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Sorption behavior of Sn(II) onto Haro river sand from aqueous acidic solutions

S. M. Hasany,* S. J. Khurshid

Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad, Pakistan

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The sorption behavior of Sn(II) onto Haro river sand has been examined with respect to nature of electrolyte, agitation time, dosage of sorbent and concentration of sorbate. Maximum sorption (95.5%) has been achieved from 0.034M hydrochloric acid solution after equilibrating sorbate ($2\cdot10^{-5}$M) and sorbent (50 mg) for 120 minutes at a V/W ratio of $90\ \mathrm{cm^3\cdot g^{-1}}$. The kinetic data have been subjected to Morris-Weber and Lagergren equations. The kinetics of sorption proceeds a two stage process consisting of a relatively slow initial uptake followed by a much rapid increase in the sorption. The rate constant of intraparticle transport, K_d, comes out to be $8.75\cdot10^{-8}\ \mathrm{mol\cdot g^{-1}\cdot min^{-1/2}}$ and the first order rate constant for sorption is $0.0416\ \mathrm{min^{-1}}$.The sorption data of Sn(II) onto Haro river sand followed Langmuir, Freundlich and Dubinin-Radushkevich (D-R) type isotherms. The Langmuir constant, Q, related to sorption capacity and, b, related to sorption energy are computed to be $10.6\pm1.1\ \mu\mathrm{mol\cdot g^{-1}}$ and $1123\pm137\ \mathrm{dm^3\cdot mol^{-1}}$, respectively. The D-R isotherm yields the values of $C_m = 348\pm151\ \mu\mathrm{mol\cdot g^{-1}}$ and $\beta = -0.01044\pm0.0008\ \mathrm{mol^2\cdot kJ^{-2}}$ and of $E = 6.9\pm0.3\ \mathrm{kJ\cdot mol^{-1}}$. In all three isotherms correlation factor (γ) is ≥0.99. The influence of common anions and cations on the sorption has been investigated. Zn(II), Mg(II), oxalate, Pb(II), Mn(II) and tartrate reduce the sorption significantly whereas Fe(II) causes substantial increase in the sorption. It is essential that all ions causing a decrease in the sorption of Sn(II) must be absent from the sorptive solution otherwise low sorption yields would result.

Introduction

The sorption behavior of radionuclides onto geological materials helps to assess safety aspects of the underground disposal of radioactive waste. Among different geological materials, sand of Haro river, a tributary of river Indus in Pakistan, has been exploited as a cheap and inexpensive sorbent for the removal or retention of toxic metal ions or radionuclides present in aqueous solutions. The search for efficient and cost effective materials for the treatment of metals bearing liquid waste is intensified due to stringent discharge limits of harmful substances into aquatic environment.

Haro river sand has been studied in detail as a sorbent for a number of metal ions like cobalt,[1] antimony,[2] europium[3] and chromium.[4] This paper reports the results of an investigation undertaken to study the sorption behavior of Sn(II) from aqueous solutions onto Haro river sand.

Experimental

Reagents and radiotracers

The sand has been collected from the left bank of Haro river near Lawrencepur, District Attock, Pakistan and treated as described earlier.[2] The results of XRD measurement, sieve analyses and surface area and pore size determination have been reported elsewhere.[3] The fraction having the average pore diameter >250 μm has been used as a sorbent for tin.

^{125}Sn ($T_{1/2} = 9.64$ d) tracer was prepared by irradiating specpure tin metal (E. Merck, Germany) in PARR-I research reactor of this Institute at a neutron thermal flux of $4\cdot10^{13}\ \mathrm{n\cdot cm^{-2}\cdot s^{-1}}$ for three days. The isotopic abundance of ^{124}Sn is 5.6% and its absorption cross section for thermal neutrons is 4 mbarns. The irradiated tin metal was dissolved in 3.4M hydrochloric acid solution. The radiochemical purity of the tracer was checked by gamma spectroscopy using a Ge(Li) detector and a Canberra multichannel analyzer. The specific activity of this radiotin solution is $0.79\ \mu\mathrm{Ci\cdot ml^{-1}}$. Radiotin is present as $\mathrm{Sn^{+2}}$ ions in the hydrochloric acid solution. Usually 50 μl radiotin solution was added to 5 ml of sorptive medium which contributes some acidity to deionized water which has been used as a sorptive electrolyte. Therefore, this deionized water is actually 0.034M HCl solution.

