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Adsorption of Strontium from Acidic Waste Solution by Mn–Zr Mixed Hydrous Oxide Prepared by Co-Precipitation

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A manganese–zirconium mixed hydrous oxide with Mn to Zr mole ratio of 1:1 was prepared to study the sorption behavior and the removal of strontium from acidic radioactive waste solutions. Mixed hydrous oxide was identified and characterized by DTA/TGA, XRD, and surface analysis. The parameters affecting strontium adsorption, such as initial pH, contact time, initial metal ion concentration, temperature, adsorbent dose, and selectivity towards competing ions were investigated. Sorption data have been interpreted in terms of Freundlich and Langmuir equations. Thermodynamic parameters such as standard enthalpy ($\Delta H°$), entropy ($\Delta S°$), and free energy ($\Delta G°$) were calculated from the slope and intercept of the plots of ln K_D versus $1/T$. The results indicated that the sorption of strontium onto manganese–zirconium mixed oxide is endothermic and spontaneous in nature.

Keywords acidic solutions; co-precipitation; MnO_x–ZrO_2; sorption; strontium

INTRODUCTION

The age that started with Becquerel's discovery of radioactivity, and gathered momentum with the advent of nuclear power, has unavoidably generated its own type of waste. Radioactive waste is generated at various stages of the nuclear fuel cycle, which includes the mining and milling of uranium ore, fuel fabrication, reactor operation, and spent fuel reprocessing. Besides these sources, radioactive waste is produced as a result of the ever-increasing use of radioisotopes in medicine, industry, and agriculture (1).

Strontium is a soft, silver-gray metal that occurs in nature as four stable isotopes. Strontium is present in nature chiefly as celestite ($SrSO_4$) and strontianite ($SrCO_3$), and it comprises about 0.025% of the earth's crust. Strontium has a variety of commercial and research uses. It has been used in certain optical materials, and it produces the red flame color of pyrotechnic devices such as fireworks and signal flares. Strontium has also been used as an oxygen eliminator in electron tubes and to produce glass for color television tubes. Sixteen major radioactive isotopes of strontium exist, but only strontium-90 has a half-life sufficiently long (2).

Strontium-90 (half-life = 28 years) a product of uranium fission, is released to the environment from nuclear plant accidents, nuclear weapons testing, waste streams associated with fuel processing, and leakage from radioactive waste storage facilities. Based on total inventory, half-life and biological activity, strontium-90 is one of the most important radionuclides released from nuclear reactors in the first one hundred years of disposal (3).

The ever increasing pressure to reduce the release of radioactive and other toxic substances into the environment requires constant improvement/upgrading of processes and technologies for treatment and conditioning of liquid radioactive waste. Treatment of liquid radioactive waste quite often involves the application of several steps such as filtration, precipitation, sorption, ion exchange, evaporation and/or membrane separation to meet the requirements both for the release of decontaminated effluents into the environment and the conditioning of waste concentrates for disposal (4).

Inorganic compounds are extremely proven candidates for the separation of cesium and strontium from aqueous waste streams (5). The good compatibility of inorganic materials with the final waste forms, such as glass and concrete, selectivity, thermal and chemical stability, and their tolerance against ionizing radiation are critical advantages of these materials over the organic exchangers (6).

Various types of inorganic ion-exchangers and adsorbents have been reported for the removal of strontium: natural and synthetic zeolites (7), titanosilicates and titanates (8–10), titanium and zirconium phosphates (11), hydrous metal oxides and their mixtures (12–18).

The lack of selectivity is one of the problems that can limit the possibility of using particular sorbents in liquid radioactive waste management, regardless of how promising the K_D or capacity data may be (12). A number of inorganic sorbents show selectivity to ^{90}Sr from alkaline

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waste solutions, but, so far, only few sorbents were reported to be selective to strontium from acidic radioactive waste streams (6). Silica-based sorbents (19–22) and metal antimonate (23,24) compounds have been identified as highly promising ion exchangers for the removal of ^{90}Sr and other key radionuclides from acidic or Ca-bearing nuclear waste effluents. New type of materials are needed for the selective removal and safe storage of ^{90}Sr from acidic nuclear waste solutions and from groundwater.

