The Accumulation of Zn(II) Ions onto Haro River Sand from Aqueous Solutions

Syed Moosa Hasany* and Munawar Hussain Chaudhary

Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad, Pakistan, <hasany@pinstech.org.pk>

ABSTRACT

The accumulation of Zn(II) ions onto Haro river sand has been studied using radiotracer (^{65}Zn) and batch techniques, optimizing nature and composition of electrolyte, concentration of Zn(II) ions (2.34×10^{-5} – 9.38×10^{-4} M), amount of sand (10-2000 mg), shaking time (1-90 min) and temperature (15-55°C) to achieve maximum sorption (~78%). The sorption data follow Freundlich and Dubinin-Radushkevich (D-R) isotherms. Freundlich parameters $1/n = 0.39\pm0.03$ and $C_m = 0.36\pm0.11$ mmole g^{-1} and D-R constants $\beta=-0.00312\pm0.00027$ kJ^2 $mole^{-2}$ and $X_m=54\pm10$ µmole g^{-1} and $E=12.6+0.5$ kJ $mole^{-1}$ have been estimated. The values of $\Delta H=48.8\pm2.3$ kJ $mole^{-1}$, $\Delta S=-174.5\pm7.7$ J $mole^{-1}$ K^{-1} and $\Delta G=-3.3\pm0.2$ kJ $mole^{-1}$ at 298 K have been evaluated. Among the ions tested, ascorbate, tartrate, oxalate, citrate, Pb(II), Y(III) and Al(III) reduce the sorption (3-25%), whereas Zr(IV) and Cr(III) enhance the sorption significantly. Cd(II), Cr(III), I(1) and Ce(III) have low sorption. This cheaper material appears to have potential applications in analytical separation/preconcentration, in industrial effluent treatment and in water purification.

INTRODUCTION

Zinc has a variety of technical and industrial applications such as protective coatings on other metals and steels, in galvanizing, alloys, brass products and sheets, electroplating, welding, dry cells and batteries. It is used in roofing, printing, ceramics, plastics, vulcanizing process, as a catalyst and reductant, in pharmaceuticals and medicines, and as a micronutrient for animals and plants /1/. Although zinc is an essential trace element, its concentration in air, water and food should be below the tolerance limits, otherwise it would be harmful to humans and animals /2/. Therefore, it is essential to keep its concentration below these limits, especially in industrial effluents before releasing them into water bodies. If the concentration of zinc is below the detection limit one needs to preconcentrate it before its analytical measurement. A variety of cheaper materials, including agricultural and industrial waste, have been used for zinc preconcentration and accumulation on solid surfaces /3,4/. The sand of the Haro river, a tributary of the river Indus in Pakistan, has been used as an effective sorbent for a number of metal ions, including antimony

* Author for correspondence.

/5/, chromium /6/, tin /7/ and cadmium /8/. This communication reports the sorption of Zn(II) ions onto Haro river sand from aqueous solutions.

EXPERIMENTAL

Materials and Methods

All chemicals used were of analytical or equivalent grade. Solutions were made in doubly distilled deionized water whose pH and conductance were 6.7 and 4 μ S cm^{-1} respectively. $^{65}Zn(t_{1/2} = 244$ d) and other radiotracers ^{51}Cr, ^{60}Co, ^{75}Sc, ^{95}Zr, ^{110m}Ag, ^{115m}Cd, ^{128}I, ^{134}Cs, $^{141+143}Ce$, $^{152+154}Eu$ and ^{203}Hg were made by irradiating spectroscopic grade metals or their appropriate compounds in the PARR-1 research reactor of this institute at a flux of 4×10^{13} n cm^{-2} s^{-1}. Their radiochemical and radionuclidic purity was checked by gamma spectroscopy, using 4 K series of 85-Canberra multichannel analyzer coupled with a 25 cm^3 Ge(Li) detector.