All the chemicals used in this study are of analytical or of equivalent grade and all the solutions are made by doubly distilled deionized water whose pH and conductance were found to be 6.8 and 4 μS, respectively.

Instruments

The istruments used for surface area, and radiometric assay have been described elsewhere.[5]

Sorption procedure

Radiotracer technique and batch method are applied to measure the sorption of tin onto Haro river sand.

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* Author for correspondence.

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Usually 50 mg of the sand is equilibrated with 4.5 cm^3 electrolyte containing known concentration of sorbate for a specific time interval using flask shaker at 500 vibrations·min^{-1}. The initial activity of the tracer before (A_i) and after sorption (A_f) is measured. By comparing the initial and final activities the extent of sorption can be estimated. The equations used to compute the distribution ratio (R_d) and percent sorption have already been described earlier.[1] The sorption measurements are carried out at 23±2 °C at least in triplicate and results are average values and precision in most cases is ±3%. The counts per minute are always between 1618 and 16355 per ml. This corresponds to a statistical error of ±2.48 to ±0.78%.

Results and discussion

Firstly the effect of agitation time on the sorption has been investigated from different electrolytes using 50 mg of the sand. The concentration of Sn(II) used was $2\cdot 10^{-5}$M. Figure 1 shows the variation of distribution ratio as a function of agitation time in the range of 1–120 minutes. From 0.01M solution of nitric and perchloric acid sorption of Sn is almost negligible (≥3.4%) even after shaking for 120 minutes. However, from deionized water which is 0.034M hydrochloric acid solution, appreciable sorption of tin is achieved. This solution has been used as an electrolyte for subsequent experiments. The sorption proceeds in a two stage process consisting of a relatively slow uptake upto 60 minutes followed by a faster increase in the sorption.

According to Morris-Weber equation[6] the sorbed concentration at time t, q_t, (mol·g^{-1}) is related to the rate constant of intraparticle transport, K_d through the following relationship:

$$q_t = K_d\sqrt{t} \tag{1}$$

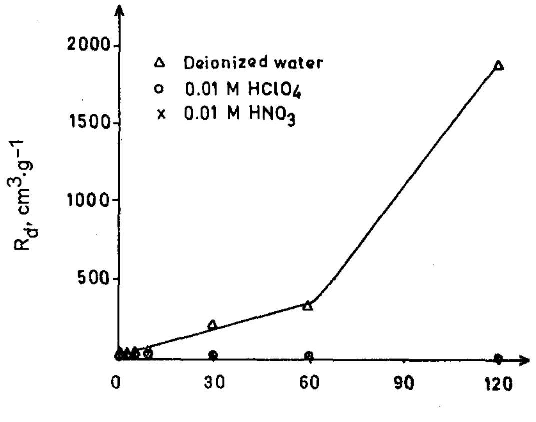

Fig. 1. Sorption of Sn(II) ($2\cdot 10^{-5}$M) onto Haro river sand (50 mg) as a function of shaking time from acidic solutions

