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# Sorption of Strontium on Hydrous Zirconium Oxide

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## ABSTRACT

Surface characteristics of hydrous zirconium oxide (HZO) and its sorption behavior toward strontium were investigated. In sodium nitrate solution, the point of zero charge (PZC) of HZO was found to be 2.88 by the pH-titration technique. The sorption edge, however, occurs at pH = 8. The lack of sorption of $Sr^{2+}$ in the pH range $2.88 < pH < 8$, seems to be due to the low dielectric constant of HZO. The beginning of sorption at pH = 8 was attributed to the hydrolysis of $Sr^{2+}$ to a lower charged $SrOH^{+}$. An estimate of enthalpy and entropy changes accompanying $H^{+}/Sr^{2+}$ exchange were determined by the temperature-variation method. The increase in the entropy of the overall system seems to favor the exchange of $H^{+}$ with $Sr^{2+}$.

## INTRODUCTION

Apart from the exceptional stability, selectivity, and resistance to radiation, the essential advantage of inorganic sorbents containing, silica, titania, zirconia, etc., is that they can be vitrified or ceramized to unleachable final form for disposal of radiowaste (1–3). Zirconolite ($CaZrTi_2O_4$) (4) is one phase assembly existing in synroc-C that acts as a host matrix for accommodating some divalent, trivalent, and rare-earth radionuclides present in the high-level liquid waste (HLLW). Single phase assemblies for strontium fixation in zirconia (5), titania (3), and conversion of zirconia to zircon ($ZrSiO_4$) (6) were also suggested for radiowaste disposal.

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Understanding the sorption behavior of metal ions from aqueous solution on hydrous oxides (SOH), requires knowledge of the chemistry of the oxide–water interface and the thermodynamic parameters governing sorption and desorption. The amphoteric nature of hydrous metal oxides, as sorbents, strongly influences the sorption of metal ions from aqueous solution (7–12). Hydrous oxides (SOH) in acidic media react with $H^+$ to produce a protonated ($SOH_2^+$) surface with an anionic exchange group as shown in Eq. (1)

$$SOH_2^+ \Leftrightarrow SOH + H^+ \tag{1}$$

In alkaline solution the hydroxyl ion reacts with the hydrous oxide to produce the deprotonated ($SO^-$) form as shown in Eq. (2)

$$SOH \Leftrightarrow SO^- + H^+ \tag{2}$$

Point of zero charge (PZC) is defined as the pH at which the $[SO^-] = [SOH_2^+]$, i.e., the net charge on the surface of the oxide is zero. PZC is a convenient reference value for characterizing hydrous oxides, even though no hydrous oxide has a unique PZC (13). The exact value of the PZC depends on the origin history, purity, crystallinity, temperature, degree of hydration, etc. (14). When $pH < PZC$, the net charge on the oxide surface is positive with exchangeable anionic groups, and when $pH > PZC$ the oxide acts as a cation exchanger. Thus recent studies (15) on the sorption of strontium on silica–titania ($PZC = 4.2$) gel suggest that the sorption of strontium begins at $pH = 4$ and it increases with increase in the fraction of negatively charged surface, which is in accordance with the predictions discussed above.

In the present work, the amphoteric nature of HZO was determined by the pH-titration method and the thermodynamics of the sorption of strontium on HZO.

## EXPERIMENTAL

### Materials

All the chemicals used were of analytical grade. $Sr^{(85+89)}$ radioisotope used for sorption studies was obtained from the Board of Radiation and Isotope Technology, Mumbai, India.

### Preparation of HZO

Hydrous zirconium oxide (HZO) was prepared by the hydrolysis of 0.15 M zirconium oxychloride ($ZrOCl_2 \cdot 8\ H_2O$) with 500 mL of concentrated ammonia at 60°C. The precipitate formed was filtered, washed with water, and dried at 60°C for 20 h. Then it was crushed and sieved to obtain $-30 + 50$ BSS particles. This product was converted to $H^+$ form by passing 1 L of 1.0 M nitric acid into the column packed with the crushed particles. This was again washed thoroughly with water followed by drying at 100°C. This $H^+$ form of the sorbent was used for the subsequent studies.

## pH Titration

pH titrations were carried out by batch equilibrium of 0.1 g of the sorbent in $H^+$ form with 20 mL of the aqueous solution prepared by mixing different volume ratios of 0.05 M sodium nitrate and 0.05 M nitric acid. For the alkaline region 0.05 M NaOH was used instead of nitric acid. The sorbent was kept in contact with the aqueous solution for 3 d with occasional shaking, and the pH of the supernatant was measured after centrifugation.

## Determination of Capacity

The total ion-exchange capacity of the sorbent was determined by passing 100 mL of 0.1 M NaOH through 0.5 g of the sorbent present in a suitable column. The capacity was calculated from the amount of sodium hydroxide consumed.

