

Preparation of TiO_2 – SiO_2 mixed gel spheres for strontium adsorption

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Abstract

A simple external gelation process, taking full advantage of the gelation features of titanium and silica, was developed to prepare TiO_2 – SiO_2 mixed gel spheres suitable for strontium adsorption. The source solutions used for the process were prepared from different mixtures of 1 M TiCl_4 and 1 M Na_2SiO_3 solutions and converted into droplets in a gelation column. The suitable spheres for strontium adsorption were obtained using a hexone (methyl isobutyl ketone) solution as the drop formation medium and ammonia as the gelling agent. The mixed oxide gels were identified and characterized by DTA/TGA, FTIR and XRD analysis. The parameters affecting the strontium adsorption, such as weight ratio of TiO_2 , pH, temperature, shaking time and selectivity towards competing ions were investigated. Sorption data have been interpreted in terms of Freundlich, Langmuir and Dubinin–Radushkevich equations. Thermodynamic parameters for the sorption system have been determined at four different temperatures. The value of $\Delta H^\circ = 39.553$ kJ/mol and $\Delta G^\circ = -16.687$ kJ/mol at 296 K prove that the sorption of strontium on mixed oxide gel is an endothermic and a spontaneous process.

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1. Introduction

A number of activities and events have caused significant radioactive contamination of areas in many states. These include: inadequate practices for the management and disposal of radioactive waste, the intentional or accidental discharge of radioactive material to the environment, nuclear accidents, testing of nuclear weapons, etc. Such contamination may present a hazard to human populations and the environment [1]. ^{137}Cs and ^{90}Sr are also well known contaminants originating from nuclear weapons tests or from failures of nuclear power plants. New type of materials is needed for the selective removal and safe storage of ^{137}Cs and ^{90}Sr from nuclear waste solutions and from groundwater. The ions to be removed are generally present in low concentrations and are associated with an assortment of other cations [2]. The problem of removing ^{90}Sr from liquid radioactive waste and groundwater is far more complicated than that of ^{137}Cs . Cesium existing in simple ion forms, strontium tends to form

complexes with complexing agents (oxalic acid and oxalates) often present in liquid radioactive waste solutions [3]. Strontium uptake is known to be highly affected by the presence of competing ions, especially calcium and limits for strontium concentration are lower than for cesium. 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. Adsorbents and/or ion exchangers used in the nuclear industry should also exhibit considerable resistance against ionizing radiation, possess high thermal and chemical stability. Inorganic ion exchangers, due to their resistance to heat and radiation, can be used for the high temperature separation of ionic components in radioactive wastes [4,5]. A large number of inorganic ion exchangers are known to have a great selectivity towards alkali and alkaline earth metal ions. Titania–silica mixed oxide gel is an interesting material for the adsorption of certain metal ions because cation exchange property of silica [6], and both cation and anion exchange properties of titania [7] are well known. The co-precipitation of hydrous oxides (titania and silica) affect seriously surface properties (specific surface area, porosity, acidic sites, etc.)

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of each component, which provides a supplementary influence on the sorption. The utilization of columns in adsorption and/or ion exchange operations of liquid radioactive wastes possesses some advantages: the system has a great flexibility and provides shielding facility. Granular shape of sorbent is preferred over the powdered one when column operations are used. It is possible to prepare granular products by general preparation methods. But the traditional preparation methods necessitates a lot of time consuming steps such as precipitation, filtering, drying of gel, grinding, sieving, etc.

In the present study, a simple method using a gelation column containing two phases (hexone and ammonia) as sphere forming and gelling medium, allowing to direct preparation of $\text{TiO}_2\text{-SiO}_2$ mixed gel spheres suitable for column operation, was developed. The adsorption behavior of mixed gel towards strontium was investigated.

2. Experimental

2.1. Reagents

Titanium(IV) chloride (98.5%, $d = 1.73 \text{ g mL}^{-1}$) was purchased from BDH Chemicals Ltd. (AnalaR grade) and was used as a main starting material. The appreciated amount TiCl_4 was dissolved in distilled water in an ice-water bath and the concentration of titanium was adjusted to 1 M.

Sodium metasilicate ($d = 1.35 \text{ g mL}^{-1}$, 7.5–8.5% Na_2O and 25.5–28.5 SiO_2) was of analytical grade, obtained from Merck and was used as a starting material. The appreciated amount Na_2SiO_3 was dissolved in distilled water and the concentration of silica was adjusted to 1 M.