The sand was collected from the left bank of the Haro river near Lawrencepur, District Attock, Pakistan. The X-ray diffraction analysis indicates that the sand contains quartz 50 %, calcite 30-32 %, albite 8-10 %, illite 5 %, tremolite 1-2 % and antigorite 1-2 %. The BET surface area of the sand measured was 1.47 m^2 g^{-1} after heating it at 120^{0}C for one hour. The sieve analysis of the sand gives the following results:

+250 μm (and above) 67.98 %, +212 μm 11.45 %,
+150 μm 14.13 %, +78 μm 5.90 %, <63 and
>45 μ m 0.18 % and <45 μm 0.36%.

A portion of sand was agitated with distilled deionized water, stirred occasionally and left for 4 hrs. The coloured water was decanted off and fresh deionized water was added. This process was repeated until a colourless supernatent was obtained. The portion of sand having +250 μm and above was heated for 8 hrs. to remove moisture completely. This portion was used as a sorbent for Zn(II) ions in these studies.

Procedure

4.5 cm^3 electrolyte (V) containing carrier and tracer of ^{65}Zn was agitated with 50 mg of sand (W) for 10 minutes. The gross gamma activity of tracer before (A_i) and after shaking (A_f) was measured by a Tennelec gross gamma counter equipped with a 30 cm^3 well-type NaI(Tl) detector after 3 minutes centrifugation for phase separation. The distribution coefficient (K_d) and percent sorption were evaluated by following equations

$$K_d = \frac{A_i - A_f}{A_f} \cdot \frac{V}{W} \left(cm^3 g^{-1}\right) \qquad (1)$$

$$\% \text{sorption} = \frac{A_i - A_f}{A_i} \times 100 \qquad (2)$$

The results quoted are the average of at least triplicate independent measurements at 29±2°C and precision in most cases is ±3%.

RESULTS AND DISCUSSION

Firstly, to select the most appropriate electrolyte, the sorption of Zn(II) ions onto Haro river sand has been measured from 0.001 M solutions of perchloric, hydrochloric and nitric acid solutions along with buffers of pH 7-10. The results are listed in Table 1 along with the concentration of zinc (4.69×10^{-5} M), amount of Haro river sand (50 mg/4.5 ml) and agitation time (10 minutes). It is evident from this table that maximum sorption of Zn(II) ions onto Haro river sand has been achieved from pH 8 buffer under the given experimental conditions. Therefore, for further investigations, this electrolyte has been selected.

Table 1

The sorption of traces of zinc(II) ions onto Haro river sand from different sorptive solutions.

Sand = 50 mg/4.5 ml Agitation time = 10 min.

[Zn] = 4.69×10^{-5} M

	$K_d(cm^3\ g^{-1})$	% Sorption
0.001 M $HClO_4$	19.3	17.5
0.001 M HNO_3	36.9	29.0
0.001 M $HClO_4$	14.8	14.0
Buffer* of pH 7	3.7	4.6
Buffer of pH 8	39.4	30.3
Buffer of pH 9	32.2	26.1
Buffer of pH 10	15.4	14.5

*0.1 M NaOH + 0.1 M boric acid

In general, the equilibration time between sorbent and sorbate also influences the sorption. Therefore, shaking time was varied from 1-90 minutes for two electrolytes, namely pH 8 buffer and deionized water. The percent sorption from pH 8 buffer is always more than that observed from deionized water for corresponding shaking times (Fig.1). The concentration of zinc and amount of sand used were the same throughout these studies, unless specified otherwise.

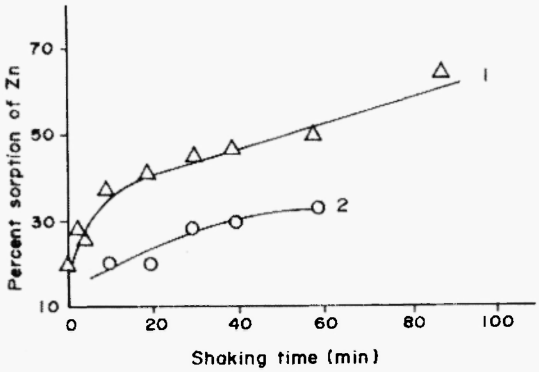

Fig. 1: Percent sorption of Zn(II) ions onto Haro river sand as a function of shaking time.