## Strontium Distribution Studies

### Effect of pH

Sorption of $Sr^{2+}$ as a function of pH was studied by equilibrating 0.05 g of the sorbent with 10 mL of the solution containing 10 ppm $Sr(NO_3)_2$ spiked with $Sr^{(85+89)}$ tracer and 0.05 M sodium nitrate at 30°C. The pH of the solution was adjusted to the desired value by adding dilute sodium hydroxide or dilute nitric acid. Radioassay of strontium isotope was performed by measuring the $\gamma$-activity of the sample with a well-type NaI(Tl) scintillation counter. Distribution coefficients ($K_d$ in mL/g) for strontium were determined using Eq. (3)

$$K_d = [A_i - A_f]/A_f(V/m) \tag{3}$$

where $A_i$ and $A_f$ (cpm/mL) are the initial activity and activity at equilibrium respectively, $m$ is the weight of the sorbent in g, and $V$ is the volume (in mL) of aqueous solution used for equilibration.

### Kinetic Studies

Sorption of strontium(II) as a function of time was studied by equilibrating 0.1 g of the sorbent with 100 mL of aqueous solution containing 0.1 M NaOH and 10 ppm strontium nitrate spiked with $Sr^{(85+89)}$. Aliquots were taken at various intervals of time and their activity was measured. From the initial activity and the activity measured at various intervals of time the fraction of strontium sorbed on HZO was calculated.

### Effect of Sodium Ion

The effect of sodium ion on the sorption of strontium(II) on HZO (in sodium form) was studied at 30°C by equilibrating 0.05 g of the sorbent with 10 mL of the solution containing 10 ppm strontium nitrate spiked with $Sr^{(85+89)}$ tracer, 0.1 M NaOH and varied quantities of sodium nitrate. The total sodium ion concentration in the solution was varied from 0.1 M to 1.5 M. The samples were analyzed as described above.

### Temperature Variation Studies

Batch experiments at 30, 35, and 40°C were conducted by equilibrating 0.05 g of hydrous zirconium oxide with 10 mL of the solution containing 0.1 M NaOH, 0.4 M sodium nitrate, and varied quantities of strontium nitrate. The concentration of $Sr^{2+}$ ion was varied from 10 ppm to 50 ppm spiked with $Sr^{(85+89)}$ tracer. The samples were analyzed as described above.

## RESULTS AND DISCUSSIONS

### Kinetics

Figure 1 shows the sorption of Sr(II) as a function of time. The uptake of Sr(II) at 30°C increases rapidly with time and saturates in about 100 min. At 35°C, equilibrium was attained within 60 min. However, further batch experiments were conducted for a sufficiently long time (360 min) to ensure equilibrium.

### Surface Characteristics of HZO

The conditional equilibrium constants $K_{a1}$ and $K_{a2}$ for reactions (1) and (2) can be given as follows

$$K_{a1} = X_{(SOH)}\, M_{H^+}/X_{(SOH_2{}^+)} \qquad (4)$$

and

$$K_{a2} = X_{(SO^-)}\, M_{H^+}/X_{(SOH)} \qquad (5)$$

where $M_{H^+}$, $X_{(SOH_2{}^+)}$, $X_{(SOH)}$, and $X_{(SO^-)}$ are the molarity of $H^+$ in solution and mole fractions of protonated ($SOH_2^+$), undissociated (SOH) and deprotonated ($SO^-$) forms of the surface hydroxyl groups, respectively, of the oxide. These equilibrium constants can be computed from the pH titration curves by the method given by Schindler and Gamesjaeger (16). The details of this approach are reported elsewhere (7, 11, 12, 15, 17). Thus, assuming that $[SOH_2^+]$ is zero in the alkaline region and $[SO^-]$ is zero in the acidic region, the conditional equilibrium constants, $K_{a1}$ and $K_{a2}$ can be written in terms of the pH-