Strontium nitrate was purchased from Merck and was used to prepare Sr(II) stock solutions (1000 mg L^{-1} , in 2% HNO_3).

Methyl isobutyl ketone, ammonia, nitric acid and sodium hydroxide used in the experiments were of analytical grade and obtained from Merck.

Ultrapur water (resistivity $18.2 \text{ M}\Omega \text{ cm}$, TOC Level 1–5 ppb) prepared with Millipore model water purification system including Elix and Mili-Q was used in the experiments.

2.2. Preparation of $\text{TiO}_2\text{-SiO}_2$ mixed gel spheres

Different ratios of mixed oxides were prepared from different mixtures of 1 M TiCl_4 and 1 M Na_2SiO_3 solutions, according to the flow sheet given in Fig. 1. The process was

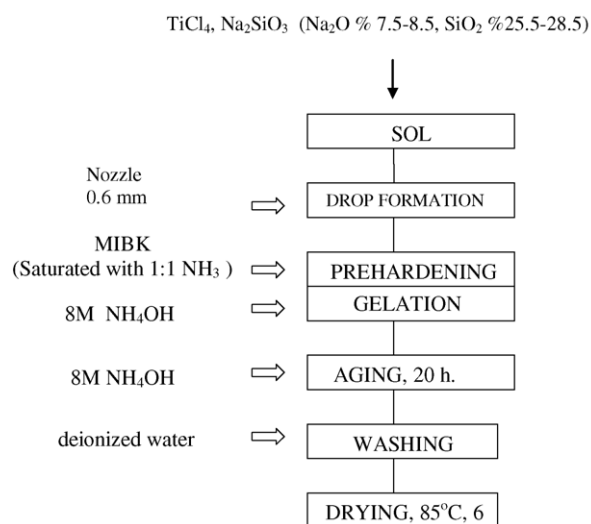


Fig. 1. Flow sheet of the process.

carried out in an apparatus consisting of a peristaltic pump, a nozzle, a glass column, and a reservoir. A stainless steel nozzle with an inner diameter of 0.6 mm was used for sol drop formation. The nozzle was adapted into a system giving permission to inner passage of sol, which is dispersed into droplets. The sol drops system was vertically placed at the top of the gelation column. Sols were added to the system using a peristaltic pump (Chromatograph AFFD SJ-1211). The gelation column contains two phases. The upper phase is hexone (saturated with ammonia 1/1, v/v) to provide prehardening and the lower phase where the spheres are gelled completely is 8 M NH_4OH . The resulting gel spheres were collected in a reservoir connected to the bottom of the column and aged in 8 M NH_4OH for 20 h to improve their mechanical characteristics. The aged spheres were washed by demineralized water and dried at 358 K (Photo 1).

2.3. Identification and characterization

$\text{TiO}_2\text{-SiO}_2$ mixed gel spheres was characterized by DTA/TGA analysis using a Shimadzu thermal analyzer, by FTIR analysis using a Shimadzu model FTIR spectrometer and by X-ray diffraction analysis using a Perkin-Elmer model diffractometer (Cu $K\alpha$ radiation $\lambda = 1.5418 \text{ \AA}$ at 32 kV/22 mA). The specific surface area was measured by the

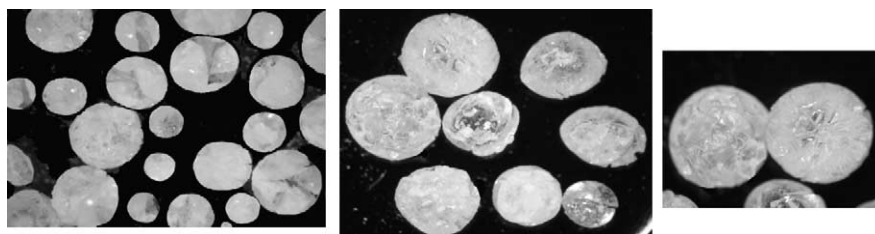


Photo 1. Optic micrographs of the $\text{TiO}_2\text{-SiO}_2$ mixed gel spheres dried at 85°C .

BET method using a High Speed Surface Area Analyzer (Micrometrics 2200 model). The chemical analyses were made using a Perkin-Elmer Optima 2000DV model ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer). All pH measurements were made by 654 Model Metrohm pH Meter.