First, studies of selectivity of MnO_2 to alkaline earth cations have been accomplished in mid-70th. Later on, its properties as a sorption material for strontium have been studied in great detail. Typical K_D values for manganese oxides are ca. 100 mL/g. Like for other materials of high affinity to strontium, the dependence of adsorption of Sr^{2+} on pH reaches a plateau in alkaline media. In order to afford the working ability of manganese oxide in more acidic solutions, which is especially valuable for technical applications, modification of MnO_2 by an acid-insoluble oxide, SiO_2, TiO_2 has been proposed. It has been shown that mixed $xMnO_2 \cdot ySiO_2$ sorbents remain active up to pH $\approx$ 4.0, having enhanced capacity for strontium and higher K_D values. Hydrous, amorphous MnO_2–TiO_2 composites have much greater affinity to Sr^{2+} ions at $pH = 7$ than single oxides. One may therefore concludes that modification of MnO_2 by acid-resistant oxides may be highly promising for the amendment of this material. Zirconia seems even more favorable, in particular, if one bears in mind its own reasonable ion-exchange property and high capacity towards Sr^{2+} (13,14).

Selectivity and cation exchange property of manganese oxides (25–30) and cation exchange and acid resistant properties of zirconia (13) are well known. As a consequence, manganese–zirconium mixed hydrous oxide seems a prospective material for the sorption of strontium.

The co-precipitation of hydrous oxides (manganese and zirconium oxide) affect seriously surface properties (specific surface area, porosity, acidic sites, etc.) of each component, which provides a supplementary influence on the sorption (12).

Numerous parameters influence the quality of precipitates, vs raw materials used (such as, manganese sulphate, nitrate, and chloride); the pH of the initial and the final solutions; the excess of the oxidant; the type of a neutralizing agent (lithium, sodium, potassium hydroxide); the washing method, and pH of leachates (31).

Previously, we prepared hydrous zirconium dioxide and studied the sorption of strontium from alkaline solutions (13). The aim of this study was to present an additional investigation on the sorption behavior of strontium, as an important fission product usually present in acidic solutions. For this aim, manganese–zirconium mixed hydrous oxide was co-precipitated and the parameters that affect strontium adsorption were investigated.

EXPERIMENTAL

Chemicals and Reagents

Zirconium(IV) chloride was purchased from Riedel De Haen. Manganese(II) nitrate tetra hydrate, strontium nitrate, hydrogen peroxide, and sodium hydroxide were purchased from Merck. Strontium nitrate was used to prepare Sr(II) stock solutions ($1000\,mg \cdot L^{-1}$, in 2% HNO_3). The working solutions were prepared by diluting the stock solutions to appropriate volumes. All reagents used in the experiments were AnalaR grade. Ultrapure water (resistivity $18.2\,MW \cdot cm$, TOC level 1–5 ppb) was prepared by the Millipore model water purification system including Elix and Mili-Q was used in the experiments.

Preparation of Mn–Zr Mixed Hydrous Oxide

11.7 g $ZrCl_4$ and 12.6 g $Mn(NO_3)_2 \cdot 4H_2O$ were dissolved in water with the addition of 20 mL hydrogen peroxide under stirring to prepare a 0.5 M 100 mL mixed solution. 1 M KOH was slowly added to the mixture under vigorous stirring at room temperature until the final pH was reached to 12. The resulting mixtures were stirred for 1 hour and left for 24 hours for aging. Then the settled solutions were decanted, and precipitates were repeatedly washed with distilled water until the constant pH value was accessed. Further operations included filtering and airdrying at room temperature. Materials obtained are uniform powders of dark chocolate color.

The composition of the material was determined by dissolving 0.120 g of hydrous Mn–Zr oxide in 3 mL of concentrated HCl in the presence of hydrogen peroxide with heating. The solution was diluted and the elements were determined by ICP–OES spectrometry. It was observed that the weight ratio of Mn/Zr in the mixed hydrous oxide was conserved as the initial weight ratio of 0.60.

The structural stability of Mn–Zr hydrous oxide against acid solution was proven by observing no weight loss for five day contact with the nitric acid solution of pH 2.

