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Adsorption of Cadmium and Zinc Ions from Aqueous Solution Using Low Cost Adsorbents

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Abstract: The wastewaters letting out from small-scale industries, like electroplating, smelting, battery manufacture, tanneries etc. are contaminating the nearby water source by increasing the heavy metal concentrations mainly Cadmium and Zinc etc. These cause acute poisoning in humans high blood pressure, kidney damage and destruction of testicular tissue, red blood cells, stomach cramps, skin irritations, vomiting and respiratory disorders. Therefore, these wastewaters are to be treated using cost effective methods. In recent years, the adsorption of metal ions using low cost adsorbents is very promising method. This study presents adsorption investigations in removal of Cadmium and Zinc using low cost adsorbents of Fly Ash and Cenospheres (derived from power plant fly ash) from aqueous solution and the results were compared with Activated Carbon. Batch adsorption experiments were conducted in order to evaluate the removal efficiency of these adsorbents and the parameters effect like temperature, contact time, pH, adsorbent dosage and initial concentration were studied. The kinetics studies were made to estimate adsorption rate constants. The thermodynamic parameters were estimated for these adsorbents. The adsorption isotherms of Langmuir, Freundlich and Temkin constants for all the adsorbents were determined and the Langmuir adsorption isotherms recommended.

Key words: Adsorption, cadmium, zinc, flyash, activated carbon, cenospheres, adsorbent dosage, pH, langmuir, freundlich, temkin, adsorption isotherms

INTRODUCTION

Several industries including metal finishing, electroplating, metallurgical, battery manufacture and chemical industries let out the huge volume of wastewaters into nearby water sources. This is a potential hazard for the environment because of introducing various contaminants such as heavy metals into soil and water resources. Heavy metals are toxic to aquatic organisms even at very low concentrations. The wastewaters containing metal ions such as Cadmium and Zinc are introduced into the bodies of water commonly because these metals are widely used and exposure of human beings to these toxic metals could be the cause of those symptoms. Memory loss, increased allergic reactions, high blood pressure, depression, irritability, poor concentration, sleep disabilities, speech disorders, cholesterol, vascular occlusion, neuropathy, autoimmune diseases and chronic fatigue. The effects of acute cadmium poisoning in humans are high blood pressure, kidney damage and destruction of testicular tissue and red blood cells. Too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting and respiratory disorders. Therefore, these wastewaters are to be treated using low cost methods. Many conventional methods for removing metal ions from Industrial Effluents suffer with high capital and regeneration costs of the materials. Therefore, these are not suitable for the small-scale industries. Thus, there is currently a need for new, innovative and cost effective methods for the removal of toxic substances from wastewaters. Among these processes Adsorption with the selection of suitable adsorbent can be an effective and versatile method and can be easily adopted in low cost to remove heavy metals from large amount of industrial wastewaters.

The Fly Ash, an inorganic residue from the combustion of powdered coal, has received particular attention as an economical adsorbent for removing heavy metals (Bayat, 2002; Barkat *et al*., 2009; Mohan Rao and Basava Rao, 2007) from wastewater due to its abundance and easy availability. Fly Ash has potential use in waste water treatment because of its major chemical components, which are alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon and its physical properties such porosity, particle size distribution and surface area. The alkaline nature of fly ash makes it a good neutralizing agent. Cenosphere derived from fly ash

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(Han *et al*., 2009; Joseph *et al*., 2007) are lightweight, inert, hollow ceramic spheres filled with inert air or gas, typically produced as a byproduct of coal combustion at thermal power plants. The color of cenospheres varies from gray to almost white and their density is about 0.4-0.8 g cm^{-3}. In this study, the batch adsorption experiments are conducted to estimate the adsorption kinetic parameters, adsorption isotherms and thermodynamic parameters.

