

## Removal of Zinc from Aqueous Phase by Charcoal Ash

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**Abstract:** The aim of present research was to investigate sorption characteristic of charcoal ash (ash) for the removal of Zn (II) from aqueous phase. The sorption of Zn (II) was carried out in a batch process. The optimum conditions of sorption were defined with a sorbent dosage of 30 g/l of aqueous solution for 120 min contact time and pH 5. At optimum condition, Zn (II) removal efficiency was 96 %. Morris-Weber, Lagergren and pseudo-second order equations were applied to evaluate kinetics of the removal process. In order to estimate sorption capacity Langmuir, Freundlich and Dubnin-Randkovich (D-R) were investigated for sorption data. It was concluded that ash had great potential to remove Zn (II) ions from aqueous solution in a wide range of metal ions concentrations. Desorption efficiency was experimented by saturated water with CO<sub>2</sub> and NaOH solution. Although the desorption data were not promising. The effect of temperature was investigated; it was found that rising temperature had positive impact on adsorption of zinc ions. The thermodynamic parameters  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  were also evaluated. Thermodynamic parameters showed that spontaneous adsorption of Zn (II) on ash at defined condition was endothermic and feasible.

**Key word:** Charcoal ash · Kinetic model · Adsorption isotherm · Zinc removal · Desorption

### INTRODUCTION

Removal of toxic heavy metals from aqueous streams is an important issue as many industries are facing challenges of the environmental constrains. Zinc is an essential element but its concentration in air, water and food should meet EPA standards or to be lower than standard limits, otherwise it would be harmful to humans and animals [1]. Many industries, especially electroplating, battery manufacturing, pigments and ammunition productions they are continuously releasing Zn (II) in their discharges [2]. High intake of Zn (II) may lead to health complications such as 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 heavy metal ions [4]. Currently,

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 highest quality treated effluents [5]. Activated carbon is commonly used as adsorbent for the removal of pollutants such as removal of heavy metals from water and wastewater. The high cost of activated carbon has restricted the widespread use of adsorption process. A variety of natural sorbents has been exploited as alternative sorbent for the removal of toxic metal ions from the discharge streams [6-8].

Fly ash is a waste material originated in massive amounts in combustion processes. Although it may contains some hazardous substances, such as heavy metals. Often fly ash is utilized in many industries. In 1994, approximately 6.74 million metric tons of coal fly ash was used in the United States as blend with cement for

production of concrete [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. Therefore, research is required to develop alternative environmental friendly applications for further exploitation of fly ash. Environmental impact of fly ash utilization has been extensively studied. It has been reported that leachates of heavy metals from ashes are relatively low [10] and thus the risks associated with the heavy metals liberation into the environment may not exceeded from an acceptable level. When ash is used for acidity control in mining and sulde or 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 from discharges [13, 15-17]. An applicability of 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 fly ashes from incinerator in comparison to coal fly ashes [18]. Ash generated from the combustion of sugar industrial wastes are recommended as most probably the ash 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 was investigated. Effects of sorbent dosage, contact time and pH value of the aqueous media of Zn (II) were also investigated. Adsorption isotherms and adsorption kinetics models were determined.

## MATERIALS AND METHODS

**Ash Preparation and Characterizations:** For preparation of ash, defined mass of charcoal was combusted in a furnace at 250°C. Remaining ash was kept at 60 °C oven for 24 hour. For determining the initial composition of ash, 750 mg dried ash sample was treated in 20 ml of 200 g/l HF, then dissolved in 80 ml of 50 g/l H<sub>3</sub>BO<sub>3</sub>. The most probable precipitate particles were CaF<sub>2</sub>. The determination of SiO<sub>2</sub> and SO<sub>3</sub> were performed according to standard methods ASTM D27956 Molybdosilicate and ASTM D1757 Gravimetric Methods, respectively. The physicochemical characterization of ash was performed according to standard procedures. Characterization of the ash was carried out by surface area

Table 1: Ash particle size distribution

Adsorbent (µm)	Size distribution (%)
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 ash.

