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Effect of Different Parameters on the Adsorption of Zn(II) onto Charcoal Ash

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The aim of this research work is to investigate sorption characteristic of charcoal ash for the removal of Zn(II) from aqueous solutions and wastewater. The sorption of Zn(II) by batch dynamic method is carried out. The optimum conditions of sorption were found to be: a sorbent dose of 10 g in 100 mL of aqueous solutions, contact time of 2 h, pH 5. In optimum condition, removal efficiency was 96.1 for the Zn(II). Three equations, *i.e.* Morris-Weber, Lagergren and pseudo second order have been tested to track the kinetics of removal process. The Langmuir, Freundlich and D-R are subjected to sorption data to estimate sorption capacity. It can be concluded that ash has potential to remove Zn(II) ions from aqueous solutions at different concentrations. Desorption efficiency had been tested by water saturated with CO_2 and by aqueous solution of acetic acid, the results was not considerable. It was found that increasing temperature has positive effect on the adsorption, the thermodynamic parameters ΔH, ΔS and ΔG are evaluated. Thermodynamic parameters showed that the adsorption of Zn(II) onto ash was feasible, spontaneous and endothermic under studied conditions.

Key Words: Ash, Zinc, Adsorption, Kinetic, Isotherm, Removal.

INTRODUCTION

The removal of toxic heavy metals from aqueous streams is an important issue facing industries discharging effluents bearing heavy metals. Zinc is an essential element but its concentration in air, water and food should be below the tolerance limits, otherwise it would be harmful to humans and animals[1]. Many industries, especially electroplating, manufacturing batteries, pigments and ammunition production release continuously Zn(II) in wastewaters[2]. Too much intake of Zn(II) can lead to respiratory incapacitation, as indicated by increased respiratory activity such as breathing rate, volume and frequency of ventilation, coughing, decrease in oxygen uptake efficiency[3].

Various treatment processes have been introduced for the removal of metal ions[4]. Current treatment processes include precipitation, oxidation/reduction, membrane filtration/osmosis, ion exchange and adsorption. Each process has its advantages and disadvantages, but ion exchange/adsorption methods do offer the most direct method of producing the highest quality treated water[5].

Activated carbon is a commonly used adsorbent for the removal of pollutants present in water and wastewater the high cost of activated carbon has restricted its more widespread use. A variety of natural sorbents has been exploited for the sorption of toxic metal ions from aqueous systems[6-8].

Fly ash is a waste material originating in great amounts in combustion processes. Although it may contain some hazardous substances, such as heavy metals, it is widely utilized in industry in many countries. For example, in 1994, approximately 6.74 million metric tons of coal fly ash was used in the United States in cement and concrete products[9]. Although fly ash utilization in construction and other civil engineering applications is expected to increase, it is unlikely that this will ever use all the fly ash generated. Research is therefore needed to develop new alternative environmental friendly applications that can further exploit fly ash. Potential environmental impacts of fly ash utilization have been extensively studied and are well understood. Leachability of heavy metals from ashes is relatively low[10] and thus the risks associated with the heavy metals liberation into the environment do not exceed an acceptable level. When used for acidity control in mining and sulfide ore treatment, the lignite fly ash reduced concentrations of dissolved metals in waters to values that meet the European regulatory limits for potable water[11]. Various kinds of ashes have been used as low-cost sorbents for the removal of heavy metals[10,12], organics[13,14], as well as dyes[13,15-17] from waters. An applicability of the fly ashes for the water treatment depends strongly on their origin. Fly ashes from waste incinerators seem to be unsuitable because of their nonstable composition and properties. It was shown that both total contents of heavy metals as well as the released (leached) amounts of these pollutants are higher in the case of the incinerator fly ashes in comparison with coal fly ashes[18]. Ash generated in sugar industry probably does not contain large amounts of toxic metals and has been widely used for adsorption of pollutants from waters[14,16].

In this study, removal of Zn(II) by ash is studied. The effects of dosage of sorbent, contact time and pH value on sorption of Zn(II) are investigated in detail, also adsorption isotherms and adsorption kinetics are obtained and then adsorbent has been used for plating wastewater treatment.