MATERIALS AND METHODS

Fly ash and cenospheres: The fly ash and cenospheres were obtained from Vijayawada Thermal Power Plant (VTPS), Vijayawada and National Thermal Power Corporation (NTPC), Ramagundam. Activated carbon of AR grade obtained from M/S R.K.Carbons, Hyderabad was, directly used as adsorbents. The activated carbon is in the form of 3 mm size diameter granules with surface area of 460.3 m^2 g^{-1}. All chemicals were used of analytical reagent grade and $3CdSO_4.8H_2O$ was obtained from SISCO Research Laboratory Pvt. Ltd., NaOH was obtained from Merks, $ZnCl_2$ and HNO_3 were obtained from Qualizens Fine Chemicals, Mumbai.

Adsorption experiments: The batch adsorption experiments were carried out in 100 mL capacity glass flasks with initially prepared stock solutions by shaking a preweighed amount of the fly ash with 50 mL of the aqueous Zinc and Cadmium metal ion solutions for effect of contact time at 30°C on a water bath shaker while maintaining the initial concentration 10 mg L^{-1}, pH 6 and adsorbent dosage 10 g L^{-1}. The adsorption kinetic rate constants for adsorbents were determined at effect of contact time. Adsorption isotherm study is carried out with different initial concentrations 1, 5, 10, 20 mg L^{-1} while maintaining the contact time 120 min and remaining are same as mentioned above. The effects of adsorbent dosage were 1, 5, 10, 15, 20 g L^{-1} studied at 30°C with remaining are same as mentioned above. Thermodynamic parameters for the adsorption of metal ions onto various adsorbents were determined at different temperatures 30, 40, 50°C while maintain the remaining are same as mentioned above. To determine the optimum pH on adsorption with varying pH values 2, 4, 5, 6, 8 while maintaining the other are same as above.

The solutions were filtered using with Whatman filter paper No. 40 after the experiments were done. The filtrate was used for determination of metal with the help of Flame Atomic Absorption Spectrophotometer (Shimadzu AA-6300). The pH of the solution was measured with a digital pH meter (Eutech Instrument pH Tutor). The initial and final metal ion concentrations were measured by Atomic Absorption Spectrophotometer (AAS). The amount of metal ion adsorbed per liter was calculated from the difference between the initial (C_i) and final (equilibrium) concentration (C_{eq}) in the solution.

The adsorption percentage was calculated by using from the following equation:

$$\text{Adsorption (\%)} = \frac{C_i - C_{eq}}{C_i} \times 100$$

ADSORPTION ISOTHERMS

Langmuir Isotherm: The Langmuir isotherm can mathematically represented as:

$$\frac{1}{q_e} = \frac{1}{Q_0 b} * \frac{1}{C_{eq}} + \frac{1}{Q_C}$$

where q_e is the equilibrium uptake (mg g^{-1}), C_{eq} is the equilibrium metal concentration (mg L^{-1}), Q_0 (mg g^{-1}) and b (L g^{-1}) the Langmuir constants are the saturated monolayer sorption capacity and the sorption equilibrium constants, respectively. The above equation shows that a plot of $1/q_e$ vs. $1/C_{eq}$ should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and intercept of this line then gives the values of constants Q_0 and b.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L also known as the separation factor, given by:

$$RL = \frac{1}{(1 + bC_{eq})}$$

The value of R_L lies between 0 and 1 for a favorable adsorption.

Freundlich isotherm: The Freundlich isotherm can be represented as:

$$\text{Log}\, q_e = \text{Log}\, K_F + \frac{1}{n} \text{Log}\, C_{eq}$$

where, K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively. The Freundlich coefficients can be determined from the plot of log q_e versus log C_{eq} based on the above equation.

Temkin isotherm: The linear form of Tempkin equation is given as:

$$q_e = A+B \text{ In } C_{eq}$$

where, the constant B is related to the heat of adsorption, A is the equilibrium binding constant (l/min) corresponding to the maximum binding energy. The slope and intercept from a plot of q_e versus ln C_{eq} determines the isotherm constants A and B.

