

# Application of *Acacia karroo* charcoal for desalinating Ni(II) and Zn(II) from aqueous solutions through batch mode

Joginder Singh, Renu Sharma and Amjad Ali

## ABSTRACT

*Acacia karroo* charcoal lumps were used for the biosorption of Ni(II) and Zn(II) from an aqueous solution using batch mode. The effect of various parameters viz., solution pH, adsorbent dose, contact time and initial metal concentrations were studied. Freundlich and Langmuir isotherm models were applied to the batch equilibrium data. The maximum biosorption capacity ( $q_{\max}$ ) for Ni(II) and Zn(II) was found to be 9.0 and 7.99 mg g<sup>-1</sup> at pH 6.0 and 4.0 respectively. Experiments were performed to study the kinetics of Ni(II) and Zn(II) biosorption and the data obtained was best fitted to the pseudo-second-order kinetic model. Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) changes were also calculated and the observed values supported the spontaneity of the biosorption process. The exhausted adsorbent was regenerated three times using 0.1 N NaOH and its regeneration capacity was evaluated. These results illustrate that *A. karroo* charcoal lumps hold good potential for removing heavy metals ions from aqueous solution and could be used for desalinating metal ions from industrial wastewater.

**Key words** | *Acacia karroo* charcoal lumps, adsorption, heavy metals, kinetics, Langmuir isotherm model, thermodynamics

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## INTRODUCTION

The disproportionate release of heavy metal ions into the aqueous streams as a result of excessive industrialisation has posed major problems worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products, hence are more dangerous (Gupta *et al.* 2001). The main industries responsible for this pollution are metal plating, mining, tanning, the chloralkali process, radiator manufacturing, smelting, alloy and battery manufacture (Singh & Ali 2012). Different conventional treatment processes, such as precipitation, membrane filtration, ion exchange, co-precipitation and adsorption, have been used and reported in the literature. Among them, adsorption emerges to be a highly effective and eco-friendly technique using activated carbon as an

adsorbent (Chand *et al.* 1994). Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material. In recent years, the need for low cost alternatives to commercially available activated carbon has been a motivation for research. Low cost agricultural waste by-products, such as sugarcane bagasse (Mohan & Singh 2002), rice husk (Munaf & Zein 1997; Ajmal *et al.* 2003), coconut husk, palm shell (Tan *et al.* 1993) and neem bark (Ayub *et al.* 2001), have been investigated by various researchers for the elimination of heavy metals from wastewater (Bailey *et al.* 1999). Currently, it is necessary that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail.

## MATERIALS AND METHODS

### Preparation of adsorbent

*Acacia karroo* charcoal was collected from charcoal manufacturing kilns near Barara, Haryana, India. It was washed with deionised water to remove dust particles and any other visible impurities, filtered and dried in hot air oven at 105 °C for 24 h. The dried charcoal was crushed into lumps. Thirty grams of charcoal lumps were boiled in 1.0 M HCl (500 mL) for 5 h to activate them and dried again at 105 °C for 24 h. The dried activated *A. karroo* charcoal lumps (AKCL) were packed in a sealed plastic bag for further experimental use.

### Preparation of adsorbate

All the chemicals used were of analytical reagent grade. Stock solution (1,000 mg L<sup>-1</sup>) of Ni(II) and Zn(II) were prepared from Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and ZnSO<sub>4</sub>·7H<sub>2</sub>O (HI-Media, India), respectively, using double-distilled water. Working solutions of Ni(II) and Zn(II) ions from 50 to 100 mg L<sup>-1</sup> were prepared from the stock solution. The pH of each test solution was adjusted to the required pH value with 0.1 M NaOH and 0.1 M HCl.

### Instruments and software

The quantification of the metal ions in solutions was done by atomic absorption spectrophotometry (AAS) (AA630, Shimadzu, Japan) and the Fourier transform infrared (FT-IR) spectrum of the adsorbent was recorded on a Shimadzu FT-IR spectrophotometer. The pH of the solution was measured by a Labtronics Digital pH meter and for shaking the samples during batch operations, an orbital shaker incubator (REMI, India) was used at the desired temperature and speed of shaking. Software Sigma Plot 11 was used for the data analysis and fitting the experimental data to the adsorption isotherms and kinetic models.