Batch Sorption Studies

The sorption experiments of strontium ions were conducted by batch process. The pH values of these solutions were adjusted with $1\,mol \cdot L^{-1}$ NH_3 and $1\,mol \cdot L^{-1}$ HNO_3 solution by using Metrohm 654 pH meter with a combined pH electrode. Batch sorption experiments were performed by a thermostatically controlled shaker at 130 rpm (GFL-1086 model). In the experiments, Mn–Zr mixed oxide was separately shaken with strontium solutions at varying experimental conditions in 25 mL Erlenmeyer flasks. The supernatants were filtered through a filter paper (Whatman No. 41) and the concentration of strontium in the solution was measured before and after equilibrium by a Perkin-Elmer Optima 2000DV ICP-OES. All the experiments were carried out in duplicate and the mean value was used in all cases. The adsorption percentages

(*Ads* %) were calculated by:

$$Ads\ \% = (C_i - C_e/C_i) \times 100 \qquad (1)$$

where C_i and C_e are the initial and equilibrium concentration of strontium in solution ($\mathrm{mg \cdot L^{-1}}$).

RESULTS AND DISCUSSION

Identification and Characterization

Thermal analysis related to Mn–Zr mixed hydrous oxide was performed by DTA/TGA analysis using a Shimadzu thermal analyzer. From the DTA curve, the endothermic peak observed at 390 K indicates the maximum value of loss of water. From the TGA data, it was calculated that the adsorbent includes 2.6 mol water. It was observed that at 1199 K, the mixed oxide is converted to oxide by losing completely its water (Fig. 1). X-ray diffraction analysis was performed using a Perkin-Elmer model diffractometer (CuKα radiation $\lambda = 1.5418\,\text{Å}$ at 32 kV/22 mA). Figure 2 shows the XRD analysis of Mn–Zr mixed oxide. From the XRD pattern, it was observed that Mn–Zr mixed oxide has an amorphous structure. Specific surface area and pore diameter were measured by High Speed Surface Area Analyzer (Micromeritics ASAP 2020 model). The specific surface area (BET) of the sorbent was measured as $254\,\mathrm{m^2 \cdot g^{-1}}$. As it can be seen from Fig. 3, Mn–Zr mixed oxide has a pore diameter of less than 20 angstroms. This data, is in good agreement with manganese types sorbents (14,16) in the literature, points out the microporous characteristics of the sorbent.

The Effect of Initial pH

25 mL of $100\,\mathrm{mg \cdot L^{-1}}$ strontium nitrate solutions were treated with 0.1000 g of Mn–Zr hydrous oxide at different pHs, in a thermostatically controlled shaker at 130 rpm, at 303 K, for 3 hours.

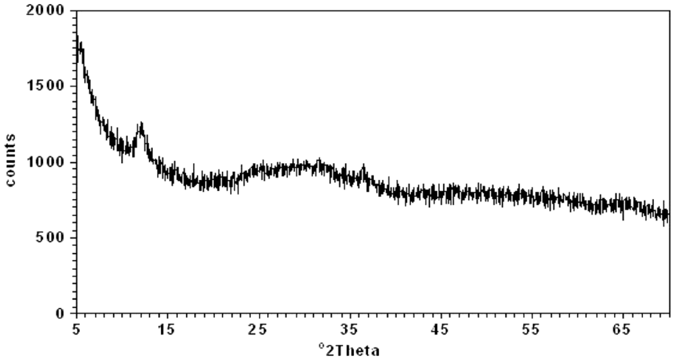

FIG. 2. X-ray diffraction pattern of Mn–Zr mixed hydrous oxide.

Figure 4 shows the effect of pH on the adsorption efficiency of strontium on Mn–Zr hydrous oxide. A sharp increase of strontium adsorption was observed between pH 3 and 4, then it becomes nearly constant between the pH range of 4–8.

pH is an important factor controlling the process of sorption. Understanding the sorption behavior of metal ions from aqueous solution on hydrous oxides, 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. Hydrous oxides (MOH) in acidic media react with H^+ to produce a protonated (MOH_2^+) surface with an anionic exchange group as shown in Eq. (2). In alkaline solution the hydroxyl ion reacts with the hydrous oxide to produce the deprotonated (MO^-) form as shown in Eq. (3) (32)

$$\underset{\text{Positive}}{MOH_2^+} \rightarrow \underset{\text{Neutral}}{MOH^0} + H^+ \qquad (2)$$