ADSORPTION KINETICS

Pseudo first order kinetics: The linear form of pseudo first-order (Lagrange) equation given by:

$$\text{Log}(q_e - q_t) = \text{Log}\, q_e - \frac{k_1 t}{2.303}$$

where, q_e and q_t are the amounts of metal adsorbed (mg g^{-1}) at equilibrium time and at any instant of time, t respectively and k_1 (l/min) is the rate constant of the pseudo first order adsorption operation. Plot of log (q_e-q_t) vs. t gives a straight line for the first-order adsorption kinetics, which allow the computation of the adsorption rate constant, k_1.

Pseudo second order kinetics: Applicability of the second order kinetics has be tested with the rate equation given by:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

where, k_2 (g mg min^{-1}) is the second order rate constant, $h = k_2 q_e^2$ that can be regarded as the initial sorption rate as t tends to zero. Under such circumstances, the plot of t/q_t vs. t should give a linear relationship, which allows the computation of q_e, k_2 and h.

Intraparticle diffusion model: The intraparticle diffusion model is expressed as:

$$\log Y_{id} = \log k_{id} + \alpha \log t$$

where, Y_{id} is the percent metal ion adsorbed, t is the contact time (min), 'a' is the gradient of linear plots, k_{id} is the intraparticle diffusion rate constant (1/min). The values of k_{id} were calculated from the slope of plots log Y_{id} vs. log t and R^2 values led to conclusion that the intraparticle diffusion process is the rate-limiting step.

THERMODYNAMIC PARAMETERS

The thermodynamic parameters, which characterize the equilibrium of a system, are the Gibbs free energy (ΔG^0), the enthalpy (ΔH^0) and the entropy (ΔS^0). The apparent distribution coefficient (K_d) of the adsorption is defined as:

$$k_d = \frac{C_i - C_{eq}}{C_{eq}} \times \frac{V}{m}$$

where, C_i is the initial concentration of metal ion in the aqueous solutions, C_{eq} is the equilibrium concentration of metal ion on the adsorbent (mg mL^{-1}), V is the volume of adsorbate solution (mL) and m is the amount of adsorbent (g).

The K_d value is used in the following equation to determine the Gibbs free energy of adsorption (ΔG^0):

$$\text{In}\, k_d = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

Van't Hoff equation is given by:

$$\Delta G^0 = -RT\text{In}\, K_d = \Delta H^0 - T\, \Delta S^0$$

where, ΔG^0 is standard Gibbs free energy change (J), R is the universal gas constant (8.314 J mol^{-1} ^{0}K) and T is the absolute temperature (^{0}K). The enthalpy (ΔH^0) and entropy (ΔS^0) can be obtained from the slope and intercept of a Van't Hoff equation of ln K_d vs. 1/T.

RESULTS AND DISCUSSION

Effect of contact time: The effect of contact time on the adsorbed of Cd and Zn metals removal is plotted in Fig. 1. It can be observed that that the adsorption rate is very