### Adsorption studies

Batch experiments for Ni(II) and Zn(II) biosorption from synthetic solutions were carried out at different pH values

(1.0–7.0) by agitating 1.5 g of AKCL in 250 mL screw-cap conical flasks with 100 mL of metal ion solutions respectively. The mixture was agitated in the orbital shaker at 120 rpm for 12 h at 30 °C. After every 30 min of agitation, 2.0 mL of the suspensions were filtered through Whatman no. 40 filter paper and the filtrates were analysed using AAS. Under optimised conditions, the effect of initial metal ion concentration from 50 to 100 mg L<sup>-1</sup> and contact time from 1 to 720 min was studied.

The percentage metal removal ( $R\%$ ) was calculated for each experiment using Equation (1):

$$R(\%) = [(C_i - C_e)/C_i] \times 100 \quad (1)$$

where  $C_i$  and  $C_e$  were the initial and equilibrium concentrations of Ni(II) and Zn(II) ions in the solution respectively. The metal biosorption capacity ( $q_e = \text{mg g}^{-1}$ ) for biosorption of Ni(II) and Zn(II) at equilibrium was determined using Equation (2):

$$q_e = \frac{(C_i - C_e)}{M_a} \times V \quad (2)$$

where  $V$  is the volume of the solution (L) and  $M_a$  is the mass of the adsorbent (g) used.

### Adsorption isotherms

In order to optimise the design of a sorption system for the removal of metals from aqueous solution, it is important to establish the appropriate correlation for equilibrium curves. Experimental data acquired for different conditions were fitted to Langmuir and Freundlich adsorption isotherm models. The equation parameters and the thermodynamic of these equilibrium models often provide some insight into the sorption mechanisms, surface properties and affinities of the sorbent.

### Adsorption kinetics

The kinetics of metal sorption govern the rate that determines the residence time and are one of the important characteristics defining the efficiency of an adsorbent. Sorption kinetics may be controlled by several independent

processes that may act in parallel or in series, such as external mass transfer, bulk diffusion, intraparticle diffusion and chemisorptions. Pseudo-first-order and pseudo-second-order kinetic equations have been used to explain the adsorption of metal ions onto AKCL.

### Desorption studies

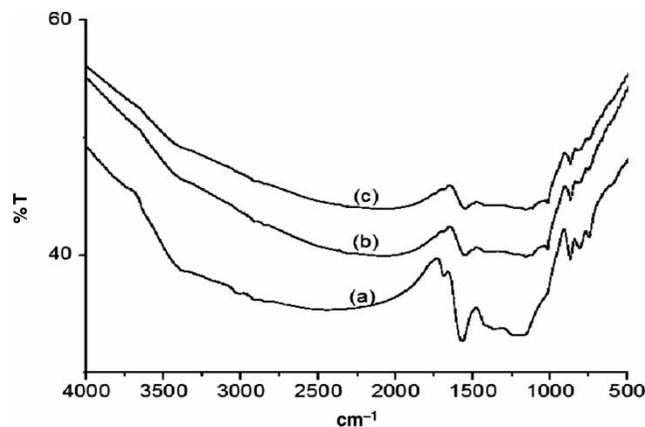
Desorption studies were conducted to check the reversibility of the adsorption process. Desorption of Ni(II) and Zn(II) ions from the exhausted AKCL was studied with the 0.1 M NaOH solution. Five grams of exhausted AKCL were transferred to a stoppered conical flask containing 100 mL 0.1 M NaOH solution. The bottle was shaken at 125 rpm for 720 min at 30 °C using an orbital shaker, and the AKCL were recovered by filtration. The concentrations of Ni(II) and Zn(II) in the aqueous solutions were determined and AKCL obtained were further reused three times.