Component	g/kg
SiO <sub>2</sub>	247.9
Fe <sub>2</sub> O <sub>3</sub>	44.1
Al <sub>2</sub> O <sub>3</sub>	128.8
Ti O <sub>2</sub>	2.4
CaO	483.8
MgO	42.6
SO <sub>3</sub>	44.3
Na <sub>2</sub> O	3.1
K <sub>2</sub> O	6.4

Table 3: Ash characterization.

Adsorbent	Ash
Surface area (m <sup>2</sup> /g)	62.1
Bulk density (g/cm <sup>3</sup> )	1.15
pH without charge	8.5
Mean diameter (m)	2.4 × 10 <sup>-4</sup>

analysis, bulk density, particle size distribution analysis and scanning electron microscope (SEM). The surface area of the ash was measured by BET (Brunauer-Emmett-Teller) nitrogen adsorption technique. The density of ash was determined by specific gravity bottle. Determination of the moisture content of adsorbent was carried out with a digital microprocessor based moisture analyzer (Mettler-LP16). The particle size distribution analysis was determined using a particle size distribution analyzer (Model 117.08, Malvern instruments, USA). The results for particle size distribution are shown in Table 1. To explain the morphology of adsorption of metals and COD on ash particles, the samples were coated with gold sputter and the image of scanning electron microscopic (SEM) micrograph was captured (Fig. 1) using SEM (Model S3400, Hitachi, Japan). SEM micrographs of the ash particles indicated that the texture of ash was porous and surface with irregular particle distribution. Table 2 shows the chemical composition of ash. Bulk density and surface area are summarized in Table 3. The zero charge point of the ash was determined by the solid addition method [19].

**Preparation of Zn (II) Solutions:** Solution of Zn (II) was prepared using analytical grade ZnSO<sub>4</sub> supplied by Merck (Darmstadt Germany) and stored at room temperature. Powder was dried at 120°C for 1 hour.

**Batch Experiments:** In order to investigate the effect of experimental conditions on Zn (II) adsorption, adsorption experiments were carried out in batch process. Adsorption isotherm, kinetics and thermodynamic evaluations were conducted for the adsorption process. The tests were performed on a magnetic mixer. The magnetic agitation rate was set at 400 rpm, throughout the studies. By dilution of 1 g/l stock solutions, 100 ml of the solution was prepared. At the end of predetermined time intervals, the sorbate was filtered and the concentration of Zn (II) was determined. All experiments were duplicated and the adsorbed concentrations were the mean value of obtained experimental data. Error analysis was conducted and the error was less than 4%. The Zn (II) removal efficiency was calculated according to the following relation:

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

where C<sub>i</sub> is the initial concentration (mg l<sup>-1</sup>) and C<sub>f</sub> is the final concentration (mg l<sup>-1</sup>). The value for q is the amount of metal adsorbed per specific amount of adsorbent (mg/g). The sorption capacity with respect to time t, q<sub>t</sub> (mg/g) was obtained as follows:

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

where C<sub>i</sub> and C<sub>t</sub> (mg/l) were the liquid-phase concentrations of solutes at initial and a given time t, V and m were the solution volume (l) and the mass of ash (g), respectively. The amount of adsorption at equilibrium, q<sub>e</sub> was defined by the following equation:

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

where C<sub>e</sub> (mg/l) was the ion concentration at equilibrium.

**Desorption Experiments:** Leaching tests by water saturated with CO<sub>2</sub> and aqueous solution of NaOH were performed. Exhaust ash samples, resulting from multi-element sorption experiments, were used.

**Test by Water Saturated with CO<sub>2</sub>:** Desorption experiments were conducted by pure water saturated with CO<sub>2</sub>. A 3g sample of exhaust ash was placed into 0.2 L of

leaching solution. After shaking for 24 h at 20°C, the mixture was filtered by 0.45 mm Millipore filter and the eluted sample was analyzed for metal ion concentration.

**Test by Aqueous Solution of NaOH:** These experiments were carried out using a 0.5 M NaOH solution. A 3g sample of exhaust ash was placed into a 0.2 L of leaching NaOH solution. The pH was adjusted to 9 during the experiments by additions of small amount of a 0.5 M NaOH solution. After shaking for 24 h at 20°C, the mixture was filtered by 0.45-mm Millipore filter; the metal ion content in the eluted sample was determined by atomic absorption.