3. Results and discussion

3.1. The effect of TiO₂ ratio

Hydrous TiO₂-SiO₂ mixed gel spheres at different weight ratios of TiO₂ (30, 40, 50, 60, and 70%) were prepared in a gelation column as mentioned above. To investigate the effect of weight ratio on strontium adsorption, 50 mL of 5 ppm strontium nitrate solution were treated with 0.200 g of mixed oxide for each weight ratio, at pH 10.6, in a thermostatically controlled shaker (GFL-1083), at 296 K for 2 h. The final concentrations of strontium were determined by ICP-OES. The instrumental parameters were given in Table 1. The adsorption percentages (Ads.%) were calculated by the equation:

$$\text{Ads \%} = \left[\frac{C_0 - C_e}{C_e} \right] 100$$

where C_0 and C_e are initial and final concentration of strontium in solution (mg L^{-1}). Fig. 2 shows the effect of weight

Table 1
Instrumental parameters of ICP-OES for Sr determination

Gas flow (L/min)	
Plazma	18
Auxiliary	0.2
Nebulizer	0.59
RF power (W)	1400
Pump (mL/min)	1.5
Wavelength (nm)	407.771
Time (s)	30
Replicate	2

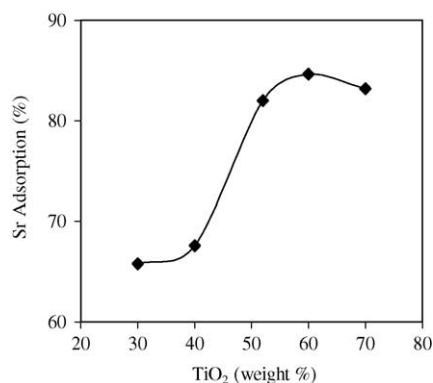


Fig. 2. Strontium adsorption yield depending on TiO₂ weight ratio. Initial concentration of strontium = 5 mg L^{-1} , 0.2 g sorbent in 50 mL solution, pH 10.6, temperature = 296 K, shaking time = 2 h.

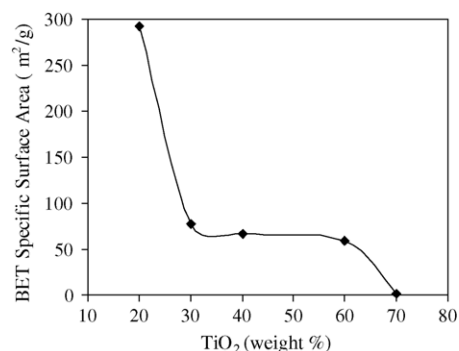


Fig. 3. Specific surface area of mixed oxides at different weight ratio of TiO₂.

ratio of TiO₂ on strontium adsorption at pH 10.6. As seen, the highest adsorption was obtained as 84.6% with 60% TiO₂ weight ratio. Sixty percent weight ratio of TiO₂ was ideal to meet the requirements necessary, such as good mechanical properties of spheres and highest strontium adsorption yield and was used at the following experiments.

The BET specific surface area of spheres at different TiO₂ weight ratios, are given in Fig. 3. The specific surface area of spheres decreases with increasing titanium dioxide ratio.

3.2. Effect of thermal treatment temperature of mixed oxide gels on strontium adsorption

The mixed oxide gel spheres were calcined in air, at 573, 773, 973 and 1173 K for 8 h. Fifty milliliters of 5 ppm strontium nitrate solution were treated with 0.200 g of the mixed oxide for each treatment temperature, at pH 10.6, in a thermostatically controlled shaker, at 296 K for 2 h. The final concentrations of strontium were determined by ICP-OES. The adsorption percentages of strontium were calculated. The relation of strontium adsorption with thermal treatment temperatures of the mixed oxide gel spheres (60% TiO₂ weight ratio) is given in Fig. 4. As clearly seen, the strontium adsorption decreases with the increasing treatment temperatures.

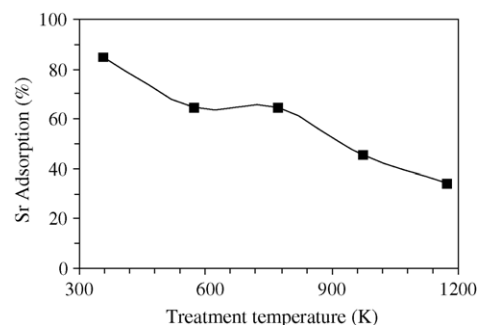


Fig. 4. Strontium adsorption percentage on the thermal treated mixed oxide gel spheres. Initial concentration of strontium = 5 mg L^{-1} , 0.2 g sorbent in 50 mL solution, pH 10.6, temperature = 296 K, shaking time = 2 h.