## RESULTS AND DISCUSSION

### Characterisation of *A. karroo* charcoal lumps

#### FT-IR studies

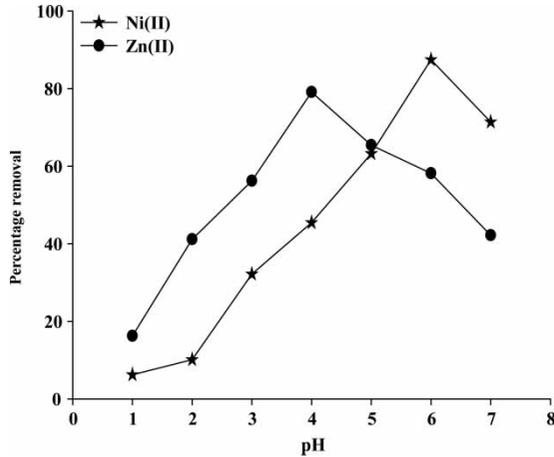
FT-IR spectroscopy is a useful tool to identify the different functional groups present in an adsorbent. The adsorption capacity of the adsorbent depends upon the porosity as well as the chemical reactivity of the functional groups at the surface. In order to determine the main functional groups of AKCL responsible for the Ni(II) and Zn(II) biosorption from the solution, FT-IR spectra of the adsorbent before and after Ni(II) and Zn(II) binding were recorded (Figure 1). As seen in Figure 1(a), the three major peaks were obtained at 1,566, 1,203 and 1,149  $\text{cm}^{-1}$ , which can be attributed to carbohydrates (cellulose and hemicelluloses) and lignin (Chen & Jakes 2002). From Figures 1(b) and 1(c) obtained after adsorption of Ni(II) and Zn(II) on AKCL, there was a shift in the peak from 1,566 to 1,543  $\text{cm}^{-1}$ , and others peaks appeared at 3,742, 3,834 and 3,865  $\text{cm}^{-1}$ , which may be due to the binding of Ni(II) and Zn(II) metal ions onto AKCL.



**Figure 1** | FT-IR spectra of AKCL: (a) AKCL before adsorption of Ni(II) and Zn(II); (b) AKCL with adsorbed Ni(II) metal ions; (c) AKCL with adsorbed Zn(II) metal ions.

*Effect of solution pH on adsorption efficiency of AKCL.* The hydrogen ion concentration is considered as one of the most important and critical parameters that influence the adsorption behaviour of metal ions in aqueous solutions. It affects the solubility of metal ions in solution, replaces some of the positive ions found in the active sites and affects the degree of ionisation of the adsorbate during adsorption (Nomanbhay & Palanisamy 2004; Vimala & Das 2009). The effect of solution pH on the adsorption of Ni(II) and Zn(II) ions onto AKCL was evaluated within the pH range 1.0–7.0. Tests were not conducted at values above pH 7.0 because of the precipitation of Ni(II) and Zn(II) ions to form hydroxides.

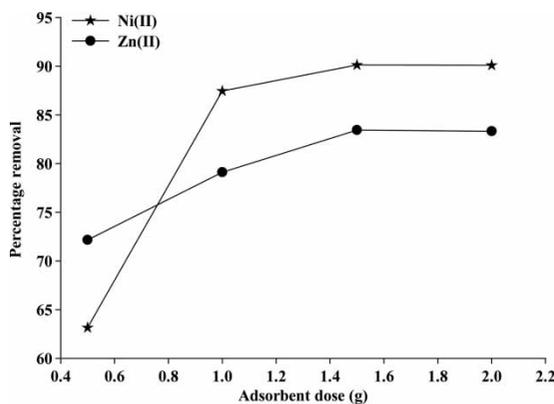
As shown in Figure 2, Zn and Ni adsorption increases with the increase in solution pH. The pH dependency of adsorption efficiency could be explained by considering the functional groups involved in metal uptake and metal chemistry. At low pH values,  $\text{H}^+$  ions occupy most of the adsorption sites on the AKCL surface and fewer Zn and Ni ions could be sorbed because of electric repulsion with  $\text{H}^+$  ions on AKCL surface. When the pH was increased, the AKCL surface became more negatively charged and the adsorption of Ni(II) and Zn(II) increased and reached equilibrium at pH 6.0 and 4.0, respectively. Further increase in pH resulted in decreased adsorption efficiency of Ni(II) and Zn(II) due to the formation of soluble hydroxylated complexes. All further studies were carried out at pH 6.0 and 4.0 for Ni(II) and Zn(II) respectively.