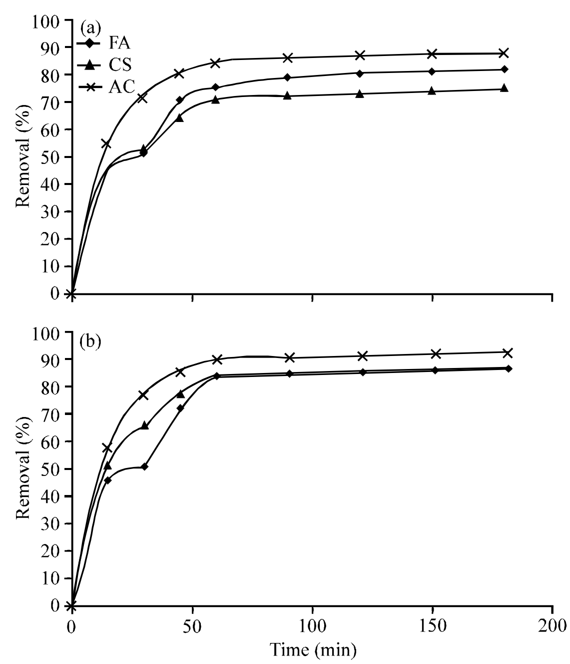

Fig.1(a-b): Effect of contact time on % removal of Cd and Zn metal at 30°C

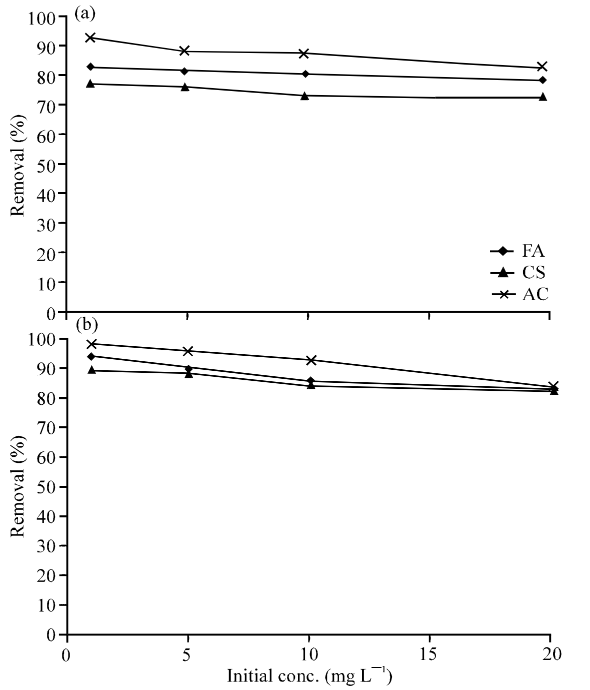

Fig. 2(a-b): Effect of initial concentration on % removal of Cd and Zn metal at 30°C

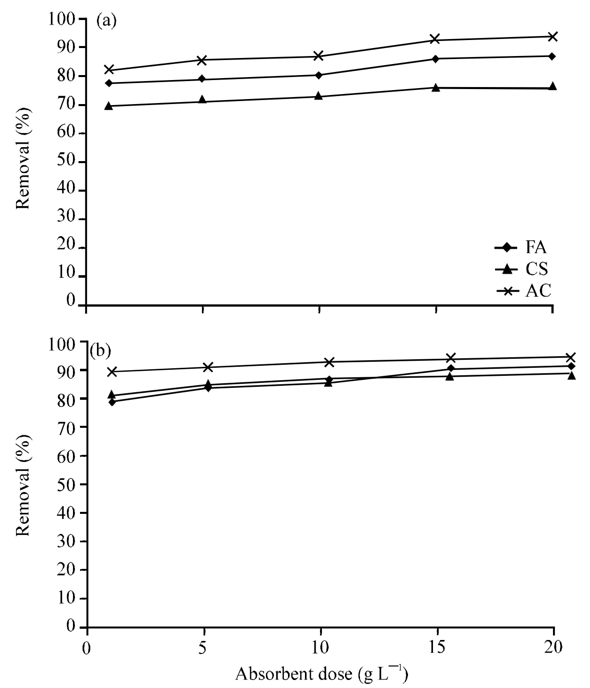

Fig. 3(a-b): Effect of adsorbent dosage on % removal of Cd and Zn metal at 30°C

rapid during the initial period of contact time and later it is very slow. However, the equilibrium is attained within 170 to 190 min. The equilibrium concentrations were following the order for Zn metal Fly Ash>Cenospheres>Activated Carbon and for the Cd metal order follows Cenospheres> Fly Ash>Activated Carbon. Fly Ash found to remove 86.9% Zn and 81.8% Cd at pH 6, temperature 30°C, initial concentration 10 mg L^{-1} and adsorbent dosage 10 g L^{-1}.