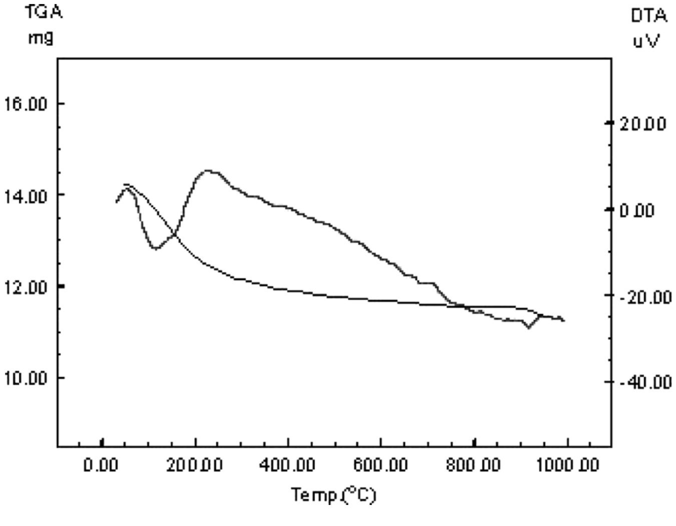

FIG. 1. DTA/TGA curves of Mn–Zr mixed hydrous oxide.

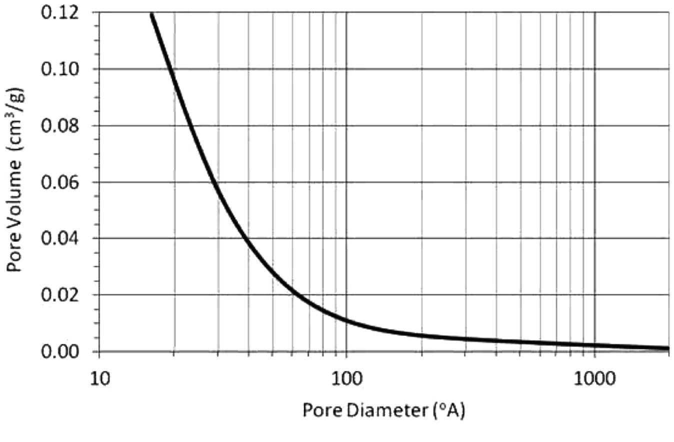

FIG. 3. Pore size distribution of Mn–Zr mixed hydrous oxide.

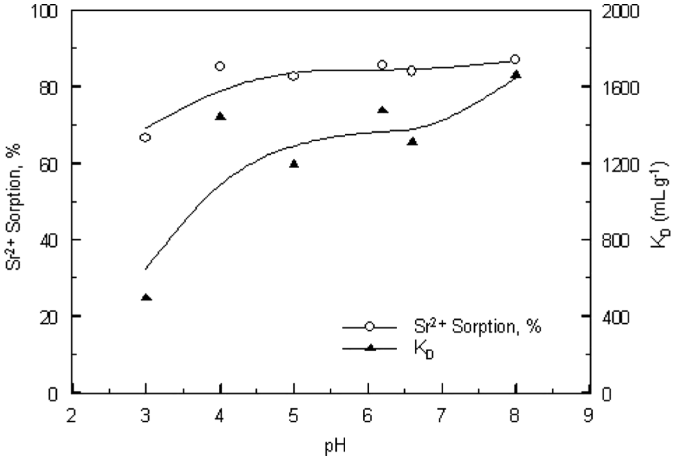

FIG. 4. Effect of initial pH on the Sr^{2+} sorption on Mn–Zr mixed hydrous oxide (Initial strontium concentration: $100\,mg \cdot L^{-1}$, temperature: 30°C, contact time: 180 min., sorbent amount: 0.1000 g).

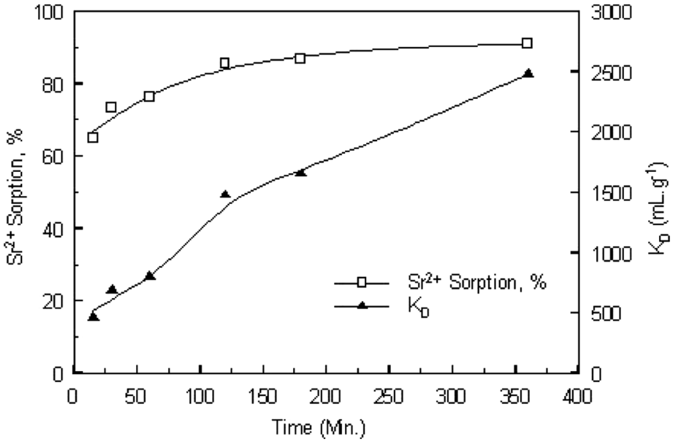

FIG. 5. Effect of contact time on the sorption of Sr^{2+} on Mn–Zr mixed hydrous oxide (Initial strontium concentration: $100\,mg \cdot L^{-1}$; initial pH: 4.1; temperature: 30°C; sorbent amount: 0.1000 g).