**Figure 2** | Effect of pH on Ni(II) and Zn(II) biosorption onto AKCL at 30 °C ( $C_i = 100 \text{ mg L}^{-1}$ , contact time = 720 min, adsorbent dose = 1.5 g).

**Effect of adsorbent dose.** The number of available sites and exchanging ions for the adsorption depends upon the amount of adsorbent in the adsorption process. The AKCL dose is an important parameter as it determines the capacity of the AKCL for a given initial metal ions concentration. The effect of adsorbent dose on the Ni(II) and Zn(II) removal is shown in Figure 3.

The Ni(II) and Zn(II) percentage removal increased with increase in adsorbent dose and was found to be maximum at an adsorbent dose of 1.5 g/0.1 L. However, with further increase in adsorbent dose, the removal efficiency was marginally lower and this may be due to reduction in concentration gradient. The maximum percentage removal of Ni(II) and Zn(II) onto AKCL was found to be 90.1 and



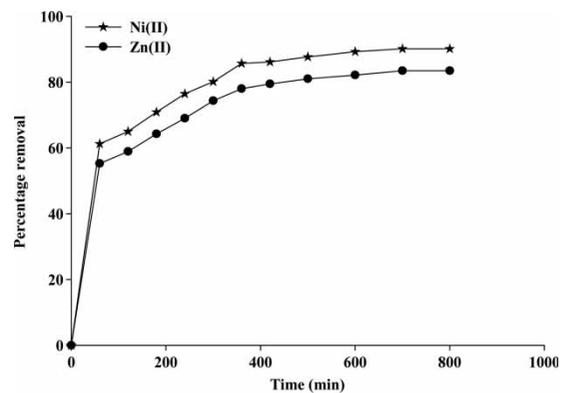
**Figure 3** | Effect of adsorbent dose on Ni(II) and Zn(II) biosorption at 30 °C ( $C_i = 100 \text{ mg L}^{-1}$ , pH for Ni(II) = 6.0 and Zn(II) 4.0, contact time = 720 min).

83.4% at AKCL dose of 1.5 g/0.1 L. This can be attributed to the increased number of exchangeable sites available for adsorption (Vimala & Das 2009).

**Effect of contact time and adsorption kinetics.** The adsorption of Ni(II) and Zn(II) onto AKCL was rapid in the first 360 min and equilibrium was reached within 720 min of contact time as shown in Figure 4. A further increase in contact time has a negligible effect on percentage removal of Zn(II) and Ni(II). This may be due to the formation of a metal ion monolayer on the adsorbent surface with subsequent control of the uptake rate depending on the rate at which the Ni(II) and Zn(II) ions are transported from the exterior to the interior sites of the AKCL particles (Semerjian 2010). It is also relevant that, since there is a fixed number of active sorption sites in a system and each active site can adsorb only one ion in a monolayer, the metal uptake by the sorbent surface will be rapid initially and then slow down as competition for the decreasing number of remaining available active sites intensifies between the metal ions remaining in the solution (Chakravarty et al. 2010).

In order to analyse the adsorption kinetics of Ni(II) and Zn(II) by AKCL, pseudo-first- and pseudo-second-order kinetic models were applied to the experimental data obtained. The first-order rate equation of Lagergren is one of the most widely used for the sorption of a solute from liquid solution and is represented in Equation (3):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$



**Figure 4** | Effect of contact time on Ni(II) and Zn(II) biosorption at 30 °C ( $C_i = 100 \text{ mg L}^{-1}$ , pH for Ni(II) = 6.0 and Zn(II) 4.0, adsorbent dose = 1.5 g).

where  $q_t$  ( $\text{mg g}^{-1}$ ) is the quantity of metal ions adsorbed at time  $t$ ,  $q_e$  is the quantity of metal ions adsorbed at equilibrium ( $\text{mg g}^{-1}$ ), and  $k_1$  is the rate constant of the biosorption ( $\text{min}^{-1}$ ).

The pseudo-first-order kinetic model considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites. The straight line in the graph of  $\ln(q_e - q_t)$  versus  $t$  suggests the applicability of this model. The quantity of adsorbed metal ions ( $q_e$ ) and  $k_1$  can be determined from the intercept and slope of the plot, respectively.