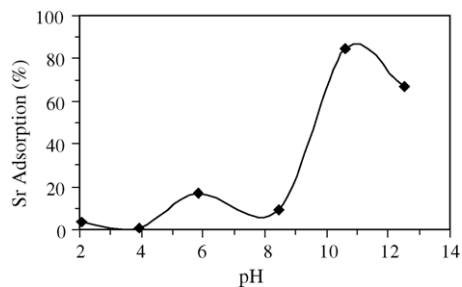


Fig. 5. Effect of pH on the adsorption of strontium on the $\text{TiO}_2\text{-SiO}_2$ mixed gel spheres. Initial concentration of strontium = 5 mg L^{-1} , 0.2 g sorbent in 50 mL solution, temperature = 296 K, shaking time = 2 h.

3.3. The effect of pH

To investigate the effect of pH on the strontium adsorption, each 50 mL of 5 ppm strontium nitrate solutions at different pH values were prepared. Different pH values of these solutions were adjusted with 1 M NaOH and 1 M HNO_3 and following the addition of 0.200 g of the mixed oxide gel spheres, the samples were shaken at 296 K for 2 h. The supernate solutions were filtered and the concentrations of strontium were determined by ICP-OES. The adsorption percentage of strontium on the mixed oxide gel spheres was calculated.

Fig. 5 shows the effect of pH on the adsorption efficiency of strontium on the mixed spheres of 60% TiO_2 weight ratio. The maximum adsorption was determined as 84.6% at pH 10.6. A sharp increase of strontium adsorption was observed between pH 9 and 11.

3.4. The effect of shaking time

The adsorption of strontium on the mixed oxide spheres was studied as a function of shaking time at pH 10.6 and 296 K. Fifty milliliters of 5 ppm strontium nitrate solution was shaken with 0.200 g of the mixed oxide spheres for different intervals of time ranging from 10 to 360 min. The concentrations of strontium were determined by ICP-OES. The effect of time on strontium adsorption is given in Fig. 6. The

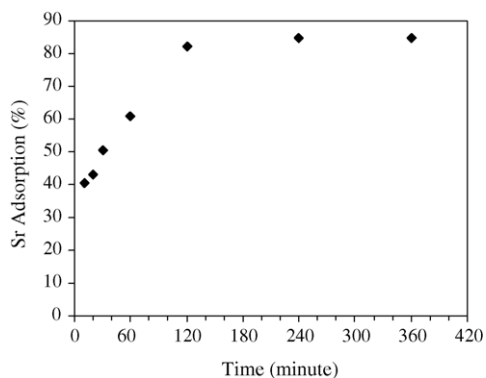


Fig. 6. Effect of time on the adsorption of strontium on the $\text{TiO}_2\text{-SiO}_2$ mixed gel spheres. Initial concentration of strontium = 5 mg L^{-1} , 0.2 g sorbent in 50 mL solution, pH 10.6, temperature = 296 K.

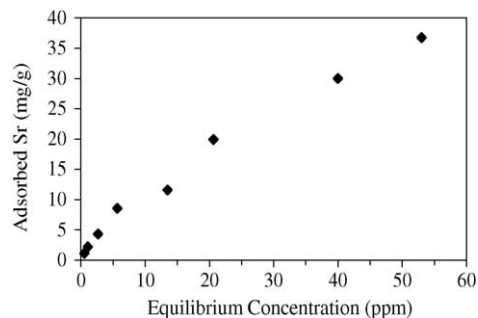


Fig. 7. Adsorption isotherm of strontium on the $\text{TiO}_2\text{-SiO}_2$ mixed gel spheres: 0.2 g sorbent in 50 mL solution, pH 10.6, shaking time = 6 h, temperature = 303 K.

adsorption yield increases with shaking time. The increase was sharp in the first 120 min. The strontium adsorption was 84.2% at the end of this time. The adsorption was slower after this time and reached to equilibrium at 240 min with 84.8% of strontium adsorption.

