ash

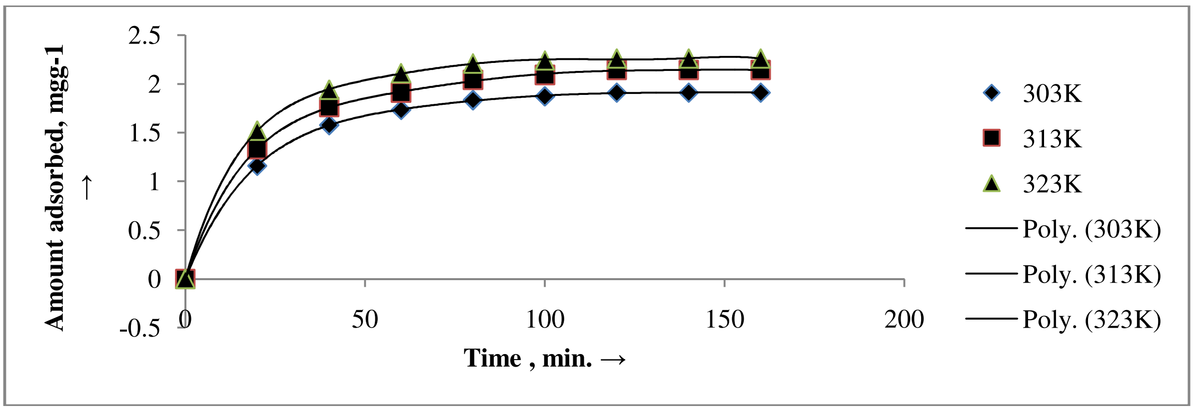


Figure-7
Effect of temperature on adsorption of Zn(II) ion on fly ash

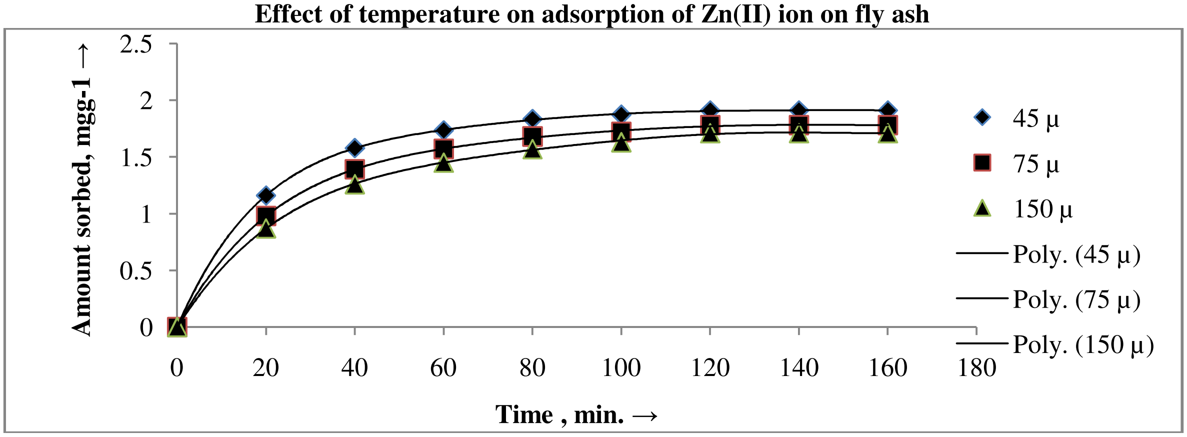


Figure-8
Effect of particle size on adsorption of Zn(II) ion on fly ash

Adsorption Isotherm: The linear form of the Langmuir and Freundlich isotherm[14] have been used to analyze the experimental data.

The Langmuir isotherm is given by the following equation
$C_e/q_e = 1/\varphi.b + C_e/\varphi$

where C_e (mgL^{-1}) is equilibrium concentration of Zn(II) and φ and b are Langmuir constants. φ is related to adsorption capacity and b is related to adsorption energy. The plot of C_e/q_e versus C_e shown in figure-9 is linear which suggests that Langmuir isotherms is applicable. Slope and intercept of the straight line obtained has been used to calculate φ and b respectively. These values have been given in table-2. It can be seen that as temperature increases values of φ and b also increases.