The fitting of the observed data according to pseudo-first-order does not fall on straight lines, indicating that this model is not suitable to describe the biosorption of Ni(II) and Zn(II) by AKCL. On the other hand, the pseudo-second-order kinetic model is based on adsorption equilibrium capacity as given in Equation (4):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where  $k_2$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ) is the rate constant of the second-order equation;  $q_t$  ( $\text{mg g}^{-1}$ ) the quantity of adsorption at time  $t$  (min), and  $q_e$  is the quantity of metal ions adsorbed at equilibrium ( $\text{mg g}^{-1}$ ). The plot of  $t/q_t$  versus  $t$  gave a straight line and the pseudo-second-order rate constant  $k_2$  and  $q_e$  were determined from slope and intercept of the plot respectively, and are presented in Table 1.

Better fitting of the experimental values were obtained by following the pseudo-second-order kinetic model. This implies that the data confirm the pseudo-second-order reaction, i.e. the adsorption has two phases of reaction: a very rapid biosorption of shorter duration at the initial stage followed by a slower phase of longer duration. It has been

**Table 1** | Parameters of pseudo-first-order and pseudo-second-order kinetic models at 30 °C ( $C_i = 100 \text{ mg L}^{-1}$ , pH for Ni(II) = 6.0 and Zn(II) = 4.0, adsorbent dose = 1.5 g)

Metal ion	Pseudo-first-order			Pseudo-second-order		
	$k_1$ ( $\text{min}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$k_2$ ( $\text{min}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$
Ni(II)	0.000036	1.245	0.110	0.000113	96.15	0.99
Zn(II)	0.000042	2.131	0.342	0.000052	98.04	0.93

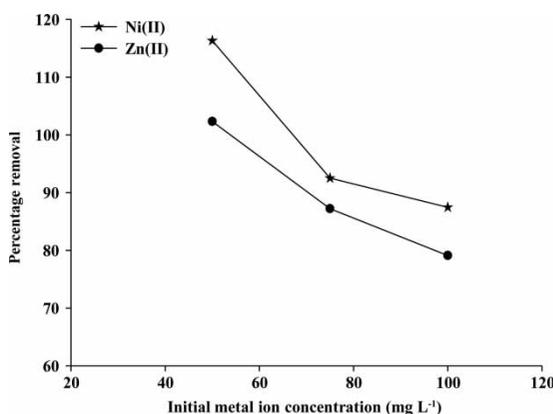
reported that the fast phase is due to exchange of electrons between sorbent and sorbate and the slow phase by diffusion of ions into the cell structure (Horsfall & Spiff 2005).

*Effect of initial metal ion concentration and adsorption isotherms.* The amount of metal ion sorbed per unit mass of AKCL (i.e. sorption capacity) was found to decrease with increase in initial metal ion concentration (Figure 5) and the maximum removal was  $50.0 \text{ mg L}^{-1}$ . The decrease in sorption capacity may be explained by the fact that, at low concentration, the available metal ions occupy adsorption sites on the adsorbent more quickly, forming a monolayer which led to saturation of biomass surface (Horsfall & Spiff 2005).

In order to represent the equilibrium behaviour between the two phases comprising the adsorption system, Langmuir and Freundlich isotherm models have been used in the present study (Kul & Koyuncu 2010). The Langmuir model assumes that the uptake of the metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions and is given by Equation (5):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b q_{\max}} \quad (5)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the quantity of metal ions adsorbed per unit mass of adsorbent and  $C_e$  is the equilibrium concentration in the solution ( $\text{mg L}^{-1}$ ) of Ni(II) and Zn(II) metal



**Figure 5** | Effect of initial ion concentration on adsorption of Ni(II) and Zn(II) on AKCL at 30 °C (pH for Ni(II) = 6.0 and Zn(II) = 4.0, shaking speed = 125 rpm, adsorbent dose = 1.5 g).