EXPERIMENTAL

Ash preparation and characterizations: In present study, for preparation of ash, charcoal was used. The procedure was putting in an oven for 24 h after burning charcoal. For determining the initial composition of fly ash, 750 mg dried ash sample was treated for 2 days with 20 mL of 200 g/L HF. Then 80 mL of 50 g/L H_3BO_3 was added to dissolve a possible precipitate of CaF_2. The determination of SiO_2 was performed according to the ASTM D 27956 molybdosilicate method and the SO_3 according to the ASTM D1757 gravimetric method. For all experiments, the measurements were carried out as triplicate runs. The physicochemical characterization of wood ash was performed using standard procedures. Characterization of the wood ash was carried out by surface area analysis, bulk density, particle size distribution analysis and scanning electron microscope. The surface area of the wood ash was measured by BET (Brunauer-Emmett-Teller nitrogen adsorption technique). The density of wood ash was determined by specific gravity bottle. The moisture content determination of adsorbent was carried out with a digital microprocessor-based moisture analyzer (mettler-LP16). The particle size distribution analysis was carried out using a particle size distribution analyzer (model 117.08, Malvern instruments, USA). The results of particle size distribution are shown in Table-1. To understand the morphology of adsorption of metals and COD on rice husk ash, the samples were gold sputter coated and the scanning electron microscopic (SEM) micrograph were taken (Fig. 1) by using SEM (model S3400, Hitachi, Japan). SEM micrographs of the wood ash indicated that the surface was highly irregular and porous in nature. Table-2 shows the chemical composition of wood ash. Bulk density and surface area are reported in Table-3. The point of zero charge of the rice husk ash was determined by the solid addition method[19].

TABLE-1
PARTICLE SIZE DISTRIBUTION OF THE ASH (400–500 μm)

Adsorbent (μm)	Ash (%)
400-420	24.2
420-440	23.4
440-460	27.1
460-480	20.3
480-500	10.2

TABLE-2
BULK CHEMICAL COMPOSITION OF FLY ASH

Oxide	g/kg
Si as SiO_2	247.9
Fe as Fe_2O_3	44.1
Al as Al_2O_3	128.8
Ti as TiO_2	2.4
Ca as CaO	483.8
Mg as MgO	42.6
S as SO_3	44.3
Na as Na_2O	3.1
K as K_2O	6.4

TABLE-3
CHARACTERISTICS OF ASH

Surface area (m^2 /g)	62.1
Bulk density (g/cm^3)	1.15
Point of zero charge, pH	8.5
Mean diameter (m)	2.4×10^{-4}

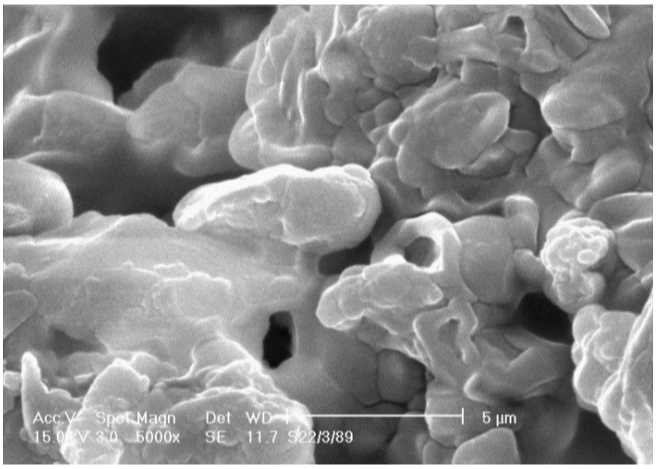

Fig. 1. Scanning electron micrographs (SEM) of ash

Preparation of Zn(II) solutions: Solution of Zn(II) was prepared using analytical grade $ZnSO_4$ provided by Merck company and stored at room temperature. powder dried for 1 h in 120 ºC.