3.5. Isotherm studies

The investigation of adsorption isotherm was conducted by batch process. Fifty milliliters of strontium nitrate solutions at different concentrations (5–200 ppm) were prepared and the pH values of these solutions were adjusted to 10.6 with 1 M NaOH. 0.200 g of the mixed oxide spheres were added to each sample. The samples were treated in a thermostatically controlled shaker at $303 \pm 1 \text{ K}$ for 6 h. The supernates were filtered and the concentrations of strontium were determined by ICP-OES. The quantity of adsorbed strontium on the mixed oxide gel spheres was calculated as the difference between initial and final concentration at equilibrium. The results are then analyzed in terms of Freundlich [8], Langmuir and Dubinin–Radushkevish (D–R) [9] isotherms.

Fig. 7 shows the relationship between the quantity of strontium adsorbed per unit mass of the mixed oxide spheres and the equilibrium concentrations at pH 10.6.

The concentration dependence study have been fitted to the classical Freundlich equation in its logarithmic form:

$$\log \frac{x}{m} = \log k + \left[\frac{1}{n} \log C_e \right]$$

where x/m is the amount of strontium ions adsorbed per unit weight of $\text{TiO}_2\text{-SiO}_2$ mixed gel spheres (mol/g) and C_e is the equilibrium concentration of strontium ions in solution (mol/L). From the slope and intercept of the linear graph of $\log x/m$ versus $\log C_e$, Freundlich constants k and $1/n$ were calculated and their values are given in Table 2.

Langmuir isotherm equation in its linear form is:

$$\frac{C_e}{\frac{x}{m}} = \frac{1}{KV_m} + \frac{C_e}{V_m}$$

where V_m and K are monolayer adsorption capacity and Langmuir constant related to energy of adsorption, respectively.

Table 2
Freundlich, D–R, Langmuir isotherm parameters for strontium adsorption on the TiO₂–SiO₂ mixed gel spheres

Freundlich parameters	
k (mol g ⁻¹)	2.177
$1/n$	0.7104
R^2	0.99
D–R parameters	
X_m (mol g ⁻¹)	0.00349
K (mol ² kJ ⁻²)	0.0060
E (kJ mol ⁻¹)	9.128
R^2	0.95
Langmuir parameters	
b (mg g ⁻¹)	54.64
K (L mg ⁻¹)	0.0311
R^2	0.85

From the slope and intercept of the linear graph of $C_e/(x/m)$ versus C_e , Langmuir constants V_m and K were calculated and their values are given in Table 2.

As an alternative to the Freundlich isotherm, the data were also fitted to the Dubinin–Radushkevich (D–R) equation:

$$\ln X = \ln X_m - K\varepsilon^2$$

where X and X_m are the amount of strontium ions adsorbed on the mixed gel spheres (mol/g) and maximum amount of Sr ions on the mixed gel spheres (mol/g), respectively, K a constant related to the sorption energy (mol²/kJ²), ε the Polanyi potential = $RT \ln(1 + 1/C)$ and C is the equilibrium concentration of strontium ions in solution (mol/L), R the gas constant (8.13×10^{-3} kJ mol⁻¹ K⁻¹), T temperature (303 K). From the slopes and intercepts of the linear graphs of $\ln X$ and ε^2 , the parameters K and X_m were calculated (Table 2). The mean energy of sorption (E) is the free energy change when one mol of ion is transferred to the surface of the solid from infinity in the solution and it is calculated from:

$$E = (-2K)^{-1/2}$$

The value of E is used to estimate the reaction mechanism occurring. If E is in the range of 8–16 kJ/mol sorption is governed by ion exchange. In the case of $E < 8$ kJ/mol, physical forces may affect the sorption mechanism. On the other hand, if $E > 16$ kJ/mol sorption may be dominated by particle diffusion. The calculated value for Sr sorption is 9.128 kJ/mol, so sorption is governed by ion exchange.

Based on the value of correlation coefficients (R^2) for Freundlich, Langmuir and D–R, it can be seen that the behavior of strontium adsorption on the mixed oxide spheres was described as an isotherm of Freundlich type and the Langmuir adsorption isotherm was non-valid.