Adsorption data have been discussed using Freundlich equation which is given as:
$\log q_e = \log K_f + 1/n \log C_e$

where q_e represents the amount of zinc ion adsorbed (mgg^{-1}), the equilibrium concentration of zinc ion in solution(mgL^{-1}) is represented by C_e. $K_f$is the adsorption capacity and n is the intensity of adsorption. Plots of $logq_e$ versus $logC_e$ has been shown in figure-10 and values of K_f, n and R^2 (correlation coefficient) value have been obtained and given in table-2. Comparing R^2 value obtained from Langmuir plots and Freundlich plots clearly shows that the experimental data fits better in Langmuir equation.

A dimensionlessseparation factor (R_L) gives important information about the nature of adsorption and is defined as[15]

$R_L = 1/1+b.C_i$

where C_i is the initial concentration in mgL^{-1} and b is Langmuir constant (L/mg) related to adsorption energy. For favourable adsorption $0<R_L<1$ and for unfavourable adsorption $R_L>1$. Besides, when b>0, adsorption system is favourable[16]. The calculated values are given in Table-3. The values $0<R_L<1$ and b>0 suggest that the process is favourable.

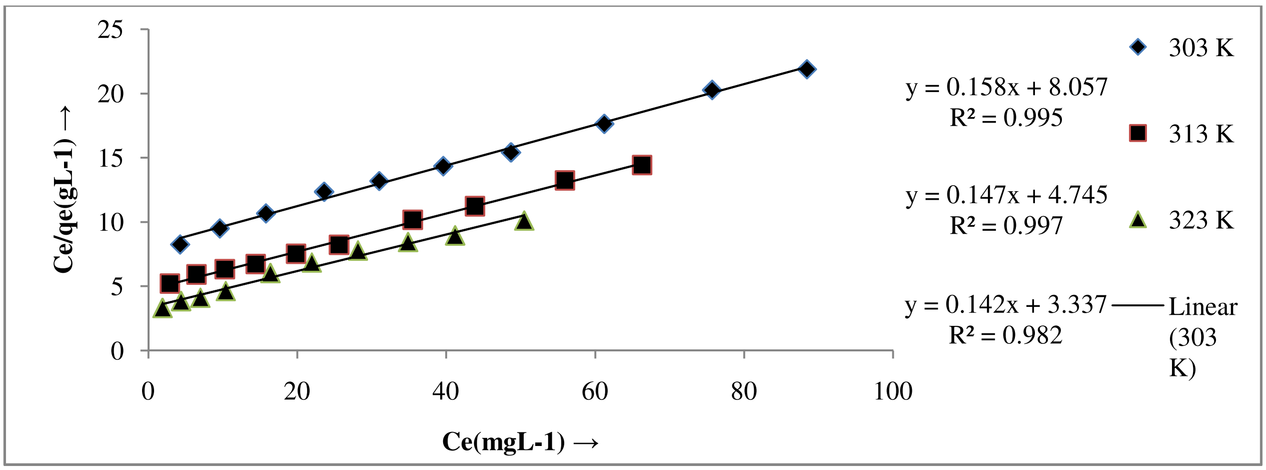


Figure-9
Langmuir adsorption isotherm for the adsorption of Zn(II) ion on fly ash