## RESULTS AND DISCUSSION

**Ash SEM Images:** The ash surface chemistry before and after adsorption were evaluated by SEM. The SEM with clear image with irregular shapes in ash before adsorption was observed (Fig. 1a). The surface texture of unused ash is clear. After adsorption the position of solid particles adsorbed on adsorbent were 50-100 nm and the position of particles on adsorption bed are uniform (Fig. 1b).

**Effect of Contact Time:** Fig. 2 shows the effect of contact time on Zn (II) adsorption by ash. For initial Zn (II) concentration of 100 mg/l, pH of 5 was used for the adsorption process. Dose of ash in 100 ml solution was 3 g. For Zn (II) sorption, maximum removal efficiency of 96% for the contact time 120 min was achieved; and the removal efficiency maintained at constant level. It was found that adsorption of Zn (II) was fast and the equilibrium was achieved for 2 h of contact time. Further experiments were performed with contact time of 2h.

**Effect of pH on Adsorption:** The pH of the solution affects on the surface charges of the adsorbents. The change in pH also affects on adsorption process and the H<sup>+</sup> ion concentration may interact with the functional groups of the active sites on the adsorption surface. In general, adsorption of cations is in favored at pH greater than pH value for point of zero charge (PZC). pH of solutions has been identified as the most important variable governing metal adsorption. This is partially due to the fact that hydrogen ions themselves are strong in competition with the other ions. Also the pH of solution may influence the chemical speciation of the metal ions as well as the ionization of the functional groups attached on the adsorbent surfaces. In order to evaluate the influence of

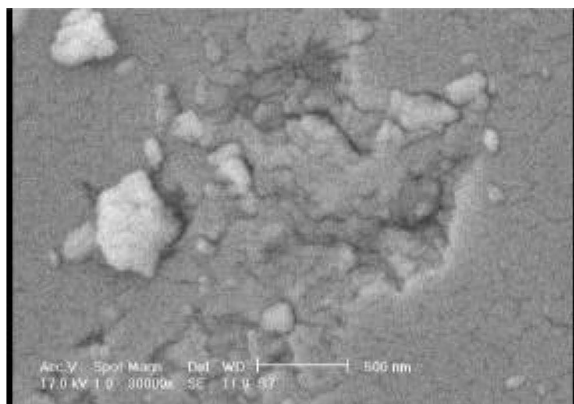


Fig. 1.a: Surface image of charcoal ash by Scanning Electron Microscope (SEM), (Before adsorption)

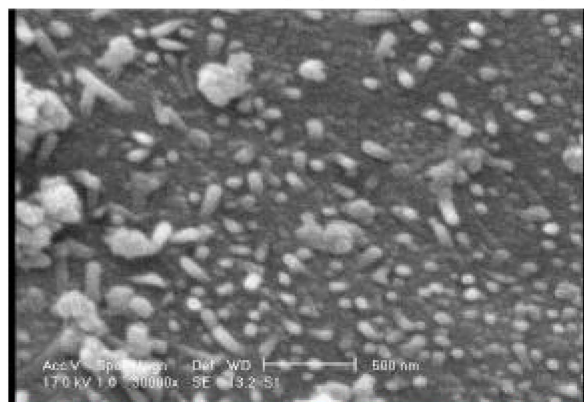


Fig. 1.b: Surface image of charcoal ash by Scanning Electron Microscope (SEM), (After adsorption)

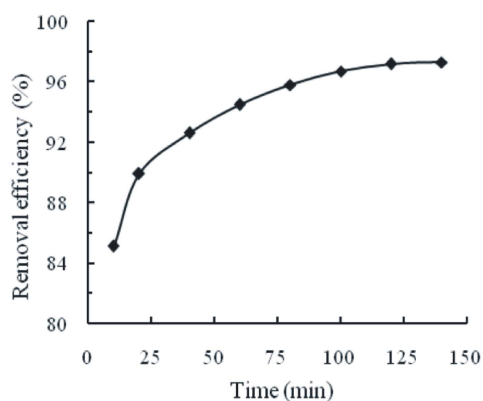


Fig. 2: Effect of contact time on zinc removal efficiency

such ionic interaction on the adsorption, the experiments were carried out with solutions in wide range of initial pH values. The effect of pH on adsorption efficiencies are shown in Fig. 3. For the maximum adsorption of Zn (II) on ash an optimum pH value of 5 was obtained. The low degree of adsorption at low pH values can be explained by the fact that at low pH values the  $H^+$  ion concentration