3.6. The effect of temperature

The experiments were carried out at 287, 296, 303, and 323 K. The other parameters were kept constant. In all experiments, 50 mL of 5 ppm strontium nitrate solution was

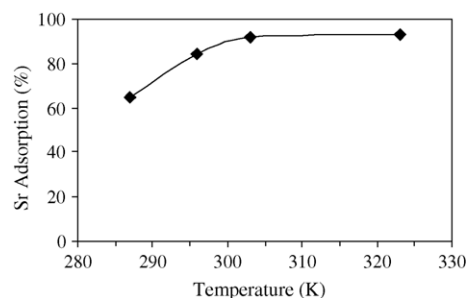


Fig. 8. Effect of temperature on the adsorption of strontium on the TiO₂–SiO₂ mixed gel spheres. Initial concentration of strontium = 5 mg L⁻¹, 0.2 g sorbent in 50 mL solution, pH 10.6, shaking time = 2 h.

shaken with 0.200 g mixed oxide spheres at pH 10.6 for 2 h. The strontium concentration was determined by ICP-OES. The distribution coefficients (K_D) were calculated from the following equation:

$$K_D = \left[\frac{C_0 - C_e}{C_e} \right] \left(\frac{V}{m} \right)$$

where C_0 and C_e are the initial and equilibrium concentrations of Sr ion in solution (mg L⁻¹), V the solution volume (mL) and m is the mass of sorbent (g).

The values of ΔH° and ΔS° are calculated from the slope and intercept of the linear variation of $\ln K_D$ with reciprocal temperature, $1/T$, using the relation:

$$\ln K_D = \left(\frac{-\Delta H^\circ}{RT} \right) + \left(\frac{\Delta S^\circ}{R} \right)$$

where K_D is the distribution coefficient (mL g⁻¹), ΔS° standard entropy, ΔH° standard enthalpy, T the temperature and R is gas constant (kJ mol⁻¹ K⁻¹). The free energy of specific adsorption ΔG° is calculated using the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The effect of temperature on strontium adsorption is given in Fig. 8. It is clearly seen that adsorption increases with increasing temperature. The maximum adsorption yield was observed at 323 K as 93.1%. 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).

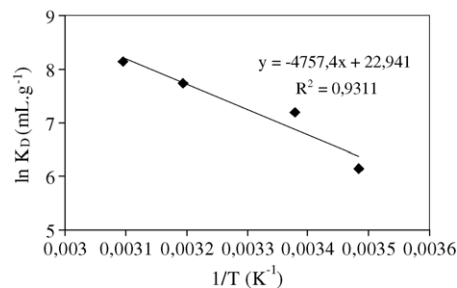


Fig. 9. Variation of $\ln K_D$ with $1/T$ for adsorption of Sr(II) on TiO₂–SiO₂ mixed gel spheres.

Table 3
Thermodynamic parameters for strontium adsorption on the mixed oxide gel spheres

ΔH° (kJ mol ⁻¹)	39.553
ΔS° (kJ K ⁻¹ mol ⁻¹)	0.190
$-\Delta G^\circ$ (kJ mol ⁻¹)	
287 K	14.977
296 K	16.687
303 K	18.017
323 K	21.817

The values of ΔH° , ΔS° , and ΔG° are given in Table 3. The value of $\Delta H^\circ = 39.553$ kJ/mol and $\Delta G^\circ = -16.687$ kJ/mol at 296 K suggest that the sorption of strontium on mixed oxide gel is an endothermic and a spontaneous process.

3.7. The influence of competing metal ions

The influence of divalent cations Ca²⁺ and Mg²⁺ on the adsorption of strontium on the mixed oxide spheres was investigated. In the experiments, 1.14×10^{-3} mol L⁻¹ strontium nitrate solutions including each 0 , 2.5×10^{-5} , 2.5×10^{-4} , and 4×10^{-4} mol L⁻¹ of calcium chloride, were treated with 0.200 g mixed oxide spheres at pH 10.6, in a shaker, during 2 h at 298 K. The same concentrations and experimental conditions were taken also for magnesium. Distribution coefficients (K_D) and strontium adsorption efficiency were determined. As clearly seen in Table 4, the decrease of strontium adsorption efficiency and K_D values for increasing concentrations of Ca²⁺ and Mg²⁺, exhibit similar trends.