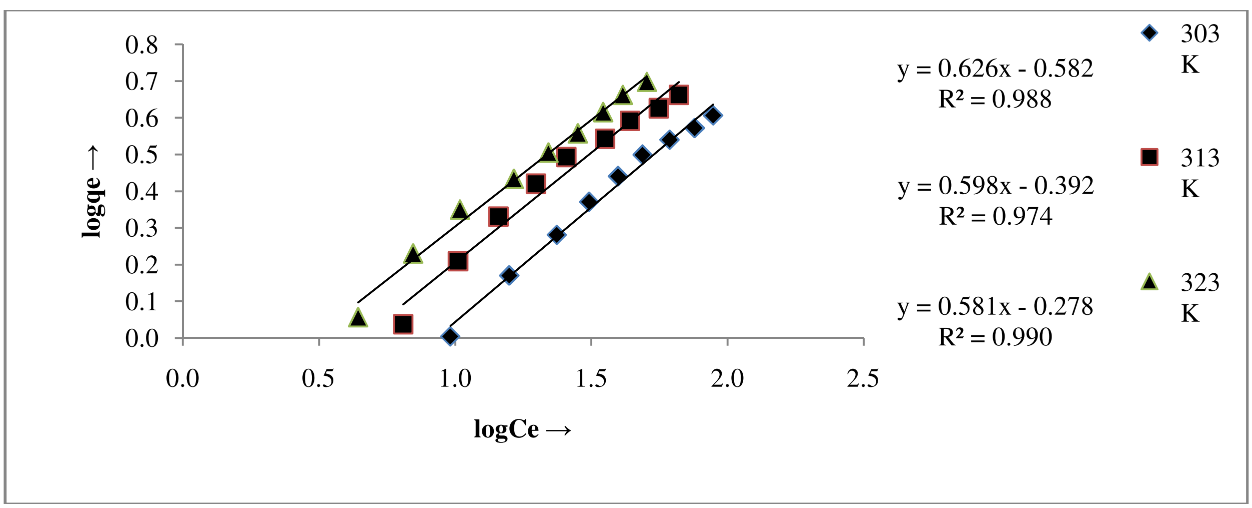


Figure-10
Freundlich adsorption isotherm for adsorption of Zn(II) ion on fly ash

Table-2
Langmuir and Freundlich isotherm constants for adsorption of Zn(II) on fly ash

Langmuir Isotherm Results				Freundlich Isotherm Results		
Temp.(K)	**R^2**	**φ**	**b**	**R^2**	**K_f**	**n**
303	0.995	6.33	0.020	0.988	0.262	1.597
313	0.997	6.80	0.031	0.974	0.406	1.672
323	0.982	6.99	0.044	0.990	0.527	1.721

Table-3
Dimensionless separation factor (R_L)

-----	R_L		
Ci (mgL^{-1})	303 K	313 K	323 K
25	0.671	0.563	0.478
50	0.505	0.392	0.314
75	0.405	0.301	0.234
100	0.338	0.244	0.187
125	0.290	0.205	0.155
150	0.254	0.177	0.133
175	0.226	0.156	0.116
200	0.203	0.139	0.103
225	0.185	0.125	0.093
250	0.169	0.114	0.084

Kinetics of adsorption: Theadsorption kinetics have been discussed by usingLagergren first order[17], pseudo-second-order[18] and Intraparticle diffusion kinetic models[19].

The Lagergren kinetic model for first order: First order rate equation of Lagergren is given as:
$\log (q_e - q_t) = \log q_e - k_1.t/2.303$

where q_e and q_t are the amounts of Zn(II) sorbed (mgg^{-1}) at equilibrium and at time t , respectively. K_1 is the first order rate constant (min^{-1}). Plots of $\log(q_e - q_t)$ *versus* t has been shown in figure- 11. From the slope and intercept q_e and K_1 have been calculated respectively and have been given in table-4.

The pseudo-second-order kinetic model: The adsorption data have been applied to pseudo-second-order kinetic model also . The equation is represented as:
$t/q_t = 1/K_2.q_e^2 + t/q_t$

where K_2 is the rate constant (g $mg^{-1}min^{-1}$). Figure-12 shows plot of t/q_t versus t. Values of K_2 and q_e have been calculated from the straight lines obtained. These values have been given in table-4.