The kinetics of the sorption of Zn(II) ions onto sorbent surface has been monitored using Lagergren

$$\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \tag{3}$$

and Reichenberg /9/ equations

$$\beta t = -0.4977 - \ln(1 - F_t) \tag{4}$$

where q_e and q_t are sorbed concentrations at equilibrium and at time 't', and F is the ratio between the two, t is agitation time and k is the first order rate constant. The results are plotted in Fig.2. The plot of Lagergren equation indicates two distinct slopes giving values of k=0.12 min^{-1} and 0.01 min^{-1}. The faster rate is approximately 11.6 times higher than the slower one. The other plot shown in Fig.2 depicts Bt vs. time.

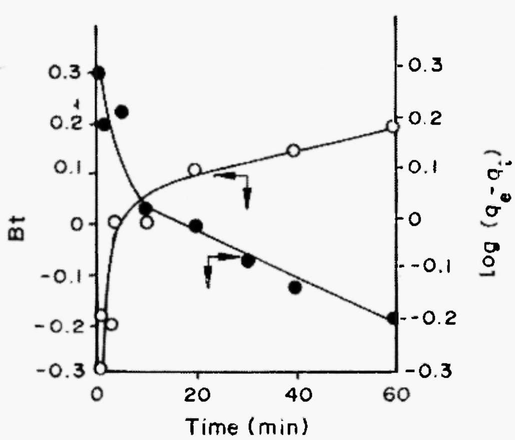

Fig. 2: Lagergren and Reichenberg plots of Zn(II) accumulation onto Haro river sand.

The influence of the amount of sand on the sorption of Zinc(II) ions on its surface has been investigated using 20 minutes agitation time. The percent sorption is plotted vs. the amount of sand in Fig.3. The percent sorption registers an increase with increasing amount of the sorbent and attains almost a constant value around 800 mg/4.5 ml aqueous solution. However, for further experiments 500 mg/4.5 ml sand has been used, because only about 4 percent sorption is gained from 85 to 89 while using 500 to 800 mg sorbent/ 4.5 ml.

The concentration of zinc was also varied over a 40 fold concentration from 2.34×10^{-5} - 9.38×10^{-4} M, to check the effect of its own concentration on its sorption onto Haro river sand from aqueous solution, using 20 minutes shaking time. The variation in percent sorption is plotted against zinc concentration in Fig.4. Percent sorption decreases with an increase in the concentration of zinc. A similar trend is noticed when cadmium metal ions concentration was varied while studying its sorption onto Haro river sand from aqueous solution /9/. The sorption data have been subjected to three sorption isotherms, namely: Langmuir, Freundlich and Dubinin-Radushkevich (D-R). The data followed both Freundlich and D-R isotherms very well over the entire metal concentration range investigated. The Freundlich sorption isotherm was tested in the following linearized form:

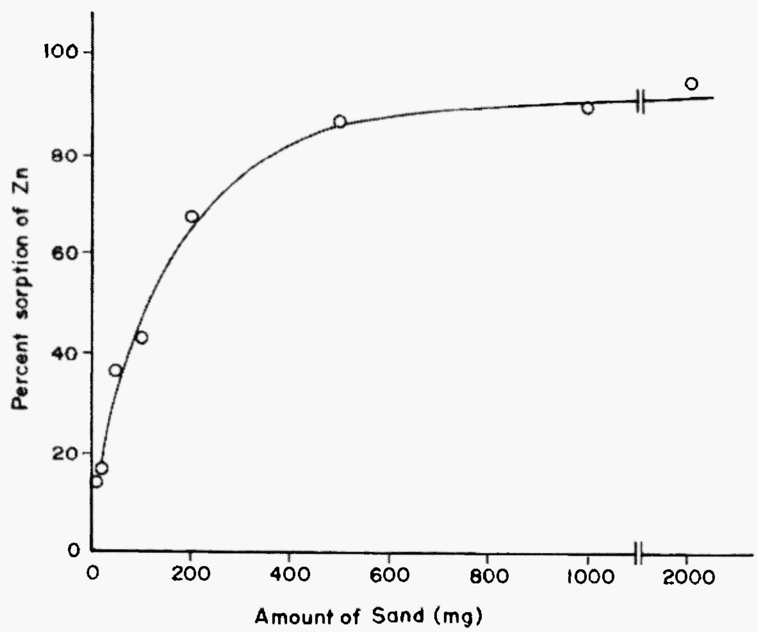

Fig. 3: Variation of Zn(II) ions sorption with the amount of sorbent.