ions respectively,  $q_{\max}$  represents the maximum biosorption capacity ( $\text{mg g}^{-1}$ ) under the experimental conditions and  $b$  is a constant related to the affinity of the binding sites ( $\text{L mg}^{-1}$ ). Further, the shape of the isotherm can be used to predict whether a sorption system is favourable or not. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant or separation factor ( $R_L$ ) and the same could be defined by Equation (6):

$$R_L = \frac{1}{1 + bC_i} \quad (6)$$

where  $C_{\text{im}}$  ( $\text{mg L}^{-1}$ ) is the initial quantity of the adsorbate in the solution and  $b$  ( $\text{L mg}^{-1}$ ) is the Langmuir constant described above. There are four probabilities for the  $R_L$  value, viz., for: (i) favourable adsorption  $0 < R_L < 1$ , (ii) unfavourable adsorption  $R_L > 1$ , (iii) linear adsorption  $R_L = 1$ , and (iv) irreversible adsorption  $R_L = 0$ .

On the other hand, Freundlich derived an empirical adsorption isotherm equation, which is based on the

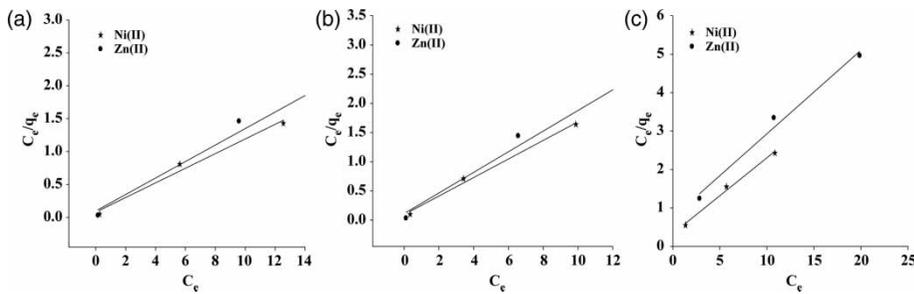
biosorption on a heterogeneous surface and is given by Equation (7):

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

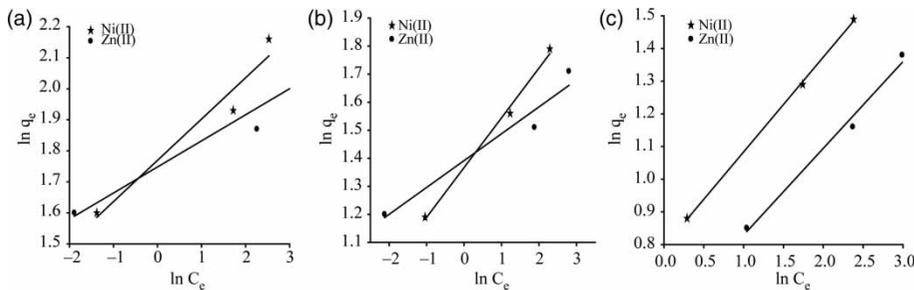
where  $K_F$  and  $n$  are the Freundlich constants and are indicators of adsorption capacity and adsorption intensity, respectively.

The plots of  $C_e/q_e$  versus  $C_e$  and  $\ln q_e$  versus  $\ln C_e$  were found to be linear indicating the applicability of both the Langmuir and Freundlich isotherm models as shown in Figures 6 and 7 respectively.

The Langmuir constants  $q_{\max}$  and  $b$  and Freundlich constants  $K_F$  and  $1/n$  were determined from the intercept and slope of the linear plots, respectively, and the values of the correlation coefficients were found to be extremely high as shown in Table 2. The values of  $1/n$  were smaller than 1 indicating that the biosorption process was favourable under the conditions studied.



**Figure 6** | Langmuir plots for adsorption of Ni(II) and Zn(II) on AKCL with (a) adsorbent dose = 1.0 g, (b) adsorbent dose = 1.5 g, (c) adsorbent dose 2.0 g (pH for Ni(II) = 6.0 and Zn(II) = 4.0, shaking speed = 125 rpm, temp. = 30 °C,  $C_i$  = 50, 75 and 100  $\text{mg L}^{-1}$ , contact time = 720 min).



**Figure 7** | Freundlich plots for adsorption of Ni(II) and Zn(II) on AKCL with (a) adsorbent dose = 1.0 g, (b) adsorbent dose = 1.5 g, (c) adsorbent dose 2.0 g (pH for Ni(II) = 6.0 and Zn(II) = 4.0, shaking speed = 125 rpm, temp. = 30 °C,  $C_i$  = 50, 75 and 100  $\text{mg L}^{-1}$ , contact time = 720 min).