$$MOH^0 \rightarrow \underset{\text{Negative}}{MO^-} + H^+ \tag{3}$$

İnan et al. (2006) have previously studied the sorption of strontium onto hydrous zirconium dioxide. The increase in the sorption of Sr(II) ions on hydrous zirconium dioxide with increasing pH of the aqueous solution is explicable on the basis of enhanced dissociation of surface hydroxyl groups of the hydrous oxide. At a lower pH, the oxide surfaces will have a positive character and less affinity for strontium ions; on the other hand at higher pH, the oxide will behave as negatively charged surface, as a result of which the uptake is a maximum in alkaline solutions (13).

Venkatesan et. al. reported that the sorption of strontium on hydrous zirconium dioxide was found to be strongly dependent on pH. The sorption edge was occured at pH = 8. When the equilibrium pH reaches 8, Sr^{2+} undergoes hydrolysis to $Sr(OH)^+$. Partial hydrolysis of Sr^{2+} to a lower charged ion $Sr(OH)^+$ could be accounted for this behavior (32,33).

Hydrous Mn oxides (HMO) in particular are important scavengers of trace metals and other contaminants in the environment because of their ubiquitous presence in clays, soils and sediments, their high surface area, and strong affinity for many elements. Sorption is affected by both electrostatic and chemical forces. Manganese oxides can exhibit a low pH point of zero charge (pH_{PZC}) and can develop a large negative surface charge over the pH range of interest in most natural waters (34).

By the co-precipitation of manganese–zirconium mixed hydrous oxide, it was achieved to remove strontium from acidic solutions which is especially valuable for technical applications.

The Effect of Contact Time

The adsorption of strontium on hydrous manganese–zirconium oxide was studied as a function of shaking time ranging from 15–360 minutes. The other parameters were kept constant. The adsorption yield increases with the shaking time (Fig. 5). At the start, the ions adsorbed and occupied selectively the active sites on the sorbent. As the contact time increased the active sites on the adsorbents were filled. The rate of adsorption became gradually slower and reached a plateau.

The Effect of Initial Metal Ion Concentration

Strontium sorption by hydrous manganese–zirconium oxide as a function of the initial metal ion concentration was studied from 5 to $300\,mg \cdot L^{-1}$. The amount of Sr^{2+} ions adsorbed on the sorbent ($mg \cdot g^{-1}$) increased with the initial concentration of the metal ions (Fig. 6). The quantity of the adsorbed strontium on hydrous manganese–zirconium oxide was calculated as the difference between initial and equilibrium concentration [Eq. (1)].

In order to understand the adsorption capacity of the adsorbents, the equilibrium data were evaluated according to the Freundlich and Langmuir isotherms. The analysis of the relationship between mixed oxide adsorption capacity and strontium concentration was performed using the Langmuir equation:

$$q = (C_i - C_e) \cdot V/W \tag{4}$$

$$C_e/q_e = 1/qsb + C_e/qs \tag{5}$$

where q_e is the quantity of strontium ion adsorbed per unit mass of the sorbent, qs indicates the maximum adsorption capacity of mixed oxide, b is a constant related to the

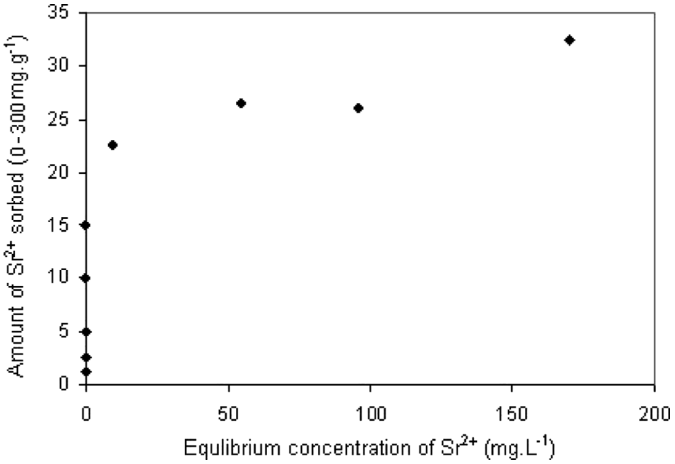

FIG. 6. Effect of initial concentration on the Sr^{2+} sorption on Mn–Zr mixed hydrous oxide (Initial pH: 4.1, temperature: 30°C, contact time: 180 min, sorbent amount: 0.1000 g).