Batch adsorption experiments: The adsorption experiments were done for the study the effect of experimental conditions on Zn(II) adsorption and determining the conditions that achieve the maximum amount of Zn(II) removal. Isotherm, kinetic and thermodynamic evaluations were also conducted in this portion of the study. The adsorption tests were conducted in magnetic mixer. The magnetic mixer was 400 rpm throughout the study with 100 mL of solution prepared from the dilution of 1 g/L stock solutions. At the end of predetermined time intervals, the sorbate was filtered and the concentration of Zn(II) was determined. All experiments were carried out twice and the adsorbed concentrations given were the means of duplicate experimental results. The experimental error was below 4 %, the average data were reported. The efficiency of Zn(II), % removal, was calculated as:

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

where C_i is the initial concentration (mg L^{-1}) and C_f is the final concentration (mg L^{-1}).

q is the amount of metal adsorbed per specific amount of adsorbent (mg/g). The sorption capacity at time t, q_t (mg/g) was obtained as follows:

$$q_t = (C_i - C_f) \times V/m$$

where C_i and C_t (mg/L) were the liquid-phase concentrations of solutes at initial and a given time t, V was the solution volume and m the mass of the ash (g). The amount of adsorption at equilibrium, q_e was given by:

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

where C_e (mg/L) was the ion concentration at equilibrium.

Desorption experiments: Leaching tests by water saturated with CO_2 and aqueous solution of acetic acid were carried out. Exhaust ash samples, resulting from multi-element sorption experiments, were used.

Test by water saturated with CO_2: Desorption experiments were carried out by using pure water saturated with CO_2 with an initial pH value of 4.6 0.1. A 10 g sample of exhaust lava ash was placed into 0.2 L of leaching solution. After shaking for 24 h at 20 ºC, the mixture was filtered by 0.45 mm millipore filter and the eluate analyzed for metal ion concentration.

Test by aqueous solution of NaOH: These experiments were carried out by using a 0.5 M NaOH aqueous solution. A 10 g sample of exhaust ash was placed into 0.2 L of leaching NaOH solution. The pH was adjusted to 9 during the experiments by small additions of aqueous solution of 0.5 M NaOH. After shaking for 24 h at 20 ºC, the mixture was filtered by 0.45-mm millipore filter and the metal ion content in the eluate was determined by atomic absorption.

RESULTS AND DISCUSSION

Effect of contact time: Fig. 2. shows the effect of contact time on sorption of Zn(II) by ash. For these cases, initial Zn(II) concentration were of 100 mg/L, pH of 5 was used for Zn(II). Also ash dose of 10 g in 100 mL were used. For Zn(II), sorption rate reaches up to 94.4 when contact time is 2 h and then little change of sorption rate is observed. This result revealed that adsorption of Zn(II) is fast and the equilibrium was achieved by 2 h of contact time. Taking into account these results, a contact time of 2 h was chosen for further experiments.

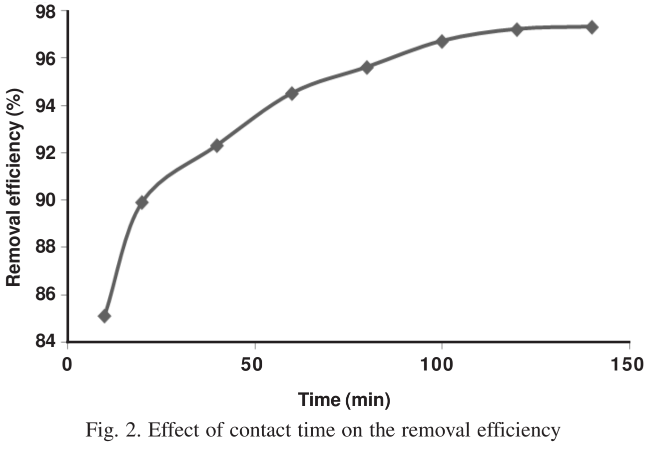

Fig. 2. Effect of contact time on the removal efficiency

Effect of pH sorption: The pH of the solution affects the charge on the surface of the adsorbents, so the change in pH also affects the adsorption process and the H^+ ion concentration may react with the functional groups on the active sites on the adsorption surface. In general, adsorption of cations is favoured at pH > pH PZC. The pH of the solutions has been identified as the most important variable governing metal adsorption. This is partly due to the fact that H^+ themselves are strong competing ions and partly that the solution pH influences the chemical speciation of the metal ions as well as the ionization of the functional groups onto the adsorbent surfaces. In order to evaluate the influence of this parameter on the adsorption, the experiments were carried out at different initial pH values. The effect of pH on adsorption efficiencies are shown in Fig. 3. Optimum pH 5 is observed for the Zn(II). The low degree of adsorption at low pH values can be explained by the fact that at low pH values the H^+ ion concentration is high and therefore protons can compete with the Pb^{2+} for surface sites. In addition when pH increases, there is a decrease in positive surface charge (since the deprotonation of the sorbent functional groups could be occurs), which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of rice husk ash, favouring adsorption.