**Table 2** | Langmuir, Freundlich isotherm constants and correlation coefficients for the biosorption of Ni(II) and Zn(II) on different adsorbent doses of AKCL at pH 6.0, 4.0 for Ni(II) and Zn(II) respectively

Adsorbent dose (g)	Metal ion	Langmuir isotherm constants			Freundlich isotherm constants		
		$q_{\max}$ (mg g <sup>-1</sup> )	$b$ (L mg <sup>-1</sup> )	$R^2$	$K_F$ (mg g <sup>-1</sup> )	$n$	$R^2$
1.0	Ni(II)	6.29	0.59	0.98	1.76	5.63	0.99
	Zn(II)	5.66	0.62	0.98	1.74	10.43	0.95
1.5	Ni(II)	9.00	0.72	0.99	1.36	7.51	0.85
	Zn(II)	7.99	0.79	0.99	1.39	11.90	0.92
2.0	Ni(II)	5.07	4.60	0.99	0.79	3.44	0.99
	Zn(II)	1.70	3.47	0.98	0.56	3.76	0.98

Further, the values of  $R_L$  (Table 3) were calculated using Equation (6) for both the metal ions with concentrations in the range of 50.0–100 mg L<sup>-1</sup> and were found to fall between zero and 1 which is again an indication of the favourable biosorption for Ni(II) and Zn(II) on AKCL.

**Table 3** |  $R_L$  for the biosorption of Ni(II) and Zn(II) on different adsorbent doses of AKCL (pH for Ni(II) = 6.0 and Zn(II) = 4.0, shaking speed = 125 rpm, temp. = 30 °C,  $C_i$  = 50–100 mg L<sup>-1</sup>, contact time = 720 min)

Adsorbent dose (g)	Metal ion	$R_L$ value
1.0	Ni(II)	0.022
	Zn(II)	0.020
1.5	Ni(II)	0.026
	Zn(II)	0.024
2.0	Ni(II)	0.002
	Zn(II)	0.003

**Table 4** | Thermodynamic parameters for the adsorption of Ni(II) and Zn(II) ions onto AKCL (pH for Ni(II) = 6.0 and Zn(II) = 4.0, shaking speed = 125 rpm,  $C_i$  = 100 mg L<sup>-1</sup>, contact time = 720 min)

Metal ion	$T$ (K)	$C_e$ (mg L <sup>-1</sup> )	$q_e$ (mg L <sup>-1</sup> )	$K_d$	$\Delta G^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\circ$ (J mol <sup>-1</sup> )
Ni(II)	283	86.48	1.352	0.016	-5,098.35	17.993	-6.108
Zn(II)		81.88	1.812	0.022	-6,194.84		
Ni(II)	293	63.58	3.642	0.057	-5,278.29		
Zn(II)		57.89	4.211	0.073	-6,413.48		
Ni(II)	303	12.55	8.745	0.697	-5,458.23		
Zn(II)		20.89	7.911	0.379	-6,632.13	21.864	-7.188
Ni(II)	313	59.85	4.015	0.067	-5,638.16		
Zn(II)		34.80	6.520	0.187	-6,850.77		

**Effect of temperature and adsorption thermodynamics.** The effect of temperature on the biosorption of Ni(II) and Zn(II) was studied at different temperatures, ranging from 10 to 40 °C with 100 mg L<sup>-1</sup> initial Ni(II) and Zn(II) concentration, adsorbent dose 1.5 g/0.1 L at pH 6.0 and pH 4.0 respectively.