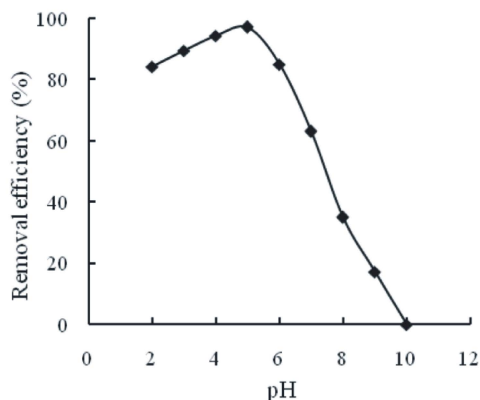


Fig. 3: Effect of pH on zinc removal efficiency

is high and therefore protons can compete with the Zinc cations attracted by the active sites. In contrary at alkaline condition (high pH), there is a decrease in positive surface charges that may cause desorption of Zn (II) from the functional groups of the active site. Desorption is resulted high electrostatic repulsion of metal ions from the surface of ash.

**Adsorption Kinetics:** Various kinetic models, namely Morris-Weber, Lagergren and pseudo second order models were validated for the experimental adsorption data of Zn (II) on ash. Adsorption is considered as physiochemical process in which mass transfer may not play major role since adsorption kinetics are involved. Therefore, adsorption kinetic studies required 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 solid-liquid interface including the diffusion process.

To investigate the change of adsorbate concentration in on sorbent with shaking time, the kinetic data of Zn (II) ions adsorption on ash were subjected to Morris-Weber models as stated as follows [20]:

$$q_t = K_{fd}(t)^{0.5} + C \quad (1)$$

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 for Morris-weber transport model,  $K_{fd}$ , is calculated from the slope of the linear plot (Fig. 4). The slope of the straight line with a correlation factor of 0.92 was calculated; the rate constant was  $k = 0.051 \text{ min}^{-1}$ .