Table 4
Effect of Ca²⁺, Mg²⁺ on the adsorption of Sr²⁺

Ca ²⁺ initial concentration (mol L ⁻¹)	0	2.5×10^{-5}	2.5×10^{-4}	24.0×10^{-4}
Sr adsorption (%)	95.40	94.60	91.86	83.40
K_D Sr (mL g ⁻¹)	5183.40	4428.13	2907.86	1307.33
Mg ²⁺ initial concentration (mol L ⁻¹)	0	2.5×10^{-5}	2.5×10^{-4}	24.0×10^{-4}
Sr adsorption (%)	96.78	96.10	88.09	84.90
K_D Sr (mL g ⁻¹)	7554.08	6155.35	1880.88	1454.63

3.8. Identification and characterization

The thermal analysis data related to TiO₂–SiO₂ mixed gel spheres (60% TiO₂ weight ratio) were evaluated. From the DTA curve the endothermic peak observed at 385 K indicates the maximum value of loss of water. From the TGA data, it was calculated that the adsorbent includes 2.29 mol water. It was observed that at 840 K, the mixed oxide gel spheres are converted to oxide by losing completely their water.

Figs. 10 and 11 show the FTIR spectra of TiO₂–SiO₂ mixed gel spheres with their enlarged low wave number region, before and after strontium adsorption, respectively. Two OH stretching bands at 3490 and 3224 cm⁻¹ in Fig. 10 are also visible in Fig. 11, at 3452 and 3236 cm⁻¹. The strong peak observed at ~ 1645 cm⁻¹ in both figures corresponds to the bending mode of adsorbed water. The peak observed in Fig. 10 at 1404 cm⁻¹ is due to the Ti–OH deformation vibration band and this peak is shifted to 1450 cm⁻¹ in Fig. 11. The bands observed in both figures at 1064 and 1056 cm⁻¹, respectively, can be attributable to O–Si asymmetric flexible vibration. The band observed in both figures at 945 cm⁻¹ is often used as evidence for Ti incorporation into the silica lattice. Indeed, some researchers have used this band to quantitatively assess the degree of Ti–O–Si heterolinkages in titania–silica samples [10]. Main differences between pure and strontium adsorbed TiO₂–SiO₂ spectra begin at the low wave number region, where the influence of strontium can be seen. In this region, the peaks at 439 and 432 cm⁻¹ disappearing with strontium adsorption, while the peak at 447 cm⁻¹ become more intense.

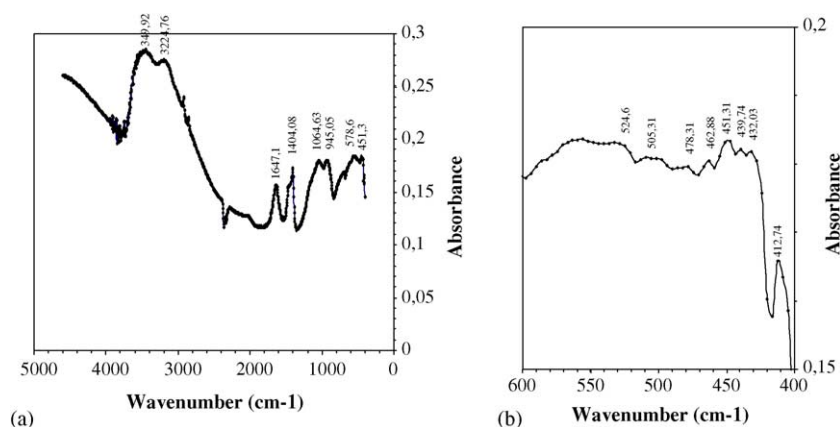


Fig. 10. The FTIR spectrum of TiO₂–SiO₂ mixed gel; (a) 400–4000 cm⁻¹ region and (b) 400–600 cm⁻¹ region.

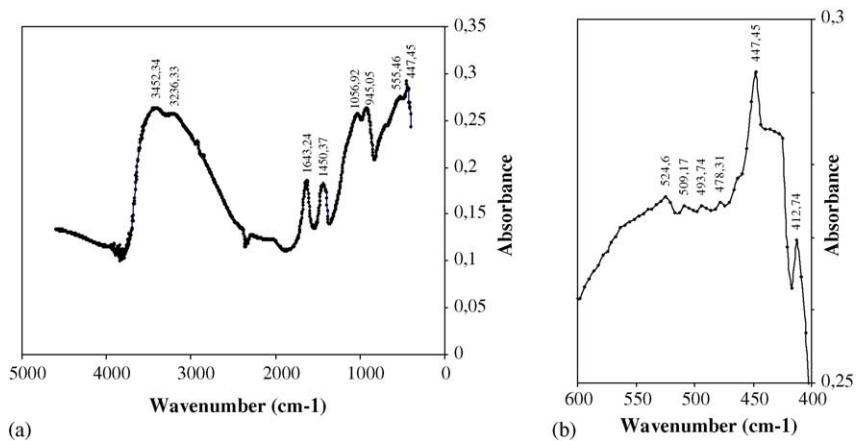


Fig. 11. The FTIR spectrum of strontium adsorbed $\text{TiO}_2\text{-SiO}_2$ mixed gel; (a) $400\text{-}4000\text{ cm}^{-1}$ region and (b) $400\text{-}600\text{ cm}^{-1}$ region.