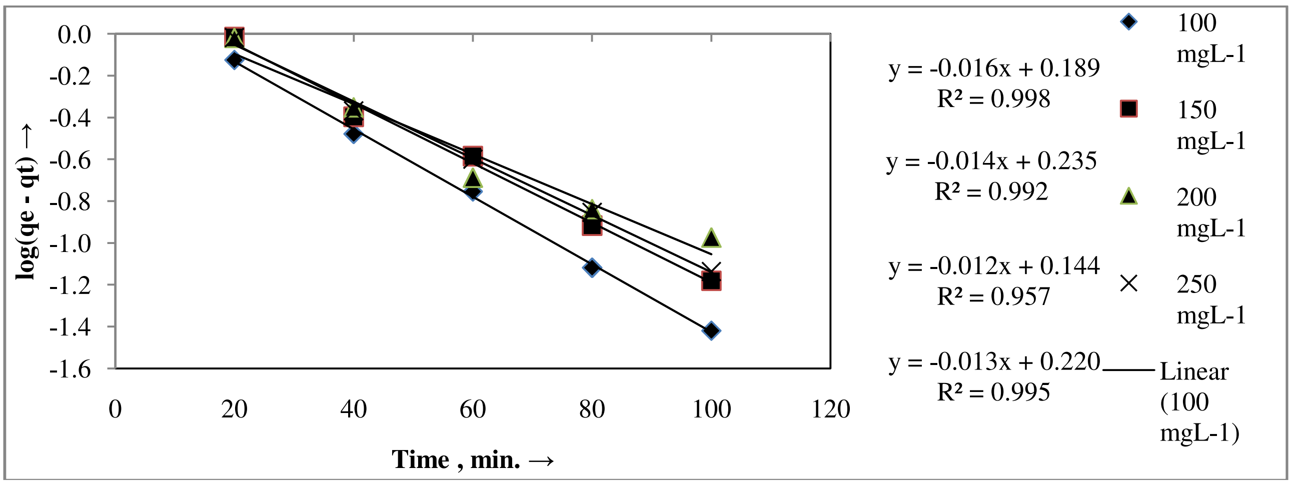


Figure-11
Lagergren first-order kinetic plot for adsorption of Zn(II) ion on fly ash

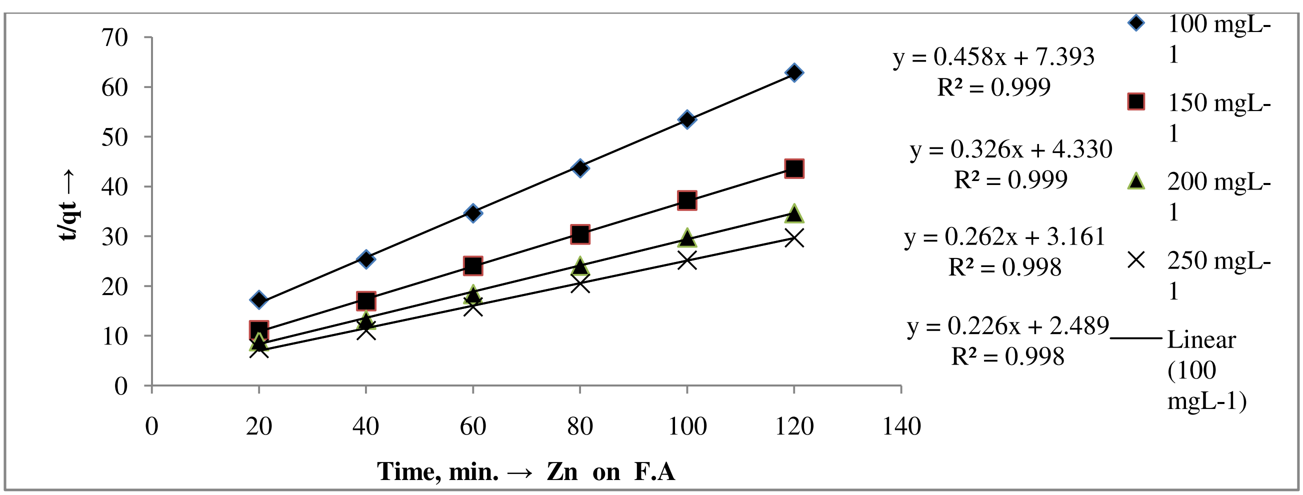


Figure-12
Peudo-second-order kinetic plot for adsorption of Zn(II) ion on fly ash

The Intraparticle diffusion model: The data obtained have been analyzed by Weber and Morris intraparticle diffusion model which is represented as:

$q_t = K_d \cdot t^{1/2} + I$

where I is the intercept . It reflects the boundary layer effect. K_d is the diffusion rate constant. Figure-13 shows the graph betweenq_t and $t^{1/2}$. Straight lines are obtained from which values of K_d and I can be calculated. Slope gives the value of K_d and intercept gives the value of I. These values have been given in table-4. Intraparticle diffusion is considered as rate-limiting step if the straight lines obtained pass through the origin. It is evident from the figure that the linear plots did not pass through the origin, so, intraparticle diffusion is not the only rate limiting step and some boundary layer effect is indicated.

It is evident from table- 4 that the kinetic data follows pseudo-second-order kinetic model as $R^2 > 0.99$ which is higher in comparison to the other kinetic models. Moreover, $q_{e(cal)}$obtained from pseudo-second-order kinetic model is in better agreement with the q_e(exp)

Thermodynamics of adsorption: Thermodynamic parameters give some insight into the process of adsorption. Whether the adsorption process is feasible or not can be predicted by the parameters such as free energy change ΔG, enthalpy change ΔH and entropy change ΔS. These parameters have been calculated using the following equations[20].