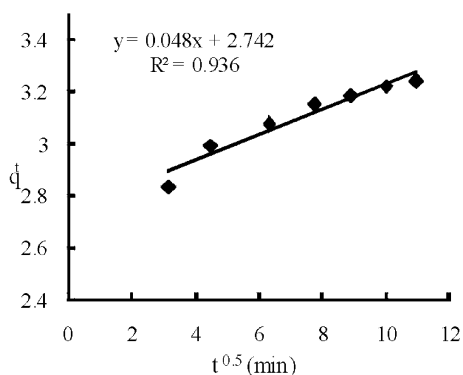


Fig. 4. Morris-Weber plot of Zn (II) adsorption on ash

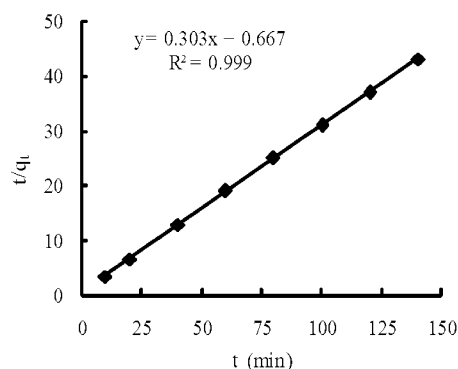


Fig. 6: Pseudo second order plot of Zn (II) adsorption on ash

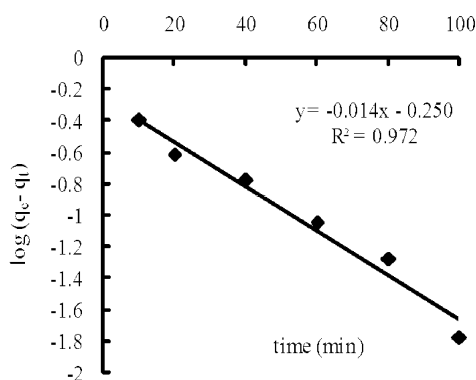


Fig. 5: Validation of Lagergren plot of Zn (II) adsorption on ash

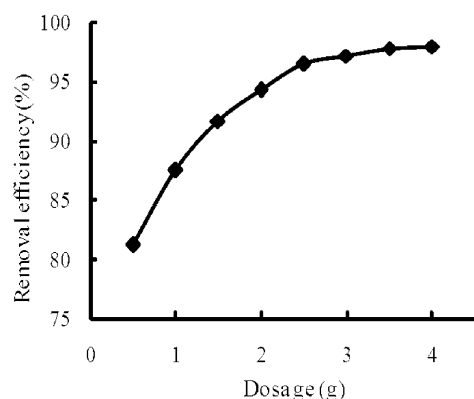


Fig. 7. Effect of dosage on zinc removal efficiency

The Pseudo first order kinetic model for the adsorption of Zn (II) on ash was evaluated by incorporating the experimental data into the following form of Lagergren rate expression given as Eq. 2 [21]. The rate constant of sorption for Zn (II) ions-ash system was determined.

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

where  $q_e$  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 (II) ions sorption on ash. The rate constant  $k = 0.03 \text{ min}^{-1}$  was calculated from the slope of the straight line with a correlation coefficient of 0.97. The kinetic data of Zn (II) ions sorption on ash was subjected to pseudo second order rate model given in Eq. 3 [22]:

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

The rate constant  $k = 0.37 \text{ min}^{-1}$  was calculated from the slope of the straight line with a correlation factor of 0.99 (Fig. 6). Also this may support 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].

**Effect of Ash Dosage on Adsorption of Zn (II):** The effect of ash dosage was investigated in the range of 0.5 to 4 g ash in 100 ml solution. The adsorption of Zn (II) carried out at optimum pH value and 20 °C. The initial metal ion concentration was 100 mg/l. The pH value of the solution was adjusted with 0.1M NaOH or 0.1N H<sub>2</sub>SO<sub>4</sub> solutions. It was observed that the adsorption percentage of Zn (II) on ash has rapidly increased as adsorbent concentration increased (Fig. 7). The data are supported because of the greater surface area were provided with additional adsorbent dosage. When the adsorbent concentration

was increased from 0.5 to 3g, the percentage of Zn (II) ions adsorption increased from 81.3 to 95.1. At high ion concentrations, the equilibrium uptake of Zn (II) did not significantly increase with the increase of ash dosage. Such behavior is expected due to the saturation level attained during the adsorption process [25]. For subsequent studies, a dose of 3g of ash in 100 ml solution was selected. In order to examine the models constants at several temperature adsorption isotherms; the obtained data depicted in Fig. 7 were fitted to Langmuir, Freundlich and Dubnin-Randkovich (D-R) models.

**The Isotherm Models:** 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.

**The Langmuir Isotherm Model:** The Langmuir isotherm model is valid for monolayer adsorption on surface containing finite number of identical sorption sites which is presented by the following equation; Eq. 4:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

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). The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants ( $K_L$ ) as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_o \cdot K_L} + \frac{1}{q_o} C_e \quad (5)$$

The values of  $q_m$  and  $K_L$  can be determined from the linear plot of  $C_{eq}/q_{eq}$  versus  $C_{eq}$ . The equilibrium data were analyzed using the linearized form the Langmuir adsorption isotherm Eq. (5). The Langmuir constants,  $K_L$  and monolayer sorption capacity,  $q_m$  were calculated from the slope and intercept of the plot provided by  $C_e/q_e$  and  $C_e$  (Fig. 8). The obtained results and equations are summarized in Fig. 8 and Table 4. As it was determined, the slope of the line is negative, so this equation is not suitable for the obtained data.

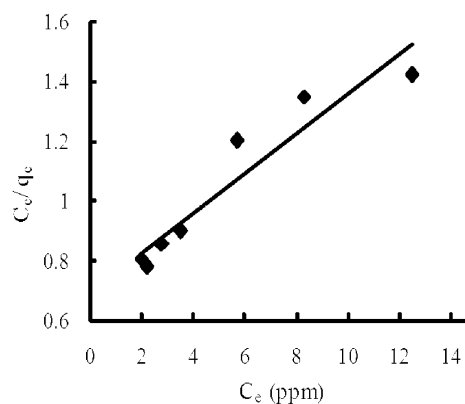


Fig. 8: Langmuir isotherm for Zn (II) adsorption on ash

Table 4: Isotherm adsorption of Zn (II) on ash

Langmuir equation		
$k_L$	$q_0$	$R^2$
10.9	1.42	0.91
Freundlich parameter		
$k$	$n$	$R^2$
0.363	0.84	0.98
D-R parameter		
$q_m$	$\beta$	$R^2$
10.86	$1 \times 10^{-6}$	0.88