In Fig. 2 q_t is plotted against $\sqrt{t}$. The slope of the straight portion of the curve shown in dotted line gives the value of $K_d = 8.75\cdot 10^{-8}$ mol·g^{-1}·$min^{-1/2}$. The kinetic data of Sn(II) sorption are subjected to Lagergren equation[7]

$$\log(q_e - q_t) = \log q_e - \frac{K_t}{2.303}, \tag{2}$$

where k is the rate constant for sorption, q_t is the sorbed concentration at time t and q_e is the amount sorbed at equilibrium. The plot of $\log(q_e - q_t)$ vs. t is shown in Fig. 3 which is a straight line upto 30 minutes agitation time. The slope of this plot gives the value of $k = 0.042$ min^{-1}. The same kinetic data have been tested by the equation given by REICHENBURG.[8] The value of B_t which is a mathematical function of $q_t/q_e = F$ can be calculated for each value of F by the expression

$$F = \left(1 - \frac{6}{\pi^2}\right)e^{-B_t}$$
$$\text{or}\quad B_t = -0.4977 - \ln(l - F) \tag{3}$$

The values of B_t against corresponding time t have also been plotted in Fig. 3. The plot is also linear upto 30 minutes but does not pass through the origin. This indicates that particle diffusion mechanism is not operative and does not control the kinetics of the sorption of tin onto Haro river sand. This conclusion has been substantiated earlier by the fact that the data do not fit the Morris-Weber equation.

The dosage of sorbent is varied between 10 mg to 500 mg. The concentration of Sn(II) has been kept constant at $2\cdot 10^{-5}$M and agitation time applied was 30 minutes. The variation of R_d as a function of the amount of sorbent is shown in Fig. 4. The distribution ratio registers a decrease with an increase in the dosage of the sorbent. A similar trend has been observed when sorption of Sb(V) on the same sand has been studied from dilute nitric acid solution.[2]

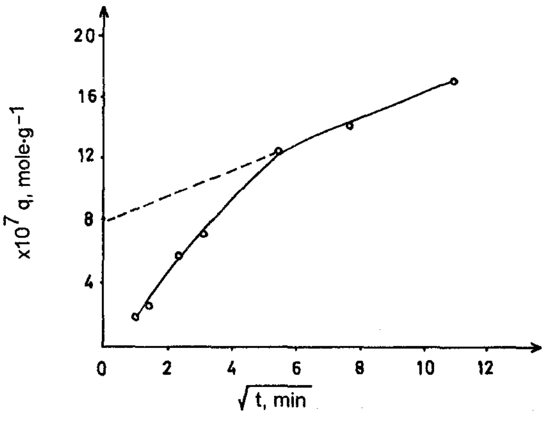

Fig. 2. Sorbed concentration (q_t) of Sn(II) onto Haro river sand from 0.034M HCl solution vs. $\sqrt{t}$

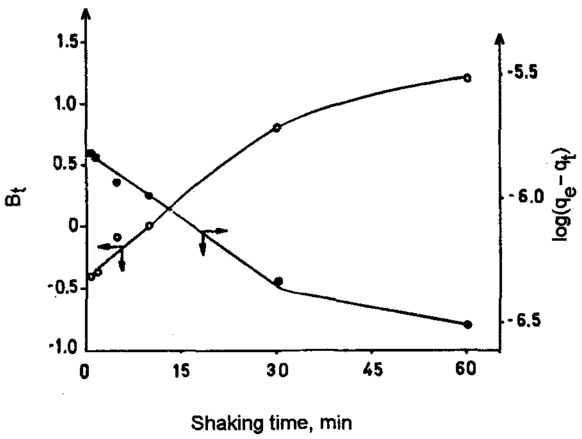

Fig. 3. Lagergren plot of Sn(II) sorption onto Haro river sand and of B_t vs. agitation time from 0.034M HCl solution

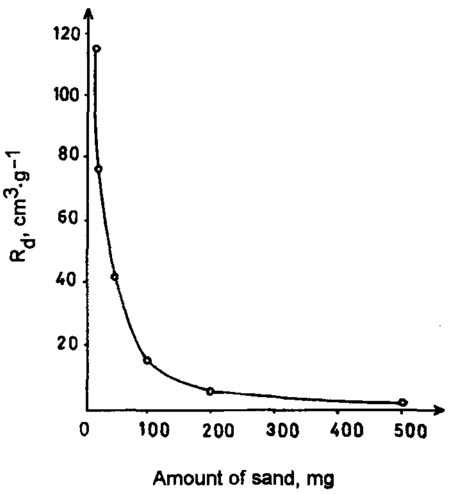

Fig. 4. Influence of sorbent dosage on the distribution ratio (R_d) of Sn(II) from 0.034M HCl solution