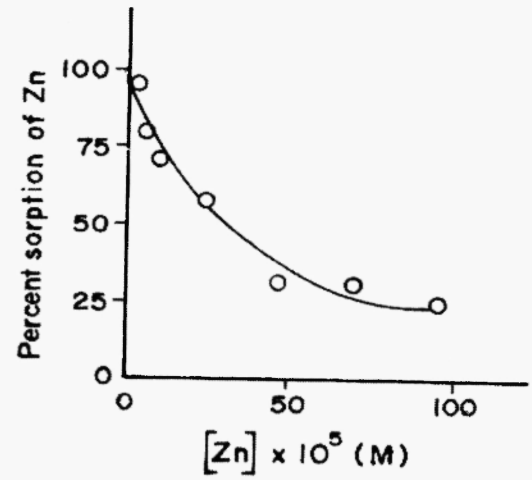

Fig. 4: Influence of Zn(II) concentration on its uptake onto Haro river sand.

$$\log C_{ads} = \log C_m + \frac{1}{n} \log C_e \qquad (5)$$

where C_{ads}, C_m and C_e are adsorbed concentration and maximum sorption capacity in mole g^{-1} and sorbate concentration in solution at equilibrium in M. 1/n is a Freundlich constant which signifies its sorption intensity and is always below unity. Fig.5 gives the graphical presentation of the isotherm where log C_{ads} is plotted against log C_e and is linear. From the slope of this plot the value of 1/n is estimated to be 0.39±0.03 and from its intercept the value of C_m = 0.36±0.11 mmole g^{-1} has been computed with a correlation factor of 0.9843. These values are of the same order of magnitude as evaluated for the sorption of cadmium onto the same sorbent[8]. The Dubinin-Radushkevich (D-R) isotherm was monitored in the following linearized form:

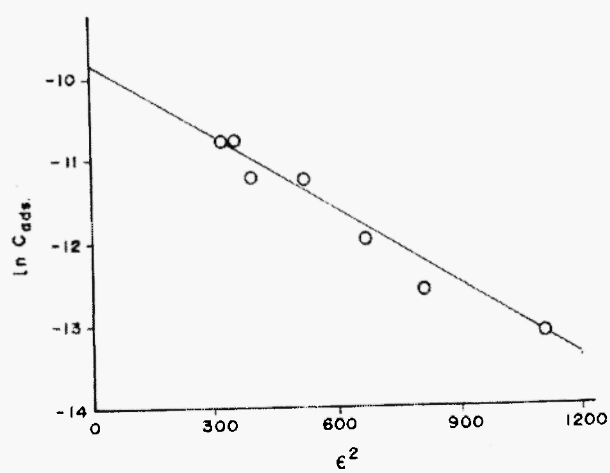

Fig. 5: D-R sorption isotherm of Zn(II) ions onto Haro river sand.

$$\ln C_{ads} = \ln C_m - \beta\varepsilon^2 \qquad (6)$$

where β is a characteristic constant and ε is Polanyi potential which is equal to

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{7}$$

where R is the universal gas constant in kJ mole^{-1} and T is temperature in Kelvin. Fig. 6 shows a linear plot where ln C_{ads} is drawn against ε^2.