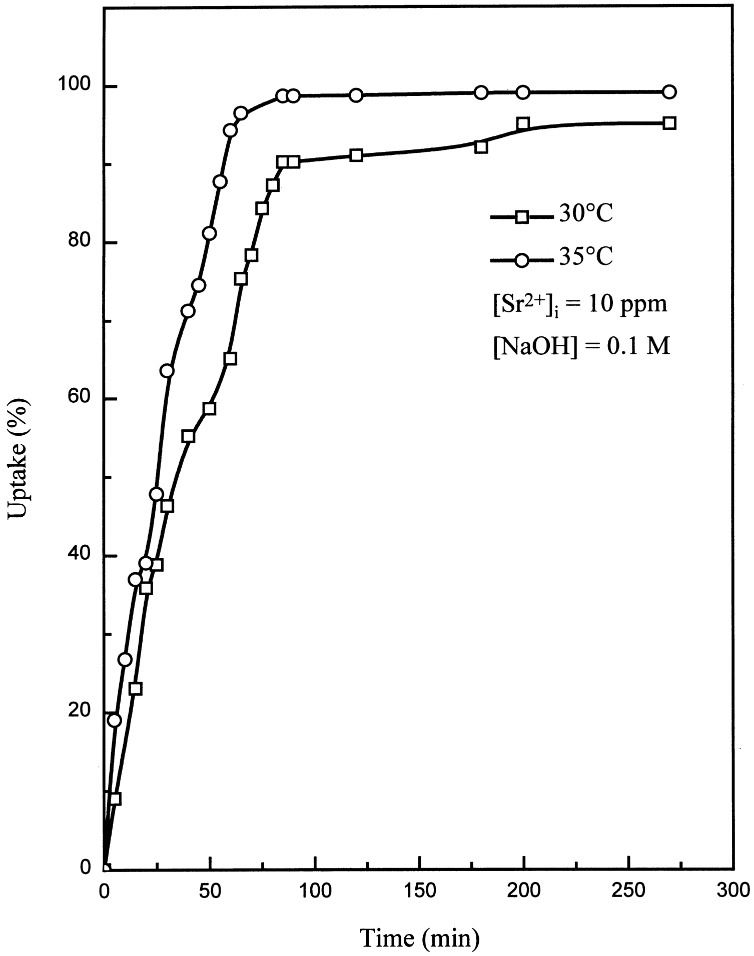

FIG. 1 Kinetics of sorption of strontium(II) by HZO.

titration data as shown in Eqs. (6) and (7), respectively

$$K_{a1} = h\,(C - q)/q \tag{6}$$

$$K_{a2} = hq/(C - q) \tag{7}$$

where $h$ is the hydrogen ion concentration in solution; $C$ is the total capacity (3.5 meq/g), and $q$ is the concentration of surface hydroxyl groups (mmol/g) either in protonated form ($SOH_2^+$) or deprotonated form ($SO^-$), depending on the acid or alkali used. The observed sodium exchange capacity of 3.5 meq/g seems to be much higher than the capacity of 1–2 meq/g normally reported for hydrous oxides and inorganic sorbents. Thus, Mishra et al. (18) reported a mercury exchange capacity of 1.5 meq/g at $\mathrm{pH} = 2.2$ for HZO. However, for titanium antimonate and cerium antimonate Aly and El-Naggar et al. (19) reported a capacity of 4.312 mmol/g based on $\mathrm{Th}^{4+}$ exchange and 2.18 mmol/g based on $\mathrm{Na}^{+}$ exchange, respectively. Yamazaki et al. reported (20) a sodium exchange capacity of 3.5 to 3.7 meq/g for hydrous silicon (IV)–titanium(IV) oxide and Bortun et al. (21) reported 6.2 meq/g for a similar system of titanosilicate. Thus it is obvious that the capacity is a strong function of the conditions employed for the preparation of the sorbent.

The plot of $pK_{ai}$ ($i = 1$ or 2) against $q$ for HZO and the linear fitting coefficients are given in Fig. (2). The intercept gives the intrinsic dissociation constant ($pK^*_{ai}$, $i = 1$ or 2) of HZO. PZC for the hydrous zirconium oxide can be calculated using the following equation

$$\mathrm{PZC} = (pK^*_{a1} + pK^*_{a2})/2 = 2.88 \text{ for HZO} \qquad (8)$$

The percentage of protonated and deprotonated forms of HZO at various $\mathrm{pH}_{\mathrm{solution}}$ were computed using Eqs. (6) and (7) and the linear equations shown in Fig. 2. A plot of the fraction of various forms of the surface against pH is shown in Fig. 3. When $\mathrm{pH} < \mathrm{PZC}$, the surface consists of positively charged and neutral sites resulting in net positive charge on the surface (22). Similarly, for $\mathrm{pH} > \mathrm{PZC}$ the net charge on the surface is negative. This fraction increases from $\mathrm{pH} = 2.88$ and reaches 0.99 at $\mathrm{pH} = 7$. Thus HZO can sorb any cation above $\mathrm{pH} = 2.88$ if the mechanism of sorption is purely governed by coulombic forces of attraction as was observed the case of silica–titania gel (15).

## Sorption Isotherms

Sorption of $\mathrm{Sr}^{2+}$ on HZO and silica–titania gel (Si–Ti) as a function of pH is shown in Fig. (4). Also shown in Fig. 4 are the percentage of the negative charged surface of HZO and Si–Ti (15) as a function of pH. Sorption of strontium on Si–Ti begins when the surface of Si–Ti ($\mathrm{PZC} = 4.22$) acquires a negative charge above the PZC, then there is an abrupt increase in sorption with the abrupt increase in the percentage of the deprotonated form ($\mathrm{SO}^{-}$). However, there is no such relationship for the sorption of $\mathrm{Sr}^{2+}$ on the negatively charged surface of hydrous zirconia gel for $\mathrm{pH} > \mathrm{PZC}$. In this case, sorption on HZO begins at $\mathrm{pH} = 8$ followed by an abrupt increase. Thus there is a delay in the sorption of strontium above the PZC even though the charge on HZO is negative.