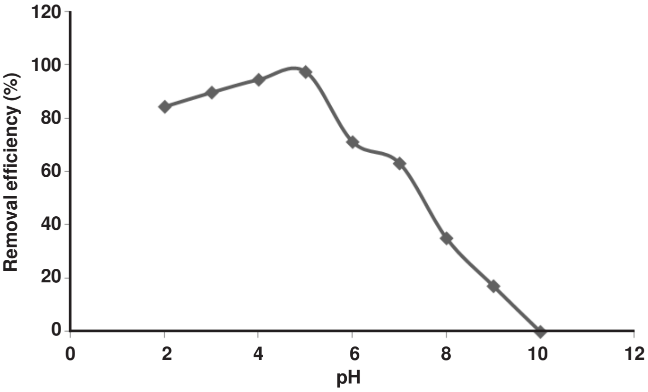

Fig. 3. Effect of pH on the removal efficiency

Kinetics of sorption: Various kinetic models, namely Morris-weber, Lagergren and pseudo second order models have been used for their validity with the experimental adsorption data for Zn(II) onto ash. It was assumed to offer no mass transfer (both external and internal external) resistance to the overall adsorption process. Therefore kinetic can be studied through the residual metal ion concentration in the solution. The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid-solution interface including the diffusion process.

To investigate the change in the concentration of sorbate onto sorbent with shaking time, the kinetic data of Zn(II) ions sorption onto ash were subjected to Morris-Weber eqn. (1)[20]:

$$q_t = K_{id}(t)^{1/2} + C \qquad (1)$$

where q_t is the sorbed concentration of Zn(II) ions at time 't'. The plot of q_t *versus* $t^{1/2}$ is given in Fig. 4. The value of rate constant of Morris-weber transport, k_{id}, calculated from the slope of the linear plot are shown in Fig. 4. The rate constant k = 0.051 min^{-1} was calculated from the slope of the straight line with a correlation factor of 0.92.

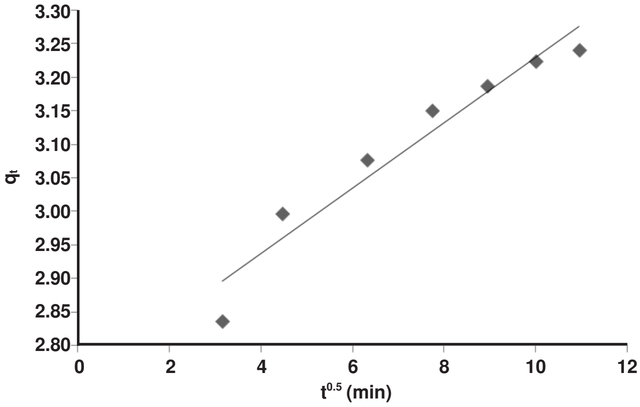

Fig. 4. Morris-Weber plot of Zn(II) sorption onto ash

The pseudo first order of the sorption of Zn^{2+} onto ash was evaluated by treating the data to the following form of Lagergren rate expression (eqn. 2)[21], to determine the rate constant of sorption for Zn^{2+}-ash system.

$$\log(q_e - q_t) = \log q_e - \left(\frac{K}{2.303}\right)t \tag{2}$$

where q_ε is the sorbed concentration at equilibrium and k is the first order rate constant. The linear plot of log (q_e -q_t) against time t (Fig. 5) demonstrates the applicability of the above equation for Zn^{2+} sorption onto ash. The rate constant k = 0.03 min^{-1} was calculated from the slope of the straight line with a correlation factor of 0.97.