adsorption intensity, C_e is the strontium concentration at equilibrium, C_i is the initial concentration of strontium, V is the volume of solution, and W is the mass of the sorbent. From the slope and intercept of the linear graph of C_e/q_e versus C_e, Langmuir constants qs and b were calculated.

Langmuir isotherm models the monolayer coverage of the adsorption surface. This model assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface. The Langmuir adsorption model further based on the assumption that all adsorption sites are energetically identical and adsorption occurs on a structurally homogeneous adsorbent (35).

The Freundlich equation, which was applied for the adsorption of strontium, is given as:

$$Q_e = KC_e^{1/n} \tag{6}$$

Eq. (6) can be rearranged to linear form:

$$\log q = \log K + \frac{1}{n}\log C_e \tag{7}$$

where q is the amount of the solute adsorbed per mass unit adsorbent, C_e is the equilibrium concentration, and K and n are the Freundlich constants characteristic of a particular adsorption isotherm and can be evaluated from the intercept and slope of the linear plot of log q versus log C_e.

The corresponding Langmuir and Freundlich parameters along with correlation coefficients are reported in Table 1.

Based on the value of the correlation coefficient ($R^2 = 0.985$) it can be seen that the behavior of strontium adsorption on the hydrous manganese–zirconium oxide is a Langmuir type isotherm (Fig. 7). The Langmuir values of qs was calculated as 30.9 mg · g^{-1} by the slope of the isotherm and $b = 0.40$ L · mg^{-1} through the ordinate at the origin of the isotherm.

TABLE 1
Langmuir and Freundlich constants for the sorption of strontium on Mn–Zr mixed hydrous oxide

Freundlich constants	
K	16.98
n	9.3
R^2	0.796
Langmuir constants	
qs (mg · g^{-1})	30.86
b (L · mg^{-1})	0.40
R^2	0.985

The Effect of Temperature

The experiments were carried out at 293, 303, 313, and 333 K. The other parameters were kept constant. Figure 8 shows that the uptake of strontium slightly increases with the increasing temperature.

The distribution coefficients (K_D) were calculated by:

$$K_D = (C_i - C_e/C_e) \cdot (V/m) \tag{8}$$

where C_i and C_e are the initial and equilibrium concentrations of Sr^{2+} ions in the solution, respectively, mg · L^{-1}, V is the solution volume (mL) and m is the mass of the sorbent (g).

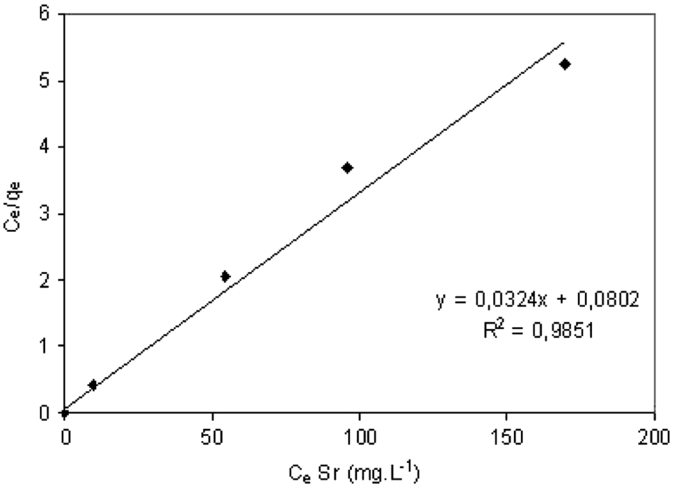

FIG. 7. Langmuir isotherm for Sr^{2+} sorption on Mn–Zr mixed hydrous oxide.