Effect of initial concentration: The effect of initial concentration of stock solution on the adsorption of Cadmium and Zinc metals were shown in Fig. 2. The percentage of metal adsorption increased with decreasing the initial metal concentration. At lower concentration, the % removal is very high and it is lower at higher concentration. This is due to the availability of same amount of adsorbent site for various amount of initial metal ion concentration. The effect of initial concentration on the removal of metals using different initial concentrations 1, 5, 10, 20 mg L^{-1} at 30°C while maintaining dosage 10 g L^{-1}, pH 6 and contact time 120 min.

Effect of adsorbent dosage: The effect of adsorbent dose on the removal of Cadmium and Zinc metal using different adsorbents 1, 5, 10, 15 and 20 g L^{-1} at 30°C with an initial concentration of Cadmium and Zincn metal ions at 10 mg L^{-1}, pH 6 and contact time is 120 min were shown in Fig. 3.

It clearly indicates that the percent removal of Cadmium and Zinc metal increases with increasing in adsorbent dose. The adsorbent dose is increased, percent removal is also increases but after optimum dose of 15 g L^{-1}, there is no appreciable change in removal. Little increase in percent removal on increasing adsorbent dose from 15 to 20 g L^{-1} of solution, then subsequent slow rise in percent removal may be due to adsorption and intraparticle diffusion takes place.

Effect of pH: All experiments were carried out in the pH range of 2.0 to 8.0 (2, 4, 5, 6 and 8) where chemical precipitation is avoided, so that metal removal could be related to the adsorption process. As shown in the Fig. 4, the maximum adsorption of Cadmium and Zinc were found between pH 5-6. This may be attributed to the surface charge development of the fly ash and the concentration distribution of metal ions, which both are pH-dependent. The percentage adsorption increased with increasing pH to a maximum value (pH 5-6) and then decline rather rapidly with further increase in pH.

Effect of temperature: Adsorption studies were conducted at 30, 40 and 50°C to determine the influence of

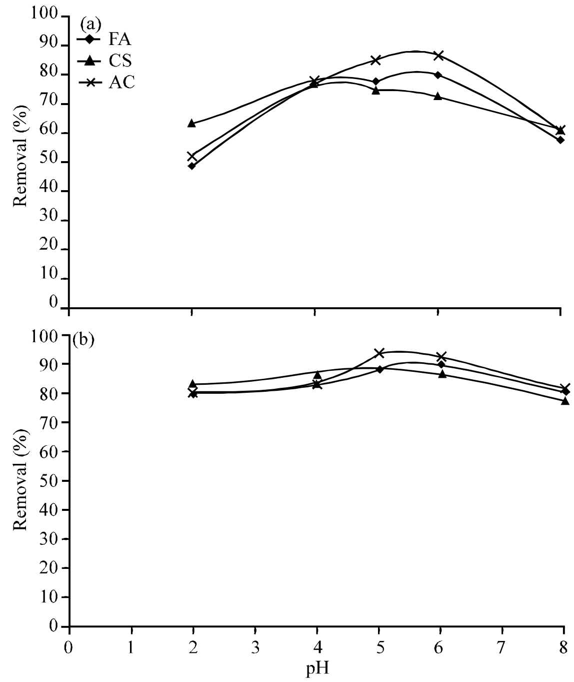

Fig. 4(a-b): Effect of pH on % removal of Cd and Zn metal at 30°C

temperature on the adsorption of Cd and Zn onto fly ash. The effects of temperature variation on the adsorption of Cd and Zn from aqueous solution were shown in Fig. 5. The extent of adsorption for both metals increases along with an increase of temperature. In fact, when the temperature increased from 30 to 40°C, an increase of adsorption was indicating the adsorption process to be endothermic.