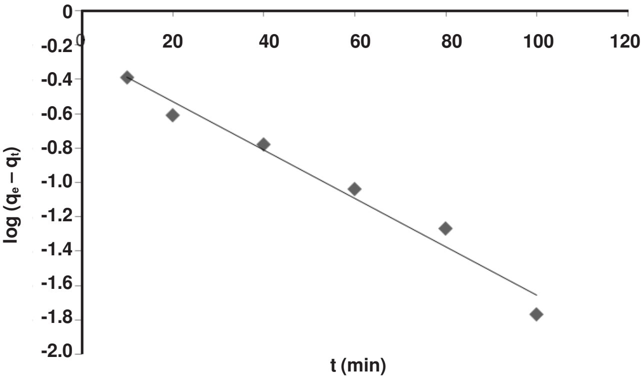

Fig. 5. Validation of Lagergren plot of Zn(II) sorption onto ash.

The kinetic data of Zn^{2+} sorption onto ash was subjected to pseudo second order eqn. (3)[22]:

$$\frac{t}{q_t} = \frac{1}{(Kq_e)^2} + \frac{t}{q_e} \tag{3}$$

The rate constant was calculated from the slope of the straight line (Fig. 6). The rate constant k = 0.37 min^{-1} was calculated from the slope of the straight line with a correlation factor of 0.99. Also this suggests the assumption behind the pseudo-second-order model that the Zn(II) uptake process is due to chemisorptions[23]. The assumption behind the pseudo-second-order kinetic model was that the rate-limiting step might be chemisorptions involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate[24].

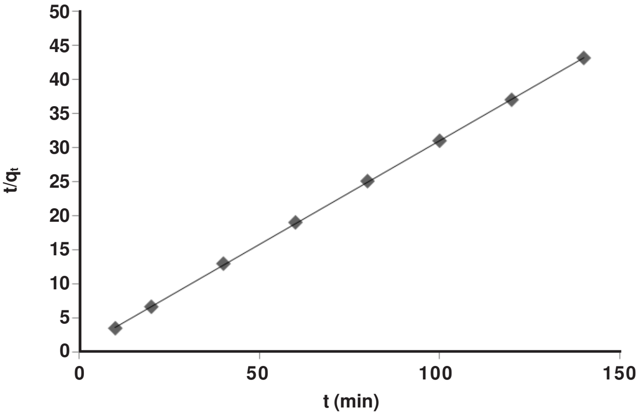

Fig. 6. Pseudo second order plot of Zn(II) sorption onto ash.

Effect of ash dosage on sorption of Zn(II): The effect of ash dose was studied for varying the dose between 0.5 g and 4 g in 100 mL aqueous solution. These tests were conducted at 20 ºC, with optimum pH value for Zn(II). The initial metal ion concentration was 100 mg/L. The pH value of the solution was adjusted with 0.1 M NaOH or 0.1 M H_2SO_4. It was observed that the adsorption percentage of Zn(II) onto the ash increased rapidly with the increasing of adsorbent concentration (Fig. 7). This result is expected because the increase of adsorbent dose leads to greater surface area. When the adsorbent concentration was increased from 0.5 to 3g, the percentage of Zn^{2+} adsorption increased from 81.3 to 97.2. At higher concentrations, the equilibrium uptake of Zn^{2+} did not increase significantly with increasing ash. Such behaviour is expected due to the saturation level attained during an adsorption process[25]. For subsequent studies, a dose of 3 g of ash into 100 mL aqueous solution was selected. The data of Fig. 7. were fitted to Langmuir, Freundlich and Dubnin-Randkovich (D-R) models in order to examine the models constants at different temperature adsorption isotherms.

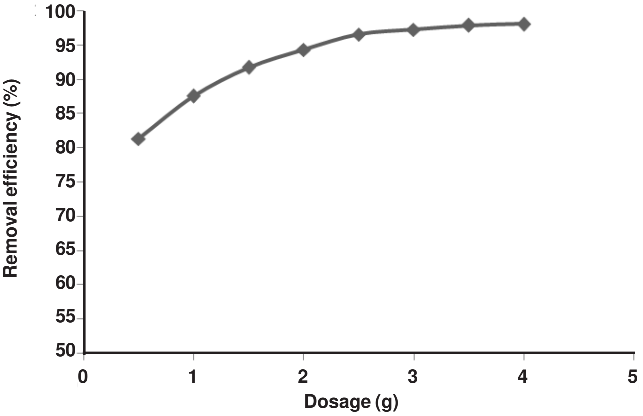

Fig. 7. Effect of dosage on the removal efficiency

Isotherm model: The adsorption isotherm is based on the assumption that every adsorption site is equivalent and independent of whether or not adjacent sites are occupied. Isotherms show the relationship between metal concentration in solution and the amount of metal sorbed on a specific sorbent at a constant temperature.