Considerable effort was made by James and Healy (10, 23) to understand the sorption behavior of hydrolyzable metal ions on various sorbents. Sorption

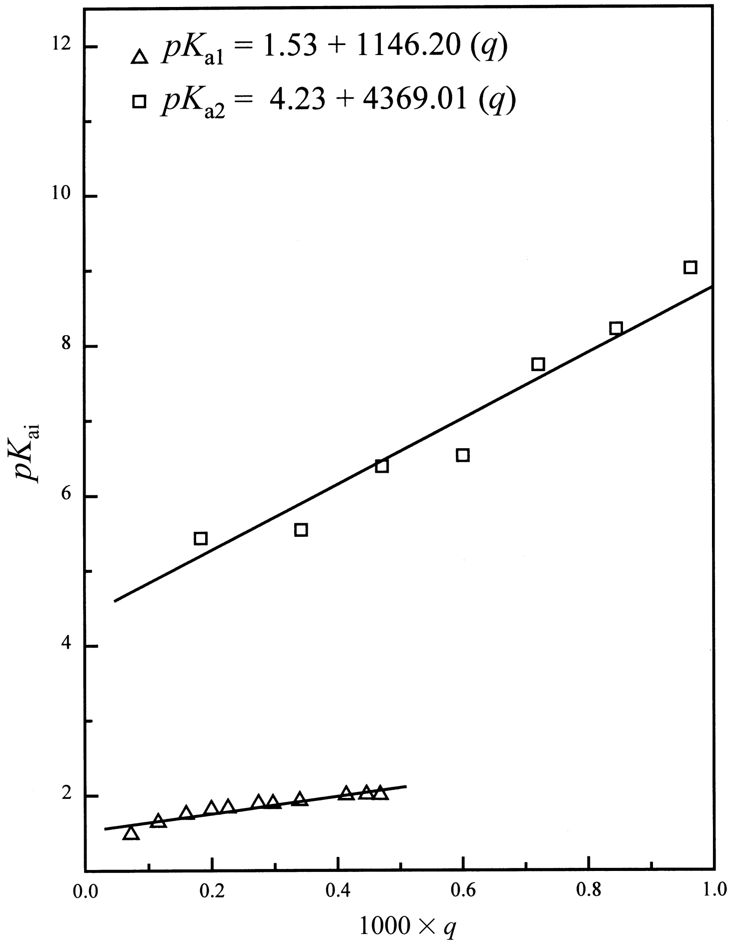

FIG. 2 Variation of $pK_{ai}$ with $q$ for HZO.

of metal ion at the oxide–liquid interface can be treated in terms of two competing free energy changes as the ion approaches the interface. They are, (a) the changes in electrostatic free energy ($\Delta G^{\circ}_{\text{coul}}$) and (b) changes in the secondary solvation energy ($\Delta G^{\circ}_{\text{solv}}$). Thus the total free energy change ($\Delta G^{\circ}_{\text{tot}}$) can be given by the following equation

$$\Delta G^{\circ}_{\text{tot}} = \Delta G^{\circ}_{\text{coul}} + \Delta G^{\circ}_{\text{solv}} \tag{9}$$

$\Delta G^{\circ}_{\text{coul}}$ is negative for the sorption of $Sr^{2+}$ on negatively charged surfaces. $\Delta G^{\circ}_{\text{solv}}$ is the free energy change accompanied by the replacement or rear-