**The 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 enthalpy of adsorption with an increase in the fraction of occupied active sites. The Freundlich equation is purely empirical based on sorption on heterogeneous surface and is given by the following equation:

$$q_e = K_F (C_e)^{1/n} \quad (6)$$

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

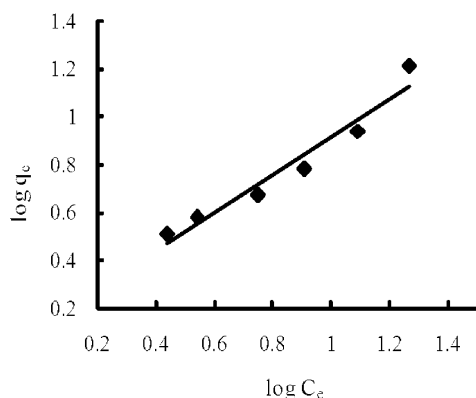


Fig. 9: Freundlich isotherm for Zn (II) adsorption on ash

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

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.

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

$$\ln(q_e) = \ln(q_m) \beta \epsilon^2 \quad (8)$$

Where  $q_e$  is the amount of Zn (II) adsorbed per unit dosage of the adsorbent (mg/g),  $q_m$  the monolayer capacity and  $\beta$  is the activity coefficient related to mean sorption energy and  $\epsilon$  is the Polanyi potential described by the following equation:

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

From the plots of  $\ln q_e$  versus  $\epsilon^2$  (Fig. 10) the values of  $\beta$ ,  $q_m$  were determined by the slope and intercept of the linear plot. The statistical results along with the isotherm constants are also summarized in Table 4. As the results show, adsorption of Zn (II) on ash can be fitted using Langmuir equation also 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.

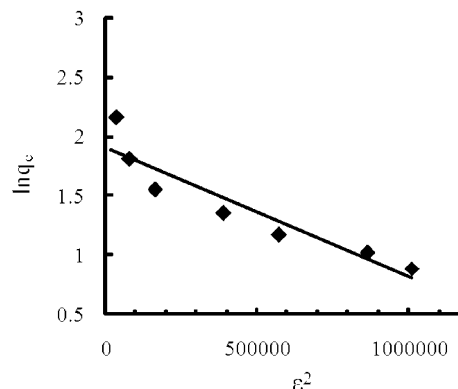


Fig. 10: D-R isotherm for Zn (II) adsorption on ash

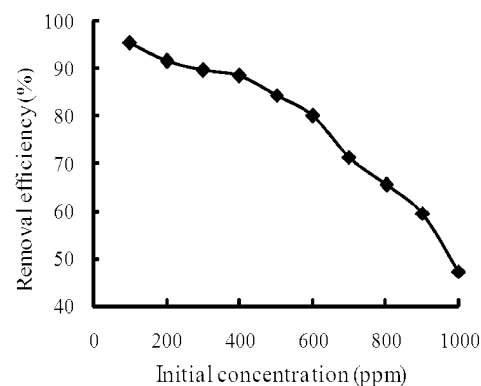


Fig. 11: Effect of initial concentration on zinc removal efficiency

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 approximated 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 adsorbent [29].

**Effect of Initial Concentration of Zn (II) on Adsorption:**

The percent sorption of Zn (II) in the range of 100-1000 ppm from aqueous solution on ash at a pH of 5 and 120 min contact time was investigated. The amount of ash was adjusted to 3 g in 100 ml solution. As data are illustrated in Fig. 11, the removal efficiency was nearly constant between 100-600 ppm. Behind the stated concentration (>600ppm) a decrease with an increase in initial concentration may occur. At the beginning, with initial concentration of 100 mg/l, the percentage of removal was high due to a larger surface area of the ash being available for the adsorption of Zn (II). When the concentration of