Langmuir isotherm model: The Langmuir isotherm model is valid for monolayer adsorption onto surface containing finite number of identical sorption sites which is presented by the following eqn. (4):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

where q_e is the amount of metal adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration of the solution (mg/L) and q_m is the maximum amount of metal ions required to form a monolayer (mg/g). Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants (K_L) as below. The values of q_m and K_L can be determined from the linear plot of C_{eq}/q_{eq} *versus* C_{eq}:

$$\frac{C_e}{q_e} = \frac{1}{q_e.K_L} + \frac{1}{q_0} C_e \tag{5}$$

The equilibrium data were analyzed using the linearized form the Langmuir adsorption isotherm eqn. (5). The Langmuir constants, K_L and monolayer sorption capacity, q_m were calculated from the slope and intercept of the plot between C_e/q_e and C_e (Fig. 8). The results and equations are indicated in Fig. 8. and Table-4. As can be seen, the correlation factor of this isotherm is very low, so this equation is not suitable for these data.

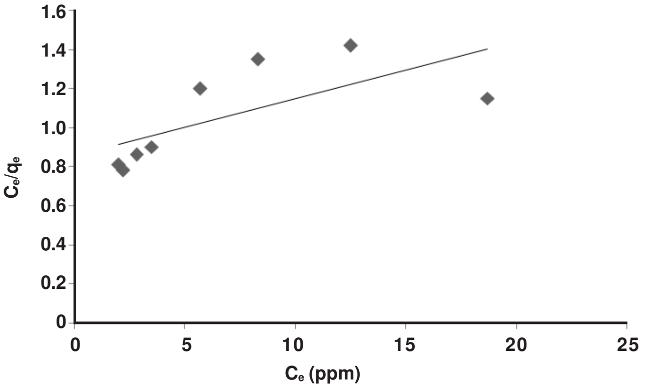

Fig. 8. Langmuir sorption isotherm for Zn(II) sorption

TABLE-4
EQUATION AND PARAMETER OF ISOTHERMS MODEL

Langmuir equations			
Material	Equation		r^2
Zn	y = 0.0288x + 0.8643		0.45
Freundlich isotherm constants for the adsorption of Zn(II) onto ash			
Material	K	n	r^2
Zn	1.4378	1.32	0.93
D-R isotherm constants for the adsorption of Zn(II) onto ash			
Material	q_m	β	r^2
Zn	8.54	8×10^{-6}	0.75

Freundlich isotherm model: While Langmuir isotherm assumes that enthalpy of adsorption is independent of the amount adsorbed, the empirical Freundlich equation, based on sorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites. The Freundlich equation is purely empirical based on sorption on heterogeneous surface and is given by:

$$q_e = K_F (C_e)^{\frac{1}{n}} \tag{6}$$

K_F and (1/n) are the Freundlich constant and adsorption intensity, respectively. Equilibrium constants evaluated from the intercept and the slope, respectively, of the linear plot of log q_e *versus* log C_e based on experimental data. The Freundlich equation can be linearized in logarithmic form for the determination of the Freundlich constants as shown below:

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e) \tag{7}$$

The slope and the intercept correspond to (1/n) and K_F, respectively. It was revealed that the plot of log q_e and log C_e yields a straight line (Fig. 9). The results are indicated in Table -4.

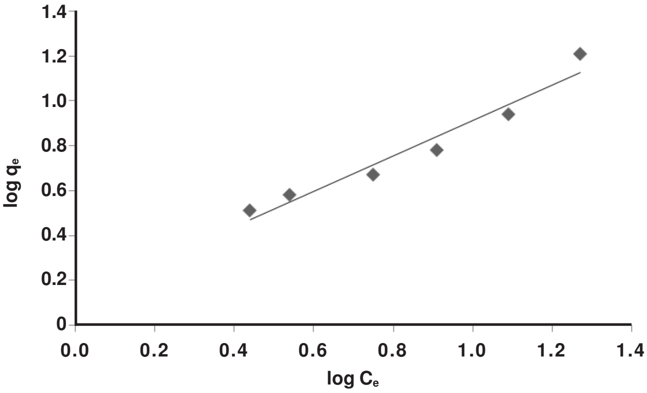

Fig. 9. Freundlich sorption isotherm for Zn(II) sorption

Dubinin-Radushkevick isotherm model: The Dubinin-Radushkevick (D-R)[26-28] isotherm was used to determine the nature of the adsorption process *viz.* physisorption or chemisorption. The linear form of this model is expressed by:

$$\ln(q_e) = \ln(q_m) - \beta\varepsilon^2 \tag{8}$$

where q_e is the amount of Zn^{2+} adsorbed per unit dosage of the adsorbent (mg/g), q_m the monolayer capacity and β is the activity coefficient related to mean sorption energy and ε is the Polanyi potential described as:

$$\varepsilon = RT\ln\left[1 + \left(\frac{1}{C_e}\right)\right] \tag{9}$$

from the plots of ln q_e *versus* ε^2 (Fig. 10) the values of β, q_m were determined by the slope and intercept of the linear plot. The statistical results along with the isotherm constants are also given in Table-4. As our results show, adsorption of Zn(II) by ash can be fitted using Langmuir equation also the D-R equation shows considerable correlation factor. Although the Freundlich isotherm provides the information about the surface heterogeneity and the exponential distribution of the active sites and their energies, it does not predict any saturation of the surface of the adsorbent by the adsorbate. Hence, infinite surface coverage could be predicted mathematically. In contrast, D-R isotherm relates the heterogeneity of energies close to the adsorbent surface. If a very small sub-region of the sorption surface is chosen and assumed to be approximately by the Langmuir isotherm, the quantity can be related to the mean sorption energy, E, which is the free energy for the transfer of 1 mole of metal ions from the infinity to the surface of the adsorbent[29].

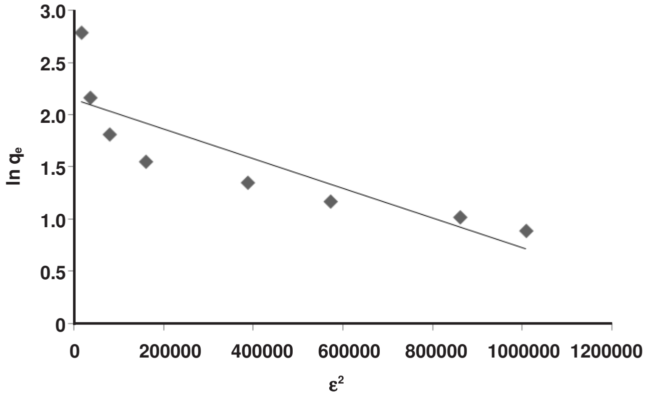

Fig. 10. D-R sorption isotherm for Zn(II) sorption

Effect of initial concentration of Zn(II) on the adsorption: The per cent sorption of Zn(II) in the range of 100-1000 ppm from aqueous solution onto ash at a pH of 5 and 2 h contact time was investigated. The amount of ash was adjusted to 10 g into 100 mL solution. As shown in Fig. 11, the removal efficiency was nearly constant between 100-600 ppm and after this concentration (> 600 ppm) decreased with an increase in initial concentration. At the beginning of initial concentrations (100 mg/L), the removal percentage was higher due to a larger surface area of the ash being available for the adsorption of Zn(II). When the concentration of the Zn(II) solution became higher, the removal percentage was lower because the available sites of adsorption became less. At a higher initial concentration, the ratio of initial number of moles of Zn(II) to the available adsorption surface area was higher and as a result adsorption percentage was less. This might be the major mechanism of the effect of the initial metal ions concentration in aqueous solution on the adsorption process.