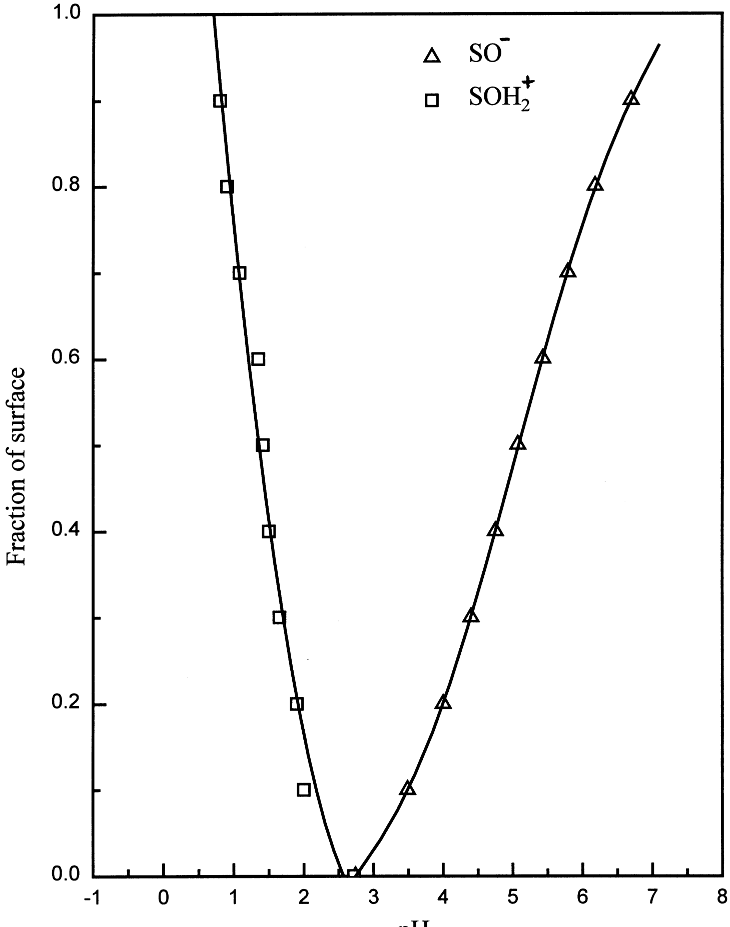

FIG. 3 Acid/base properties of HZO.

rangement of the solvation sheath as the strontium ion is sorbed from the medium (water) of a particular dielectric constant to another phase (HZO) with a different dielectric constant. The dielectric property of the oxide makes a major contribution to the changes in the secondary solvation energy ($\Delta G^\circ_{solv}$) as the ion approaches the interface (10, 23). It was found (10, 23) that for insulating oxides whose dielectric constant ($\varepsilon_{solid}$) is low, the $\Delta G^\circ_{solv}$ is of considerable magnitude. But for semiconducting oxides with an infinitely large dielectric constant, the change in solvation energy is small and the sorption process is solely governed by coulombic interactions ($\Delta G^\circ_{tot} \approx$

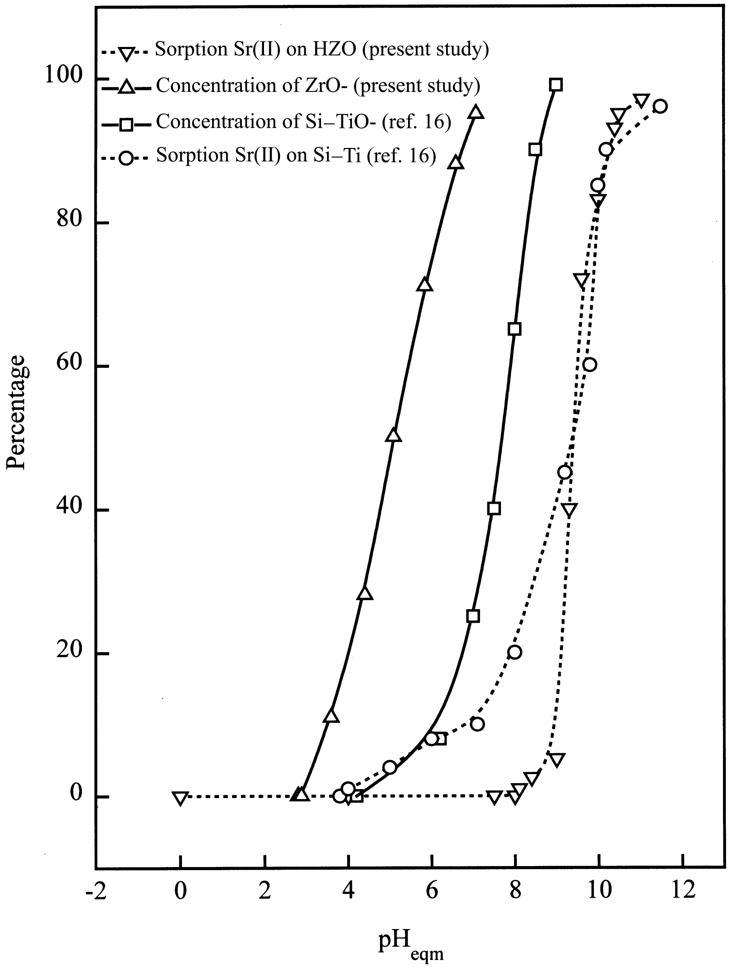

FIG. 4 Variation of the percentage of deprotonated form of the sorbent and Sr(II) sorption on HZO and silica–titania gel (Si–Ti)(16) with pH.