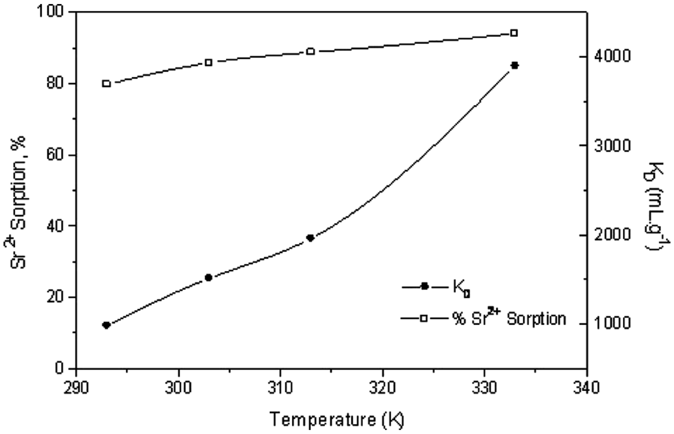

FIG. 8. Effect of temperature on the Sr^{2+} sorption on Mn–Zr mixed hydrous oxide (Initial strontium concentration: 100 mg L^{-1}; initial pH: 4.1; contact time: 180 min; sorbent amount: 0.1000 g).

The values of ΔH° and ΔS° were calculated from the slope and intercept of the linear variation of ln K_D with reciprocal temperature, $1/T$ (Fig. 9) by:

$$\ln K_D = (-\Delta H^\circ/RT) + (\Delta S^\circ/R) \tag{9}$$

where K_D is the distribution coefficient ($mL \cdot g^{-1}$), ΔS° is the standard entropy, ΔH° is the standard enthalpy, T is the temperature, and R is the gas constant ($kJ \cdot mol^{-1} \cdot K^{-1}$).

The free energy of specific adsorption ΔG° was calculated by:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{10}$$

TABLE 2
Thermodynamic parameters for strontium sorption on Mn–Zr mixed hydrous oxide

ΔH° ($kj \cdot mol^{-1}$)	27.47
ΔS° ($j \cdot mol^{-1} \cdot K^{-1}$)	150
$-\Delta G^\circ$ ($kj \cdot mol^{-1}$)	
293 K	16.48
303 K	17.98
313 K	19.48
333 K	22.48

The values of ΔH°, ΔS°, and ΔG° are given in Table 2. The value of $\Delta H^\circ = 27.47\ kJ \cdot mol^{-1}$ and $\Delta G^\circ = -17.98\ kJ \cdot mol^{-1}$ at 303 K suggest that the sorption of strontium on mixed oxide is an endothermic and a spontaneous process.

The Effect of Sorbent Dose

The volume of solution (25 mL) and the concentration of strontium ($100\ mg \cdot L^{-1}$) were kept constant while the amount of Mn–Zr mixed oxide varied from 0.0500 to 0.1500 g. The results of the dependence of strontium sorption on the amount of sorbent dose are shown in Fig. 10. It is seen that, an increase in the sorbent concentration causes an increase in the strontium adsorption. This is expected because increasing sorbent particles in the solution causes more strontium ions interact to these particles.

Selectivity Towards Competing Metal Ions

The influence of divalent cations Ca^{2+} and Ba^{2+} for the adsorption of strontium on the mixed oxide was investigated. In the experiments, $1.14 \times 10^{-3}\ mol \cdot L^{-1}$ strontium nitrate solutions including each 1.25×10^{-4}, 1.25×10^{-3}, and $2.5 \times 10^{-3}\ mol \cdot L^{-1}$ of calcium nitrate and 3.65×10^{-5}, 3.65×10^{-4} and $7.3 \times 10^{-4}\ mol \cdot L^{-1}$ of barium nitrate were treated with 0.1000 g mixed oxide at pH 4.1, during 3 h at 303 K. Distribution coefficients (K_D) and strontium