$K_c = C_s/C_e$

$\Delta G = - RT \ln K_c$

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

In the above equation C_e represents the concentration of Zn(II) in solution in mgL^{-1} at equilibrium. C_s represents the concentration of Zn(II) on the fly ash in mgL^{-1} at equilibrium. K_c is the equilibrium constant. The value of K_c was used to calculate the value of ΔG . Plot between $\log K_c$ and 1/T gives a straight line shown in figure-14. The slope and intercept of this straight line has been used to calculate ΔH and ΔS. These values have been given in table-5.

Table-4
Kinetic parameters for adsorption of Zn(II) ion on Fly ash

Conc. mgL^{-1}	First order Lagergren				Pseudo- second- order			Intraparticle diffusion		
	K_1 min^{-1}	q_{exp} mgg^{-1}	q_{cal} mgg^{-1}	R^2	K_2 g/mg/min	q_{cal} mgg^{-1}	R^2	K_d $mg/g.min^{1/2}$	I	R^2
100	3.68×10^{-2}	1.91	1.55	0.998	2.84×10^{-2}	2.183	0.999	0.110	0.787	0.891
150	3.22×10^{-2}	2.76	1.72	0.992	2.45×10^{-2}	3.067	0.999	0.139	1.329	0.89
200	2.76×10^{-2}	3.47	1.39	0.957	2.17×10^{-2}	3.817	0.998	0.171	1.722	0.821
250	2.99×10^{-2}	4.04	1.66	0.995	2.05×10^{-2}	4.425	0.998	0.190	2.126	0.809