$\Delta G^\circ_{\text{coul}}$). These predictions compare well with the observed sorption isotherm for $Sr^{2+}$ sorption on HZO ($\varepsilon_{\text{zirconia}} = 12$) (24) and on Si–Ti ($\varepsilon_{\text{titania}} = 78$; $\varepsilon_{\text{silica}} = 4$) (10). The titania ($\varepsilon_{\text{titania}} = 78$) component in silica–titania gel is capable of disturbing the solvation sphere of strontium ion in solution to a considerable extent, making $\Delta G^\circ_{\text{solv}}$ negligible. Hence the sorption process is purely governed by the attractive forces operating between the Si–Ti and $Sr^{2+}$. These forces increase with the increase in pH of the solution, thus leading to sorption of strontium at pH $\geq$ PZC. However, for HZO, because of its poor dielectric constant, the strontium(II) ion in aqueous solution cannot be dehydrated and it requires large changes in the solvation energy. Hence $\Delta G^{o}_{\text{solv}}$ is of considerable magnitude, which opposes the attractive forces. Thus there is a delay in the sorption above pH $>$ PZC. The sorption edge for strontium occurs at pH $= 8$, and at pH 9 there is an abrupt increase in sorption on HZO. This increase in sorption could also be due to the hydrolysis of $Sr^{2+}$ to $SrOH^{+}$ (10, 23), which is of considerable importance when the pH $\geq 8$. The bigger size of $SrOH^{+}$ and low effective charge on it would reduce the magnitude of change in solvation energy ($\Delta G^{o}_{\text{solv}}$) and the coulombic interactions would start operating. The existence of partially hydrolyzed $SrOH^{+}$ is supported by the plot shown in Fig. 5, which is arrived at with the assumption that the sorption of strontium on HZO is governed by the stoichiometric ion-exchange reaction presented in equation (10)

$$2\,\mathrm{Na}_s^+ + \mathrm{Sr}_a^{2+} \Leftrightarrow \mathrm{Sr}_s^{2+} + 2\,\mathrm{Na}_a^+ \tag{10}$$

where the subscripts *a* and *s* denote the aqueous and sorbent phases, respectively. The equilibrium constant *K* for this reaction is related to the distribution coefficient ($K_d$) by the following Eq. (11)

$$\log K_d = \log K + 2\log\,[\mathrm{Na}^+]_s - 2\log\,[\mathrm{Na}^+]_a \tag{11}$$

where $K_d = [\mathrm{Sr}^{2+}]_s/[\mathrm{Sr}^{2+}]_a$. Since strontium is present in trace quantities, the concentration of sodium in the solid phase can be assumed as constant. Therefore a plot of log $K_d$ against log $[\mathrm{Na}^+]_a$ should have resulted in a straight line with a slope (25) of $-2$. But the obtained slope of $-1.4$ from Fig. 5 supports the idea that strontium is partially hydrolyzed to $SrOH^{+}$, which is coexisting with $Sr^{2+}$. Thus the observed sorption of strontium at pH $>$ PZC could be in the form of $Sr^{2+}$ or $SrOH^{+}$ or both. Further studies are required to establish the actual species being sorbed.

## Freundlich Model

A Freundlich plot for the sorption of strontium on HZO at various temperatures is shown in Fig. 6. The classical Freundlich equation governing the amount of metal ion sorbed and its concentration in solution is given by

$$\Gamma = k[C]^{\beta} \tag{12}$$

where $\Gamma$ indicates the amount of strontium ion sorbed in mg/g, $C$ is the amount of strontium in aqueous solution (mg/L) and $k$ and $\beta$ are the empirical parameters of positive value. According to Sposito (26) the magnitude of $\beta$ determines the energetic heterogeneity of the sorbent (27) and $k$ is called the affinity parameter (or the average distribution coefficient), which is the indicator

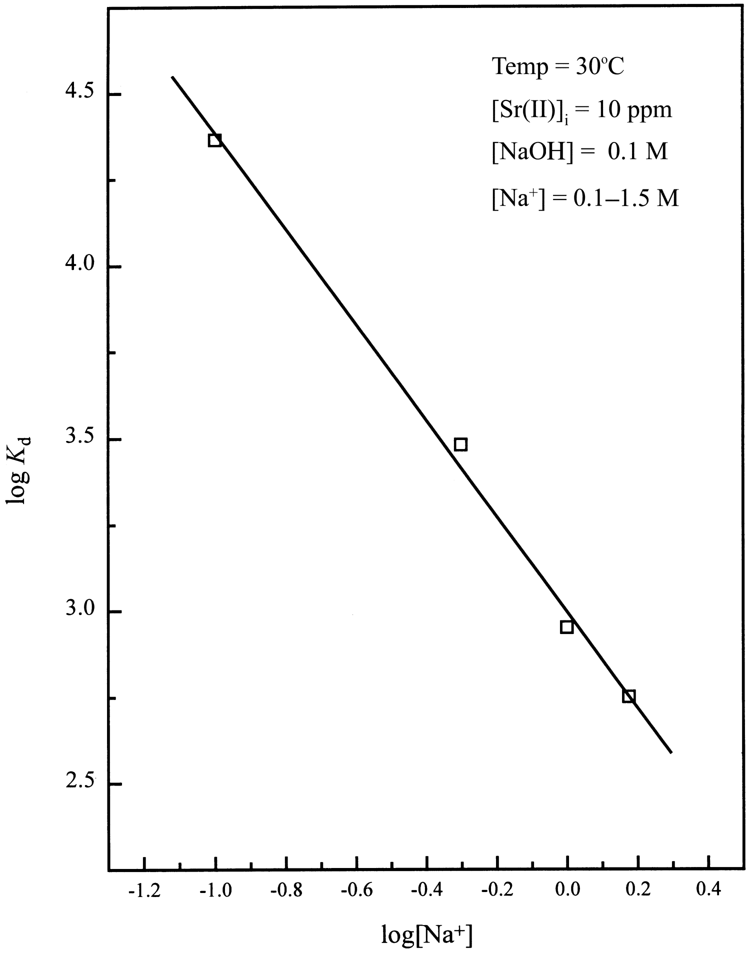

FIG. 5 Variation of $K_d$ of Sr(II) with $Na^+$ concentration.