The temperature affected the equilibrium uptake as shown in Table 4. The equilibrium Ni(II) and Zn(II) ion biosorption capacity of the AKCL was better at higher temperature and this could be attributed due to the increase in molecular diffusion or to the availability of more active sites on the surface of the AKCL by expansion of the pores at the same temperature. The spontaneity of the biosorption process was decided by several thermodynamic parameters viz., Gibb's free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ). These thermodynamic parameters were calculated using Equations (8) and (9):

$$\Delta G^\circ = -RT \ln K_d \quad (8)$$

where  $R$  is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),  $T$  is the temperature (K) and  $K_d$  is the equilibrium constant. The value of  $K_d$  was calculated using Equation (9):

$$K_d = \frac{q_e}{C_e} \quad (9)$$

where  $q_e$  and  $C_e$  are the equilibrium concentrations of metal ions on the adsorbent and in the solution, respectively. The enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) of

biosorption were calculated from Equation (10):

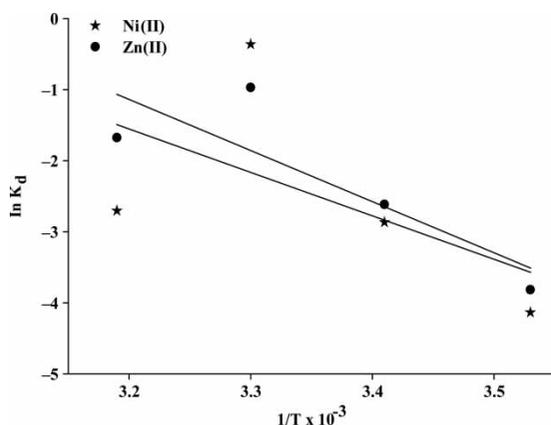
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

Equations (8) and (10) can be combined as:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

A plot of  $\ln K_d$  versus  $1/T$ , as shown in Figure 8, would give the values of the  $\Delta H^\circ$  and  $\Delta S^\circ$  from the slope and intercept, respectively, and the values of  $\Delta G^\circ$  were calculated from Equation (10).

The negative values of  $\Delta G^\circ$  as shown in Table 4 supported the spontaneity of the biosorption process of Ni(II) and Zn(II) on the AKCL while the negative value of  $\Delta H^\circ$  indicated that the process was exothermic in nature. The observed values of  $\Delta H^\circ$  could be used to predict the type of biosorption, viz., physical or chemical. The value of  $\Delta H^\circ < 4.2 \text{ kJ mol}^{-1}$  indicates physical adsorption while a value of  $\Delta H^\circ > 21 \text{ kJ mol}^{-1}$  for the same indicates chemical adsorption. In the present study, the observed values of  $\Delta H^\circ$  for the biosorption of Ni(II) and Zn(II) ions on AKCL at 303 K was found to be  $-7.188 \text{ kJ mol}^{-1}$  and hence, supported the physical nature of the adsorption process. Further, the positive value of  $\Delta S^\circ$  supports the idea that randomness at the



**Figure 8** | Effect of temperature on adsorption of Ni(II) and Zn(II) on AKCL ( $C_i = 100 \text{ mg L}^{-1}$ , contact time = 720 min, pH for Ni(II) = 6.0 and Zn(II) = 4.0, adsorbent dose = 1.5 g).

solid/liquid interface increases during the biosorption of Ni(II) and Zn(II) ions on the AKCL.

### Desorption studies

The adsorbent was regenerated three times using 0.1 M NaOH and it was found that the regeneration capacity of the adsorbent decreases in consecutive steps. Moreover, the metal uptake capacity was also found to decrease. It can be concluded that the adsorbent starts to deteriorate during regeneration cycles with basic elutions.

### CONCLUSIONS

In the present study, removal of Ni(II) and Zn(II) from aqueous solution was carried out using AKCL. The operating parameters, solution pH, adsorbent dose, contact time, initial Ni(II) and Zn(II) concentration and temperature, were effective in the removal of Ni(II) and Zn(II) ions. Langmuir and Freundlich isotherm models were applied to the equilibrium data obtained and the maximum metal uptake capacity ( $q_{\max}$ ) of the AKCL for Ni(II) and Zn(II) were 9.0 and 7.99  $\text{mg g}^{-1}$  respectively. The kinetic studies showed that the pseudo-second-order kinetic model was obeyed better than the pseudo-first-order model. The thermodynamic parameters obtained indicated the feasibility, and exothermic and spontaneous nature of adsorption of Ni(II) and Zn(II) ions onto AKCL. It can be concluded that the AKCL is a cost effective and alternative adsorbent for the removal Ni(II) and Zn(II) ions from an aqueous solutions.

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