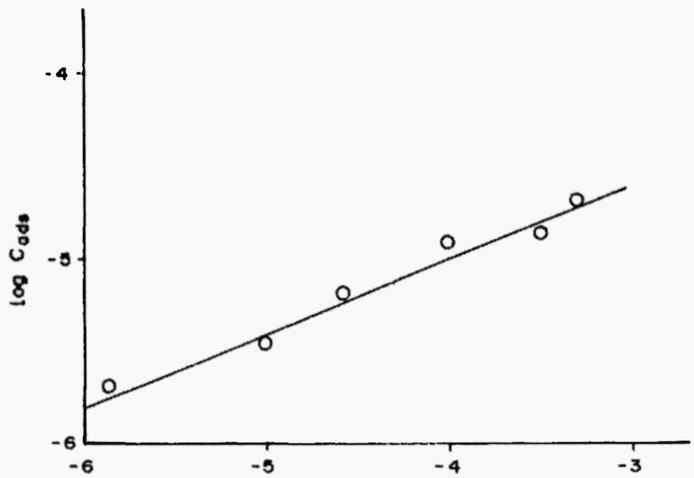

Fig. 6: Freundlich sorption isotherm of Zn(II) ions onto Haro river sand.

The sorption energy, E, can be correlated to β by the following relationship

$$E = \frac{1}{\sqrt{-2\beta}} \tag{8}$$

The values of $\beta = -0.00312 \pm 0.00027$ kJ^2 mole^{-2} and of $C_m = 54 \pm 10$ µmole g^{-1} have been evaluated from the slope and intercept of the plot shown in Fig.6 with a correlation factor of 0.9815 which is close to unity. The value of E has been calculated to be 12.6 ± 0.5 kJ mole^{-1}. The values of characteristic D-R constants of Zinc(II) sorption onto Haro river sand are compatible with the corresponding values of these constants evaluated for europium sorption onto Haro river sand /10/. The variation of sorption of Zn(II) ions onto sorbent surface with temperature has been studied from 15 to 55°C. The K_c, equilibrium constant has been evaluated using the following equation:

$$K_c = \frac{F}{1-F} \tag{9}$$

where F is the fraction sorbed at equilibrium. Fig.7 depicts the variation of log K_c with temperature which is a straight line up to 40°C. The thermodynamic parameters ΔH, ΔS and ΔG have been estimated using following relationships:

$$\log K_c = \frac{\Delta H}{2.303\,RT} + \frac{\Delta S}{2.303\,R} \quad (10)$$

$$\Delta G = -RT \ln K_c \quad (11)$$

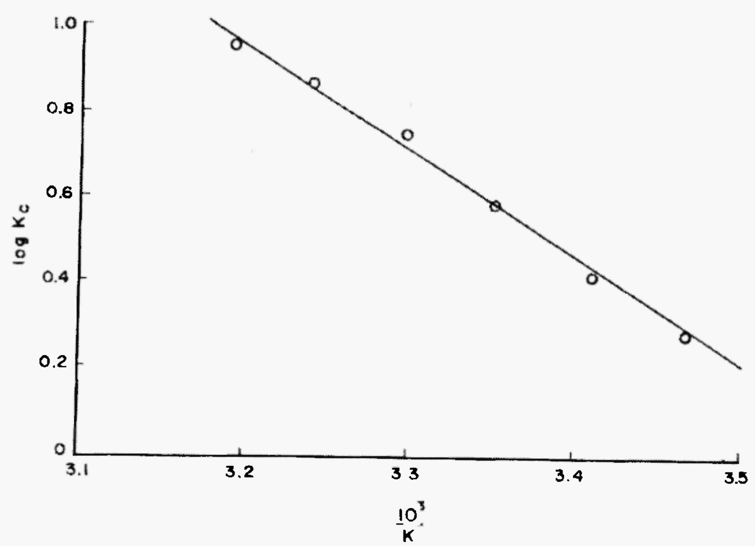

Fig. 7: Effect of temperature on the accumulation of Zn(II) ions onto Haro river sand.

The slope and intercept of the linear plot of Fig.7 give the values of $\Delta H = 48.8 \pm 2.3$ kJ mole^{-1} and of $\Delta S = 174.5 \pm 7.7$ J mole^{-1} K^{-1} and of $\Delta G = -3.3 \pm 0.2$ kJ mole^{-1} at 298 K with a correlation factor of 0.9955.