for the exchange feasibility. The values of $k$ and $\beta$ for the sorption of strontium on HZO are given in Table 1, which shows that the affinity parameter ($k$) increases with increase in temperature, and there is negligible difference in the magnitude of the heterogeneity parameter.

## Effect of Temperature

Figure 7 shows the plot of the affinity parameter (or the average distribution coefficient) log($k$), against $1/T$ for strontium sorption on HZO from 0.1 M

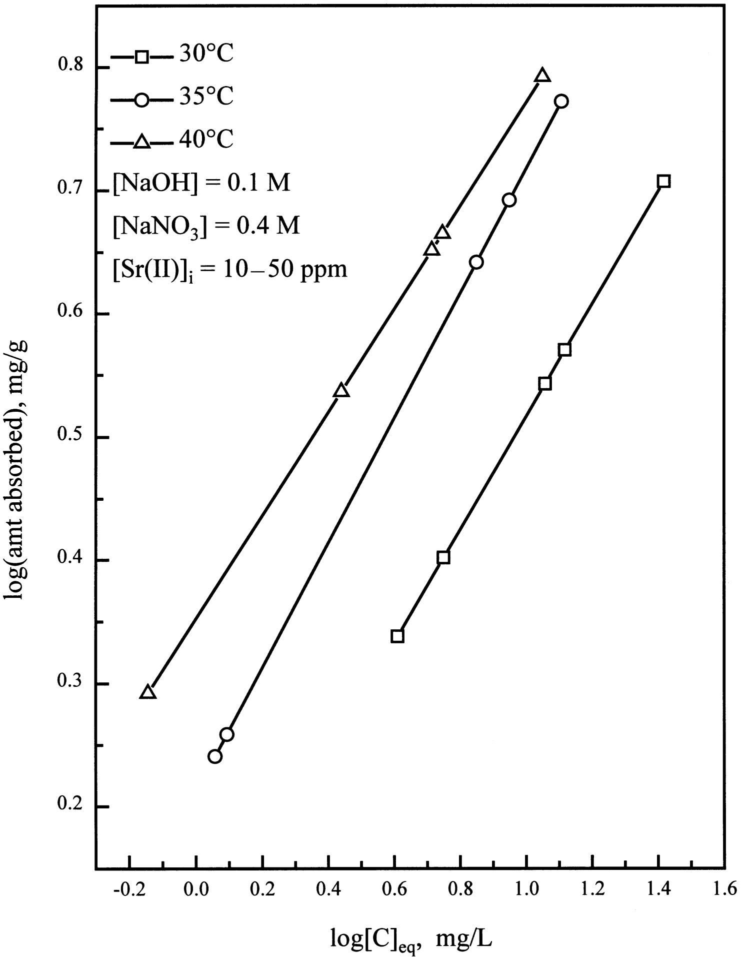

FIG. 6 Freundlich plot for sorption of Sr(II) on HZO.

TABLE 1
Freundlich Parameters (β and *k*) and the Enthalpy and Entropy Changes for the Sorption of $Sr^{2+}$ on HZO from 0.1 M NaOH

| *T*, K | β | log (*k*) L/g | $\Delta H^\circ_{tot}$, kJ/mol | $\Delta S^\circ_{tot}$, J/mol·K |
|---|---|---|---|---|
| 303 | 0.4373 | 0.0585 | 56.27 | 186 |
| 308 | 0.5062 | 0.2111 | | |
| 313 | 0.4188 | 0.3522 | | |