Table 5: The effect of temperature on the removal efficiency

Temperature°C	Removal efficiency (%)
20	96.2
30	97.9
40	98.8

Table 6: Thermodynamic properties for Zn (II) adsorption

$\Delta H$ (kJ/kmol)	$\Delta S$ (kJ/kmol)	T°C	$\Delta G$ (kJ/mol)	R <sup>2</sup>
50.53	0.2	20	-48.7	0.98
		30	-75.6	
		40	-104.1	

Table 7: Influence of concentration of different cations on the removal efficiency of Zn (II)

Cations	Removal efficiency of Zn (%)
Ni(II)	89.32
Pb(II)	91.73
Co(II)	87.18
Cr(III)	85.65

Table 8: Desorption efficiency test by CO<sub>2</sub> or NaOH aqueous solution

Element	Desorption using NaOH (%)	Desorption using CO <sub>2</sub> (%)
Zn	35.4	30

Zn (II) solution became greater than 100 mg/l, the removal percentage was lower because the available sites of adsorption became less. At a high initial concentration, the ratio of initial number of moles of Zn (II) to the available adsorption surface area was high 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 phase on adsorption process.

### Adsorption Thermodynamics

**Effect of Temperature on Adsorption of Zn (II):** To study the effect of temperature on adsorption process was investigated. The experiments were carried out at 20-50 °C at optimum pH value of the solution and adsorbent dosage level of 3 g in 100ml solution. The equilibrium contact time for adsorption was kept constant at 2 h. The percentage of adsorption increased with the rise of temperature from 20 to 40°C. The results are shown in Table 5. The results revealed the endothermic nature of the adsorption process which later utilized for determination of changes in Gibbs free energy ( $\Delta G_0$ ), heat of adsorption ( $\Delta H_0$ ) and entropy ( $\Delta S_0$ ) of the adsorption of Zn (II) from aqueous phase. Increase in adsorption with the rise of temperature may be due to the strengthening of adsorptive forces between the active sites of the adsorbents and adsorbate species and also between the adjacent molecules of the adsorbed phase.

### Effect of Temperature on Thermodynamics Parameters of Zn (II) Adsorption:

To investigate the thermodynamics of adsorption of Zn (II) on ash, thermodynamic properties such as enthalpy change  $\Delta H$ , free energy change  $\Delta G$  and entropy change  $\Delta S$  were calculated using equations (10-12). The values of these parameters are given in Table 6. Thermodynamic parameters such as  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for Zn (II) ions-ash system were calculated using the following equations:

$$K_c = \frac{F_e}{1 - F_e} \quad (10)$$

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

$$\Delta G = -RT \ln K_c \quad (12)$$

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

**Influence of Diverse Cations:** The influence of different cations on the sorption of Zn (II) ions is very important because in the environmental samples the ions other than the targeted ions greatly affect the sorption of the required ion in aqueous medium. Sorption of Zn(II) ions (50ppm) was studied in the presence of different cations. The results are given in Table 7. The sorption of Zn(II) ions is reduced to some extent in the presence of a number of competitive ions like Co(II), Pb(II), Ni(II) and Cr(III) ions. The foreign ions which caused appreciable reduction in the sorption of Zn(II) ions, may not be present in the sorptive medium, otherwise lower sorption yields may be obtained.

**Desorption Experiments:** To check whether metal ion can be desorbed from the exhaust ash, two sets of experiments were carried out to simulate the leaching by rainwater (tests conducted with carbon dioxide saturated water) as by NaOH percolates. Table 8 reports the desorption efficiency is not considerable. Results indicate that the low reversibility of the sorption process at the pH values of both tests. Leaching by NaOH is more effective than by CO<sub>2</sub> -saturated water.



## CONCLUSIONS

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 3 g in 100 ml of Zn(II) solution, contact time of 120 min, pH 5 for the Zn (II) solution. The obtained results 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 solution and by water saturated with CO<sub>2</sub>; it was found that the maximum desorption efficiency was 35%. The effect of temperature has been studied; it was found that increasing temperature has positive impact on tZn(II) adsorption. The thermodynamic properties of the adsorption process such as  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  were evaluated. Thermodynamic evaluations showed that the adsorption of Zn (II) on ash was feasible, spontaneous and endothermic under the stated conditions.

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