ADSORPTION ISOTHERMS

As mentioned earlier, the isotherm constants for isotherm models at specific initial concentration values were determined from the respective plots and were presented in Table 1 and 2 along with the correlation regression coefficients (R^2). As shown in Table 1 and 2, R^2 of Cd and Zn metals for the Langmuir isotherm were higher than for the Freundlich and temkin isotherm, therefore, the experimental data was better fitted to the Langmuir isotherm. Langmuir constant "Q_0" represents the monolayer saturation at equilibrium or maximum adsorption capacity of adsorbents. The other mono component Langmuir constant "b" represents the affinity for the binding of metals. A high "b" value indicates a high affinity. The dimensionless parameter (R_L), which is a measure of adsorption favorability, is found in the range between 0 and 1, which confirms that the favorable adsorption process for metals (Cd and Zn) removal using

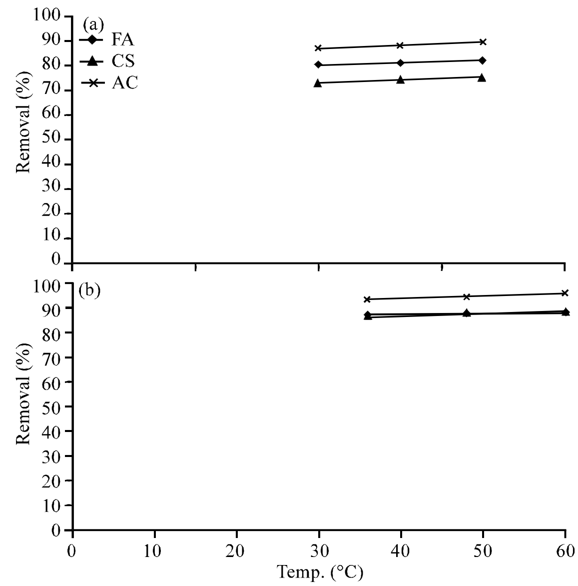

Fig. 5(a-b): Effect of temperature on % removal of Cd and Zn metal at contact time 2 h, pH 6.0, (a) Initial concentration 10 mg L^{-1} and (b) Adsorbent dose 10 g L^{-1}

Table 1: Isotherm constants for adsorbents at different initial concentrations for cadmium metal ions

Isotherms		Fly ash	Cenospheres	Activated carbon
Langmuir	Q_o	4.6685	4.7259	1.6664
	B	0.1042	0.0719	0.759
	R^2	0.9999	0.9999	0.9978
	R_L	0.1164	0.4897	0.5817
Freundlich	K_f	0.4192	0.3030	0.6669
	n	1.0927	1.0852	1.3068
	R^2	0.9995	0.9993	0.9985
Temkin	A	0.5191	0.6773	0.9174
	B	0.918	0.9871	0.8885
	R^2	0.8425	0.8543	0.863

Table 2: Isotherm constants for Adsorbents at different Initial concentrations for Zinc metal ions

Isotherms		Fly ash	Cenospheres	Activated carbon
Langmuir	Q_o	1.4465	2.9516	1.241
	B	1.0425	0.2827	3.545
	R^2	0.9977	0.9998	0.9971
	R_L	0.0274	0.0875	0.2613
Freundlich	K_f	0.6725	0.5898	0.958
	n	1.3906	1.2009	1.719
	R^2	0.999	0.9961	0.9839
Temkin	A	0.9175	0.8538	1.1203
	B	0.8315	0.9582	0.7162
	R^2	0.8513	0.8695	0.9291

all adsorbents (FA, CS and AC). Freundlich isotherm does not describe the saturation behavior of the adsorbent as well as Langmuir isotherm. From Table 1 and 2 all measured values of log K_f showed easy uptake of metals with high adsorptive capacity of adsorbents. Temkin

Table 3: Adsorption Kinetic rate constants for Adsorbent at different times for Cadmium metal

Kinetic model	Pseudo first order			Pseudo second order			Intraparticle diffusion		
Adsorbent	K_1	q_e	R^2	K_2	q_e	R^2	K_{id}	A	R^2
Fly Ash	0.00759	0.10897	0.9989	0.2195	0.8407	0.9999	6.3841	0.0476	0.9996
Ceno spheres	0.00253	0.17286	0.9924	0.2281	0.7705	0.9998	5.8304	0.0479	0.9864
Activated carbon	0.01543	0.1051	0.9994	0.2797	0.8993	1	7.2393	0.038	0.9834