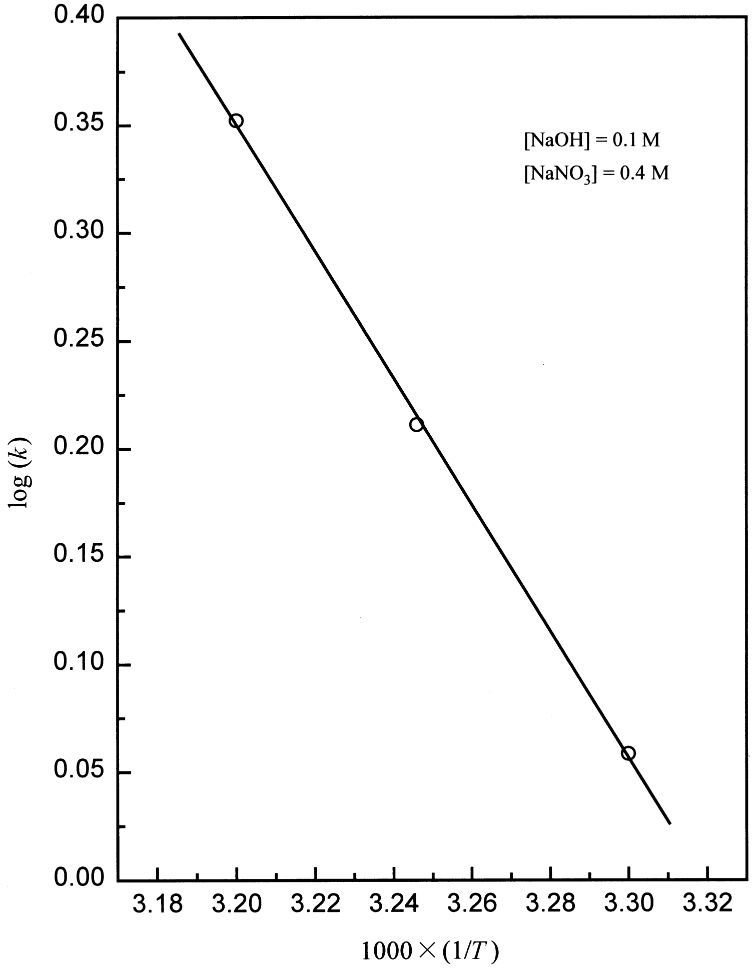

FIG. 7 Variation of log(*k*) with 1/*T* for the sorption of Sr(II) on HZO.

NaOH. An estimate of enthalpy and entropy of the $H^+/Sr^{2+}$ exchange on HZO can be obtained (28–30) from the slope and intercept of this plot according to Eq. (13), and the values are tabulated in Table 1

$$\log(k) = (-\Delta H^{\circ}_{\mathrm{tot}}/2.303RT) + (\Delta S^{\circ}_{\mathrm{tot}}/2.303R) \qquad (13)$$

It can be seen from Table 1 that sorption of $Sr^{2+}$ by HZO is endothermic. Thus, it would appear that the sorption process is made possible [log(*k*) = positive] through the contribution from the $T\Delta S$ term. The observed entropy change can be divided into two parts shown in Eq. (14)

$$\Delta S^{\circ}_{\text{tot}} = \Delta S_{\text{ex}} + \{2S^{\circ}(\text{H}^{+}) - S^{\circ}(\text{Sr}^{2+})\} \qquad (14)$$

where $\Delta S_{\text{ex}}$ represents the entropy difference between the $Sr^{2+}$ and $H^{+}$ forms of the sorbent and $\{2S^{\circ}(\text{H}^{+}) - S^{\circ}(\text{Sr}^{2+})\}$ is the difference in entropy of hydrated ions in solution. The value of $\Delta S_{\text{ex}}$ primarily reflects the entropy change associated with the net transfer of water molecules across the oxide–water interface (31). The magnitude of the second term is obtained from Hayashi et al. (28), as 20 J/K·mol, and the value of $\Delta S_{\text{ex}}$ thus works out to be 166 J/K·mol. Hence the exchange of $Sr^{2+}/H^{+}$ has resulted in an increase in the entropy of the sorbent phase. This can be viewed as follows. The $H^{+}$ present in the rigid HZO is initially solvated by water molecules. These water molecules are arranged in a more orderly fashion and have less degrees of freedom. Although $Sr^{2+}$ is more strongly solvated in solution than $H^{+}$, the whole hydration sphere cannot enter into the rigid HZO. Upon exchange of $H^{+}$ from the sorbent with dehydrated $Sr^{2+}$ from solution, some amount of water molecules that were originally present as a solvation sphere for $H^{+}$ in the sorbent are transferred to the solution phase to accommodate the large strontium ion. Therefore, this net transfer of water molecules from sorbent to solution increases the entropy of the sorbent phase. The observed endothermic nature of the sorption of strontium from the aqueous phase on a rigid matrix of HZO suggests the requirement of the removal of the solvation sheath before sorption, which happens at higher temperatures.

## CONCLUSIONS

The point of zero charge of HZO was found to be 2.88. Negligible sorption of strontium is observed when $2.88 < \text{pH} < 8$, even though the charge on the surface is negative above the PZC. This delay in sorption is due to the low dielectric nature of HZO causing unfavorable solvation energy changes. The sorption edge occurs at $\text{pH} = 8$ followed by an abrupt increase in the sorption. Partial hydrolysis of $Sr^{2+}$ to a lower charged ion $SrOH^{+}$ could account for this behavior.

The positive magnitudes of enthalpy and entropy changes indicate the endothermic nature of ion exchange and the net transfer of water molecules from the sorbent to solution, thus increasing the entropy of the exchanger phase.

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