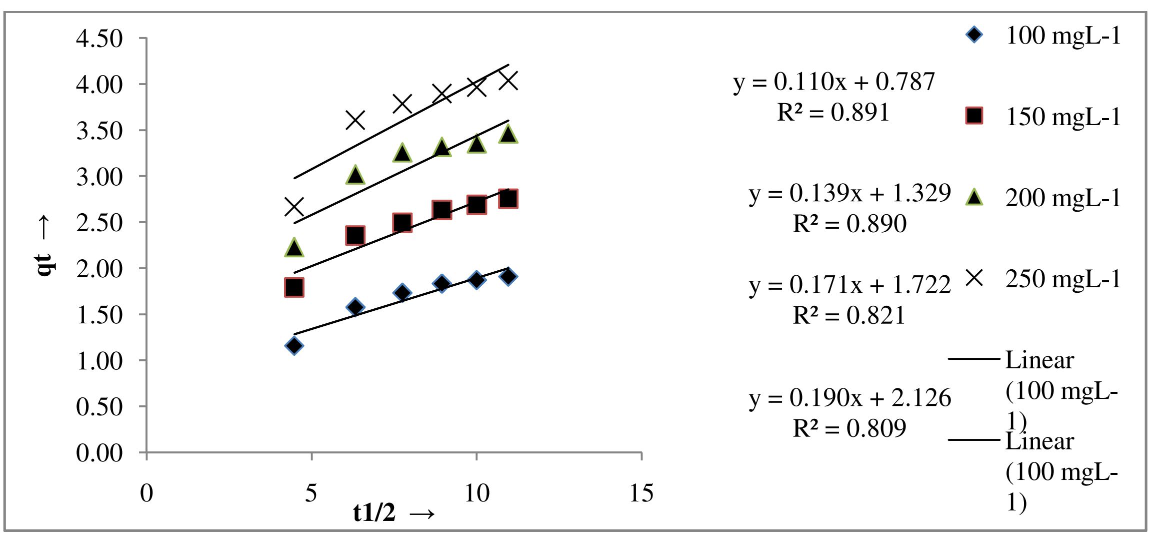


Figure-13
Intraparticle diffusion model for adsorption of Zn(II) ion on fly ash

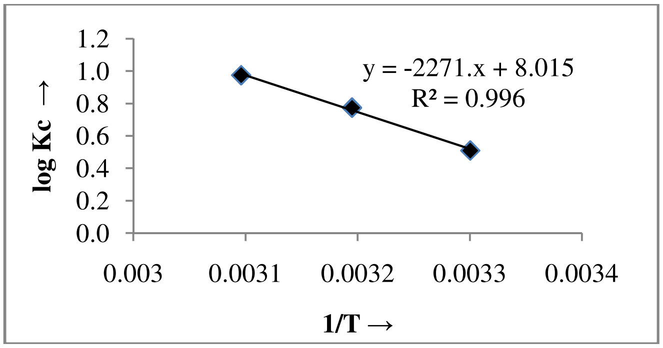


Figure-14
logK_c *vs* 1/T

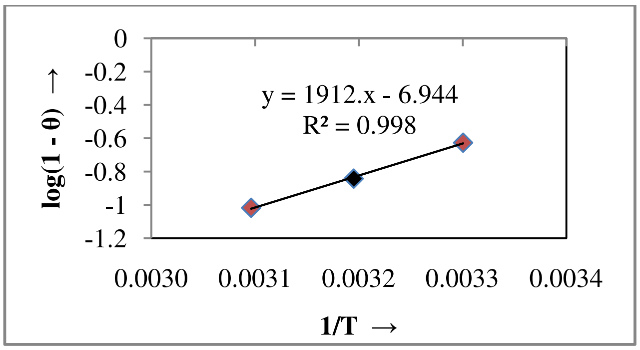


Figure-15
log(1 – θ) *vs* 1/T

Sticking probability (S*) and activation energy (E_a) also give insight into the process and mechanism of adsorption. These parameters have been calculated by using modified Arrhenius equation. This equation, related to surface coverage (θ) is represented as[21]:

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

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

The sticking probability, S*, is a function of the adsorbate/adsorbent system and should satisfy the condition 0<S*<1. Plot of ln(1- θ) versus 1/T gives straight line (figure-15). The slope and intercept of this straight line have been used to calculate E_a and S* respectively and have been given in table-5.

Table-5
Thermodynamic parameters for adsorption of Zn(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	-2.959	43.48	153.46	36.61	1.138X10^{-07}
313	-4.639				
323	-6.023				

Table-5 shows that as ΔG values are negative, the process is spontaneous. Positive ΔH value indicates that the nature of adsorption is endothermic. Positive ΔS shows the affinity of the adsorbent for the Zn(II) ions. The value of E_a has been found to be 36.61 kJ mol^{-1}. Positive value of E_a also indicates the endothermic nature of the process. Since S*<<1, it indicates that the probability of Zn(II) ion to stick on surface of fly ash is very high[22].

Mechanism: Speciation[23] of Zn(II) with varying pH has been shown in figure-16.

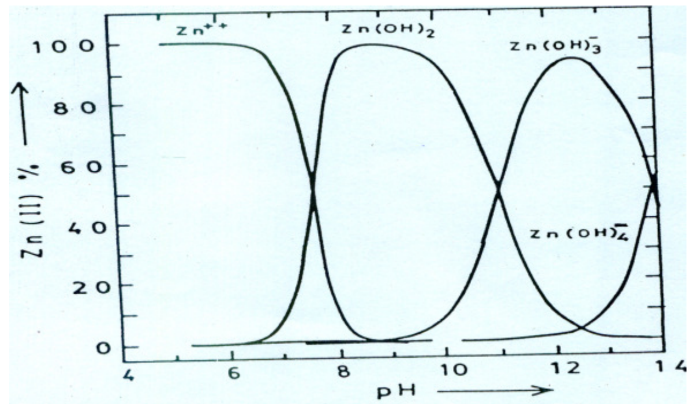


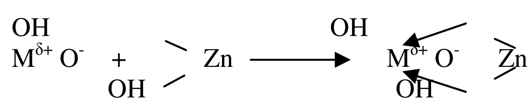
Figure-16
Speciation of Zn(II) with varying pH

It is evident that at lower pH, zinc is in the form of Zn^{+2} and at pH ≥ 8 it is in the form of $Zn(OH)_2$. 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 Zn^{+2} species[24,25]. $Zn(OH)_2$ may possibly be adsorbed on adsorbent as shown below :

$M{-}OH \xrightarrow{OH^-} MO^-$

$MO^- + Zn^{+2} \longrightarrow MOZn^+$

$MO^- + MOZn^+ \longrightarrow (MO)_2Zn$



Conclusion

It is evident that initial Zn(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 due to chemical composition, structure, more adsorption sites, cheap, availability in plenty etc. fly ash may prove to be an efficient adsorbent.

Acknowledgement

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