Another parameter influencing the sorption is the concentration of sorbate itself. This has been checked from $2\cdot10^{-5}$ to $4\cdot10^{-4}$M using 50 mg of the sand and 30 minutes shaking time. The results are subjected to different sorption isotherms. The Langmuir equation is tested in the following form:

$$\frac{C_e}{C_{ads}}=\frac{1}{Qb}+\frac{C_e}{Q}, \qquad (4)$$

where C_e is the equilibrium concentration of Sn in solution (M), C_{ads} is the amount sorbed (mol·g^{-1}), and Q and b are Langmuir constants related to sorption capacity and energy of sorption, respectively. A linear plot is obtained (Fig. 5) when C_e/C_{ads} has been plotted against C_e. The slope of this straight line gives the value of $Q = 10.6\pm1.1$ μmol·g^{-1} and the intercept yields the value of $b = 1123\pm137$ dm^3·mol^{-1}. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter,[9] R_L which is defined as $R_L = 1/(1+bC_i)$ where b is the Langmuir constant and C_i is the initial concentration of Sn(II). The value of R_L was found to be in the range of 0.96–0.69 i.e., $0<R_L<1$. This indicates a favourable sorption of Sn(II) onto Haro river sand at all concentrations studied.

The Freundlich sorption isotherm is also applied in the following form:

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

where C_m is the maximum sorption at equilibrium. The plot of log C_{ads} vs. log C_e is shown in Fig. 6. This indicates that sorption seems to follow the Freundlich isotherm model as well. The values of C_m and $1/n$ are found to be 73.4 ± 13 m·mol·g^{-1} and 1.17 ± 0.06, respectively. Another isotherm i.e., the Dubinin-Radushkevich (D-R)[10] type can be expressed as:

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

where β is a constant and ε (Polanyi potential) can be correlated to

$$\varepsilon = RT\ln(1+\frac{1}{C_e}), \qquad (7)$$

where R is the gas constant in kJ·mol^{-1} and T is the absolute temperature in Kelvin. The value of β gives the mean free energy of sorption per molecule of the sorbate when it is transferred to the surface of the sorbent from infinity in the solution and can be computed using the relationship:[11]

$$E = \frac{1}{\sqrt{-2b}}. \qquad (8)$$

The plot of ln C_{ads} vs. ε^2 gives a straight line (Fig. 7). The D-R isotherm appears to follow the data reasonably well and useful parameters β and C_m are estimated from the slope and the intercept of the plot shown in Fig. 7.