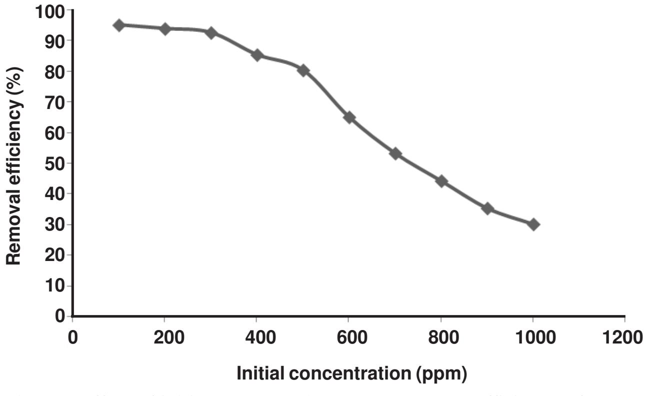

Fig. 11. Effect of initial concentration on the removal efficiency of Zn(II)

Adsorption thermodynamics

Effect of temperature on adsorption of Zn(II): To study the effect of temperature adsorption experiments are carried out at 20-50 °C at optimum pH value of materials and adsorbent dosage level of 3 g in to 100 mL of solutions. The equilibrium contact time for adsorption was maintained at 2 h. The percentage of adsorption increases with rise of temperature from 20 to 50 °C. The results were shown in Table-5 and it revealed the endothermic nature of the adsorption process which later utilized for determination of changes in Gibbs free energy (ΔG_0), heat of adsorption (ΔH_0) and entropy (ΔS_0) of the adsorption of Zn(II) from aqueous solutions. The increase in adsorption with rise in temperature may be due to the strengthening of adsorptive forces between the active sites of the adsorbents and adsorbate species and between the adjacent molecules of the adsorbed phase.

TABLE-5
EFFECT OF TEMPERATURE ON THE REMOVAL EFFICIENCY

Temperature (°C)	Removal efficiency of Zn(II)
20	97.2
30	97.9
40	98.8
50	99.6

Effect of temperature on thermodynamics parameter on adsorption of Zn(II): To study the thermodynamics of adsorption of Zn(II) on ash, thermodynamic constants such as enthalpy change ΔH, free energy change ΔG and entropy change ΔS were calculated using eqns. 10-12. The values of these parameters are given in Table-6. Thermodynamic parameter ΔH, ΔS and ΔG for Zn(II) ions-ash system were calculated using the following equations:

$$K_e = \frac{F_e}{1 - F_e} \tag{10}$$

$$\log(K_c) = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{11}$$

$$\Delta G = -RT \ln K_e \tag{12}$$

where F_e is the fraction of Zn(II) ions sorbed at equilibrium. A perusal of Table-6 indicated that the enthalpy change ΔH is positive (endothermic) due to increase in adsorption on successive increase in temperature. The negative ΔG values indicated thermodynamically feasible and spontaneous nature of the sorption. The positive value of ΔS reveals the increased randomness at the solid-solution interface during the fixation of the ion on the active sites of the sorbent.

TABLE-6
THERMODYNAMIC PARAMETER

	ΔH (KJ/kmol)	ΔS (KJ/kmol)	T (°C)	ΔG (KJ/mol)	r^2
Zn	50.53	0.2	20	- 48.7	
			30	- 75.6	0.93
			40	- 104.1	
			50	- 134.3	

Desorption experiments: To check whether metal ion can be desorbed from the exhaust lava ash, two tests were carried out to simulate the leaching as well by rainwater (test by water saturated with carbon dioxide) as by NaOH percolates. Table-7 reports the desorption efficiency is not considerable. Findings indicate the low reversibility of the sorption process at the pH values of both tests. Leaching by NaOH is more effective than by CO_2-saturated water.

TABLE-7
DESORPTION EFFICIENCY TEST BY CO_2 OR NaOH AQUEOUS SOLUTION

Element	Desorption using NaOH (%)	Desorption using CO_2 (%)
Zn	35.4	30

Conclusion

The ash showed considerable potential for the removal of Zn(II) from aqueous solutions. The optimum conditions of sorption were found to be: a sorbent dose of 10 g in 100 mL of Zn(II) contact time of 2 h, pH 5 for the Zn(II). The results gained from this study were well described by the theoretical Freundlich. The kinetic data indicated that the adsorption process was controlled by pseudo-second-order equation. Desorption of zinc from ash have been studied using 0.1 M NaOH and by water saturated with CO_2, maximum desorption efficiency was 35 %. The effect of temperature has been studied; it was found that increasing temperature has positive effect on the adsorption, the thermodynamic parameters ΔH, ΔS and ΔG are evaluated. Thermodynamic parameters showed that the adsorption of Zn(II) onto ash was feasible, spontaneous and endothermic under studied conditions.

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