To check the selectivity, the effect of common anions and cations on the sorption of Zn(II) ions has been investigated under the optimized conditions selected for sorption. The anions were mostly added as their sodium salts and cations were included as their nitrates. The results are given in Tables 2 and 3. Only Zr(IV), Cr(III) and fluoride enhance the sorption whereas Pb(II), Cr(III), Y(III) Al(III), ascorbate, tartrate, oxalate, citrate and Fe(III) reduce the sorption significantly. In the presence of Pb(II), Cr(III) and Zr(IV) white precipitates were observed. The ions which drastically reduce the sorption must be absent from the sorptive solution, otherwise low sorption yields would result.

Table 2

The influence of anions on the sorption of Zn(II) ions onto Haro river sand.

Anion	$K_d(cm^3\ g^{-1})$	% Sorption
Nil	68.9	43.3
Ascorbate	0.56	5.9
Tartrate	2.67	22.9
Oxalate*	2.88	24.2
Citrate	3.42	27.6
Sulphate	10.8	54.6
Phosphate	13.7	60.3
Iodide	14.8	62.1
Bromide*	16.0	64.0
Thiocyanate	16.3	64.4
Acetate	18.7	66.9
Chlorate	19.4	68.3
Chloride	20.7	69.7
Molybdate	33.4	78.7
Fluoride	93.0	91.2

*Potassium salts used.

Table 3

The effect of cations on the sorption of zinc(II) ions onto Haro river sand.

	$K_d(cm^3\ g^{-1})$	% Sorption
Nil	68.9	43.3
Zr(IV)*	949	97.0
Cr(III)*	77.0	89.5
Mg(II)	25.0	73.2
Ba(II)	14.8	62.1
Co(II)	9.42	51.5
La(III)	9.28	50.7
Ni(II)	7.90	46.7
Sr(II)	7.18	44.4
Fe(III)	3.96	30.5
Al(III)	1.32	12.8
Y(III)	0.97	9.7
Pb(II)	0.30	3.2

*White ppt or emulsion observed.

The sorption of other metal ions on the sand has been measured under similar experimental conditions as those chosen for zinc(II) sorption. The results are reported in Table 4 along with the separation factors (•). Cd(II), Cr(III), I(I), Ce(III) and Ag(I) have shown very low sorption as compared to Zn(II) ions. Therefore, Haro river sand column can be used to separate Zn(II) ions from other elements showing low sorption. Moreover, it can also be concluded that this sorbent can be used to preconcentrate or remove Zn(II) ions from its very dilute solutions. This cheaper and cost-effective sorbent can be utilized to decontaminate water or industrial effluents containing zinc or radioactive zinc. In other words, this sorbent has potential applications in analytical, radio, environmental and pollution abatement studies.

Table 4

The sorption of other metal ions onto Haro river sand.

	K_d(cm^3 g^{-1})	% Sorption	α=K_d(Zn(II)/K_d(M)
Zn(II)	68.9	43.3	-
Cd(II)	0.81	9.2	85.0
Cr(III)	0.85	8.6	81.0
I(I)	1.38	13.3	49.9
Ce(III)	1.50	14.3	45.1
Ag(I)	1.71	16.0	40.3
Hg(II)	3.07	25.5	22.4
Zr(IV)	14.0	60.9	4.9
Co(II)	16.4	64.5	4.2
Se(IV)	21.2	70.1	3.3
Eu(III)	25.7	73.8	2.7
Cs(I)	48.5	84.3	1.8

CONCLUSIONS

1. Haro river sand, a cheaper and abundantly available material, can be used to remove traces of Zn(II) ions from aqueous solutions.
2. The accumulation of Zn(II) ions onto Haro river sand obeys Freundlich and Dubinin-Radushkevich (D-R) isotherms.
3. Among the common ions tested oxalate, tartrate, Al(III), Y(III), ascorbate and Pb(II) reduce the sorption significantly (3-25%) whereas Zr(IV) enhances the sorption.
4. The kinetics of Zn(II) sorption onto Haro river sand follows the Lagergren equation giving two distinct first order rate constants.
5. Zn(II) ions can be separated from Cd(II), Cr(III), I(I) and Ce(III) using Haro river sand column.

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