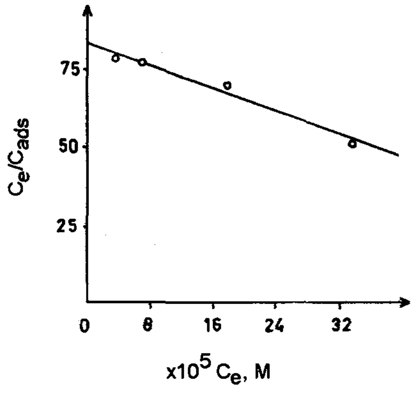

Fig. 5. Langmuir isotherm of Sn(II) sorption onto Haro river sand

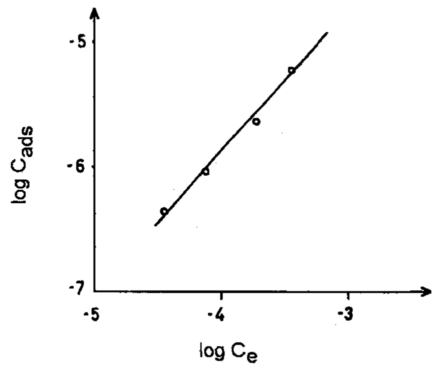

Fig. 6. Freundlich sorption isotherm of Sn(II) onto Haro river sand

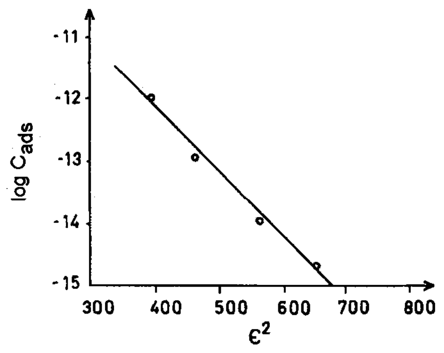

Fig. 7. Dubinin-Radushkevich (D-R) isotherm of Sn(II) sorption onto Haro river sand

Table 1. The effect of anions on the sorption of tin(II) ($2\cdot10^{-5}$M) onto Haro river sand (50 mg) from 0.034M HCl solution

Anion	R_d, $cm^3\cdot g^{-1}$	Sorption, %
Nil	207.5	69.8
EDTA	86.2	48.9
Iodide	84.8	48.5
Bromide	79.8	47.0
Citrate	33.7	27.3
Sulphate	20.2	18.3
Phosphate	16.7	15.6
Chromate*	16.3	15.3
Carbonate	13.0	12.6
Tartrate	12.6	12.3
Oxalate	7.6	7.7

* Potassium salt used.

The values of $\beta = -0.01044 \pm 0.0008$ $mol^2\cdot kJ^{-2}$ and $C_m = 348 \pm 151$ $\mu mol\cdot g^{-1}$ have been estimated for the system. The value of E using Eq. (8) is evaluated to be 6.9 ± 0.3 $kJ\cdot mole^{-1}$. This value is of the same order of magnitude as heat of reaction found for ion exchange process or physical sorption (≤ 8 $kJ\cdot mol^{-1}$) which could be attributed to the weaker bond between Sn(II) and sorbent surface.[12] The correlation factor (γ) for all the three isotherms tested comes out to be ≥ 0.99, close to unity.

Table 2. The influence of cations on the sorption of tin(II) ($2\cdot10^{-5}$M) onto Haro river sand (50 mg) from 0.034M HCl solution

Cation	R_d, $cm^3\cdot g^{-1}$	Sorption, %
Nil	207.5	69.8
Fe(II)	637.2	87.6
K(I)	25.7	22.1
Sr(II)	24.6	21.5
Ni(II)	23.6	20.8
Ba(II)	19.5	17.8
Cu(II)	13.1	12.7
Mn(II)	12.3	12.0
Pb(II)	7.61	7.80
Mg(II)	6.94	7.16
Zn(II)	6.87	7.09

The effect of common anions and cations on the sorption of Sn(II) ($2\cdot10^{-5}$M) has been investigated using 30 minutes shaking time and 50 mg of the sand. The concentration of anions and cations is kept around 10^{-2}M. The anions have been added as their sodium salts whereas cations are included as their nitrates. The results are given in Tables 1 and 2. Except Fe(II) all the ions tend to reduce the sorption. Zn(II), Mg(II), oxalate, Pb(II), Mn(II) and tartrate cause substantial decrease in the sorption whereas Fe(II) increases the sorption appreciably. In other words all the ions which cause a decrease in the sorption need to be removed from the sorptive solution otherwise low sorption yields would be achieved.

These results signify that Haro river sand can be effectively used for the removal of traces of Sn(II) from aqueous solutions. It can also be utilized to decontaminate large volumes of solutions containing small amounts of Sn(II) or to preconcentrate tin on the Haro river sand bed. This solid material appears to have wide applications in analytical and radiochemistry and in pollution abatement studies, especially for the treatment of radioactive and industrial liquid waste containing soluble Sn(II) ions.

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