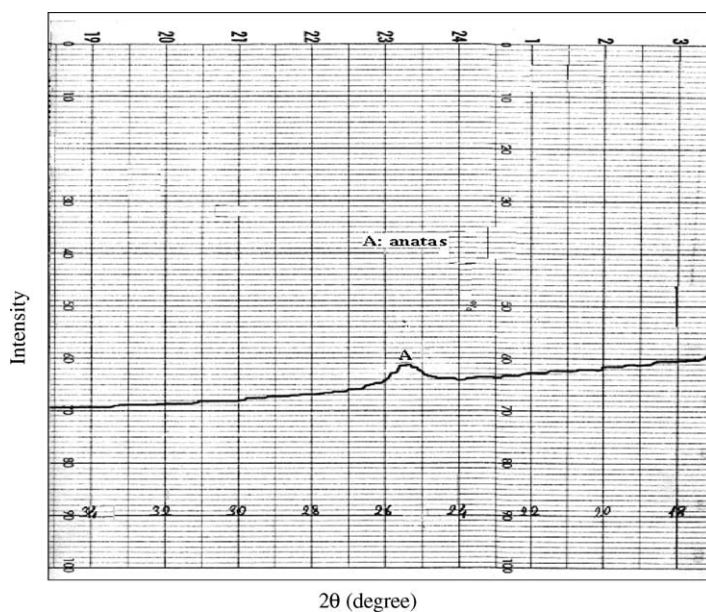


Fig. 12. X-ray diffraction pattern of the $\text{TiO}_2\text{-SiO}_2$ mixed gel spheres heat treated at 973 K.

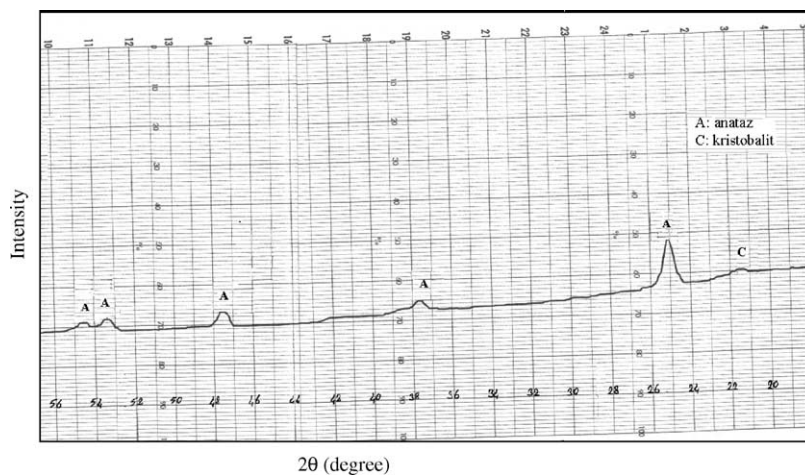


Fig. 13. X-ray diffraction pattern of the $\text{TiO}_2\text{-SiO}_2$ mixed gel spheres heat treated at 1173 K.

Figs. 12 and 13 show the XRD patterns of $\text{TiO}_2\text{-SiO}_2$ mixed gel spheres calcined at 973 and 1173 K, respectively. At both temperature titanium dioxide shows anatase type crystal structure and the data are in good agreement with the ASTM data (ASTM File no. 21-1272 for TiO_2). At 973 K, no peak was observed for SiO_2 and the structure was amorphous. The peak observed at $2\theta = 21.5^\circ$ for the gels calcined at 1173 K can be attributed to cristobalite structure of SiO_2 (ASTM File no. 4-359 for SiO_2 Cristobalite) [11].

4. Conclusion

The overall results indicate the possibility of using the synthesized $\text{TiO}_2\text{-SiO}_2$ mixed gel spheres for efficient removal of Sr(II) from aqueous and radioactive waste solutions. Beside its spherical shape allowing being used in column separation processes, its production simplicity provide to $\text{TiO}_2\text{-SiO}_2$ mixed gel many advantages on the other sorbents.

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