Table 4: Adsorption Kinetic rate constants for Adsorbents at different times for Zinc metal

Kinetic model	Pseudo first order			Pseudo second order			Intraparticle diffusion		
Adsorbent	K_1	q_e	R^2	K_2	q_e	R^2	K_{id}	a	R^2
Fly Ash	0.000207	0.731	0.9857	0.3578	0.8813	0.9999	7.5927	0.0253	0.9369
Ceno spheres	0.00046	0.6524	0.9887	0.3335	0.8925	0.999	7.5823	0.0279	0.9666
Activated carbon	0.07276	0.0081	0.9924	0.3413	0.9479	1	8.0816	0.0276	0.9928

Table 5: Thermodynamic parameters for the adsorption of Cadmium metal onto each adsorbent

Adsorbent	Fly ash			Cenospheres			Activated carbon		
temperature	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	ΔG^0
30	2.43	13.045	-1.53	2.03	10.325	-1.09	4.08	20.303	-2.08
40			-1.64			-1.21			-2.26
50			-1.79			-1.30			-2.48

Table 6: Thermodynamic parameters for the adsorption of Zinc metal onto each adsorbent

Adsorbent	Fly ash			Cenospheres			Activated carbon		
temperature	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	ΔG^0
30	2.85	15.805	-1.93	1.71	12.329	-2.02	7.15	32.583	-2.73
40			-2.09			-2.15			-3.03
50			-2.25			-2.27			-3.38

parameters A and B were also listed in the Table 1 and 2 for metals Cadmium and Zinc form that tables the binding energy (A) is more in the AC than the other two adsorbents. The heat of adsorption is more in the CS than the other two adsorbents.

Adsorption kinetics: The study of adsorption kinetics describes the solute uptake rate and evidently, this rate controls the residence time of adsorbate uptake at the solid solution interface. The kinetics of metals adsorption on the adsorbents was analyzing using pseudo first and second order and intraparticle diffusion kinetic models. The conformity was expressed by R^2. A relatively high R^2 value indicates that the model successfully describe the kinetics of both metal adsorption. In this experiment pseudo second order is the best model for the both metals and all three adsorbents. The results including with constant values of the kinetic models for the Cadmium and Zinc metals had shown in Table 3 and 4.

Thermodynamic studies: Values of the standard Gibbs free energy change for the adsorption process obtained from the above stated equation were listed in Table 5 and 6 for the Cadmium and Zinc metals, respectively.

The negative values of ΔG^0 indicate that the process involved is spontaneous with a high affinity of Cadmium and Zinc used for the adsorbents. Further, the positive values of enthalpy (ΔH^0) and entropy (ΔS^0) changes suggest the endothermic nature of adsorption and the increased randomness at the solid-solution interface during the adsorption of Cadmium and Zinc ions on adsorbents, respectively.

CONCLUSION

The results obtained in this study clearly demonstrated the potential use of a high fly ash from coal-fired power plant for the removal of Cadmium and Zinc from aqueous solutions. The following conclusions can be drawn based on the investigation:

The kinetic studies indicated that equilibrium in the adsorption of Cadmium and Zinc on the fly ash was reached in 3 h of contact between the fly ash and the wastewater. The adsorption dynamic studies indicated that the pseudo second order kinetic described the best sorption kinetic. Langmuir isotherm was better fitted for the experimental data since the correlation coefficients for Langmuir isotherm was higher than the Freundlich and Temkin isotherms for both metals. The constant value, R_L, in Langmuir isotherm gives an indication of favorable adsorption. The endothermic nature of the adsorption process was indicated by the thermodynamic parameters. Although the fly ash from thermal power plant had, a low metal adsorption capacity compared to that of activated carbon, it is cheaper than the activated carbon and it may be used as neutralizing agent in the treatment processes.

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