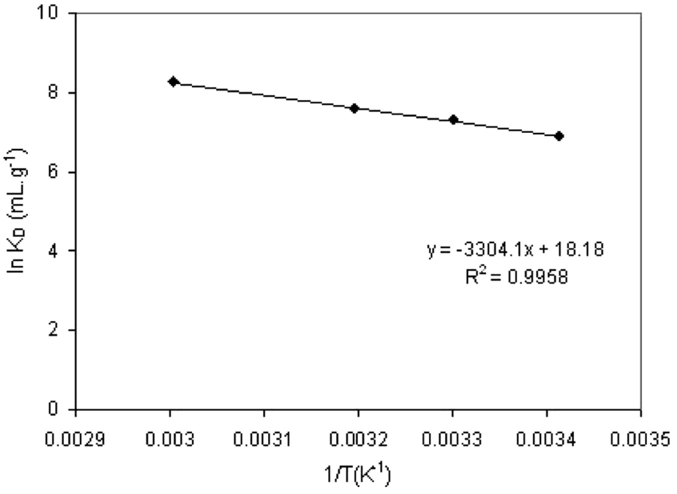

FIG. 9. Variation of ln K_D with $1/T$ for sorption of Sr^{2+} on Mn–Zr mixed hydrous oxide.

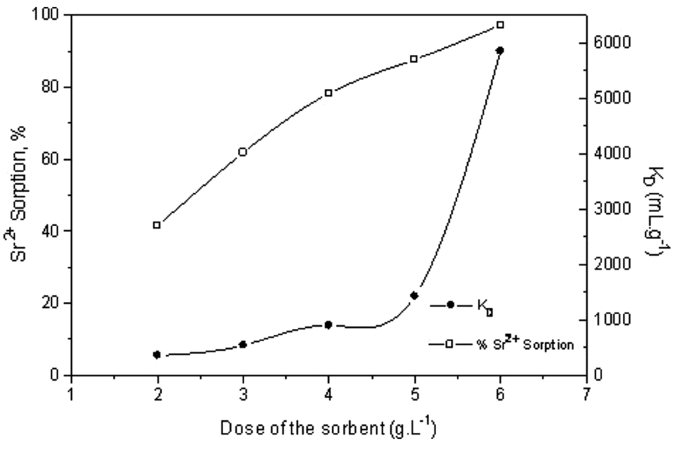

FIG. 10. Dependence of Sr^{2+} sorption on dose of the sorbent (Initial strontium concentration: 100 mg L^{-1}; initial pH: 4.1; temperature: 30°C; contact time: 180 min).

TABLE 3
The effect of Ca^{2+}, Ba^{2+} on the sorption of Sr^{2+}

Ca^{2+} initial concentration ($mol \cdot L^{-1}$)	0	1.25×10^{-4}	1.25×10^{-3}	2.50×10^{-3}
Sr^{2+} adsorption (%)	85.7	75.3	53.6	38.9
K_D Sr ($mL \cdot g^{-1}$)	1498.3	761.7	288.4	159.1
Ba^{2+} initial concentration ($mol \cdot L^{-1}$)	0	3.65×10^{-5}	3.65×10^{-4}	7.30×10^{-4}
Sr^{2+} adsorption (%)	86.2	83.6	76.0	61.6
K_D Sr ($mL \cdot g^{-1}$)	1561.6	1269.8	792.1	400.5

adsorption efficiency were determined. As seen in Table 3, for increasing concentrations of Ca^{2+} ions, the strontium adsorption efficiency and K_D values decrease. However, in the presence of Ba^{2+} ions, mixed oxide showed more selectivity for Sr^{2+} ions than Ba^{2+} ions.

CONCLUSION

A novel Mn–Zr mixed hydrous oxide for effective strontium removal from acidic solutions has been prepared by a simultaneous oxidation and co-precipitation method. The prepared Mn–Zr mixed oxide with a high surface area ($254 \, m^2 \cdot g^{-1}$) was amorphous. Manganese and zirconium in this material existed mainly in the oxidation state +IV. The mixed hydrous oxide showed high Sr^{2+} uptake in the acidic region which is important to handle acidic waste solutions. The maximum sorption capacity for Sr^{2+} was $30.9 \, mg \cdot g^{-1}$.

Among the tested cations, calcium was the greatest competitor with strontium for sorptive sites on the sorbent and the strontium removal was not significantly decreased when relatively low concentration of these cations occurred. Furthermore, mixed hydrous oxide has a greater affinity for Sr^{2+} in the presence of Ba^{2+} ions. The selectivity of the mixed oxide for alkaline-earth metals increased in the series $Ba < Sr < Ca$.

The overall results indicate that, Mn–Zr mixed hydrous oxide is a good candidate for the removal of Sr^{2+} especially from acidic waste solution.

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