



Preparation of ZrO_2 and ZrO_2 – TiO_2 microspheres by the sol–gel method and an experimental design approach to their strontium adsorption behaviours

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ABSTRACT

ZrO_2 and ZrO_2 – TiO_2 mixed gel spheres were prepared via sol–gel process. The source sols of Zr and Zr–Ti (with 1:1 molar ratio) were prepared by the ammonia addition method starting from $ZrOCl_2$ and $TiCl_4$ solutions. A simple method, using a gelation column containing two phases (methyl isobutyl ketone and ammonia) as sphere forming and gelling medium, allowing to direct preparation of ZrO_2 and ZrO_2 – TiO_2 mixed gel spheres. The adsorption behaviours of each adsorbent towards strontium were determined by the experimental design method for the possible application to its removal from radioactive waste solutions. pH, temperature, strontium concentration and shaking time were chosen as independent variables and the efficiency of strontium removal as dependent output variable. Central composite design (CCD), with seven replicates at the centre points and thus a total of 31 experiments were employed in this study for each synthesized ZrO_2 and ZrO_2 – TiO_2 microspheres. Sorption data have been interpreted in terms of Freundlich, Langmuir and Dubinin–Radushkevich equations. Thermodynamic parameters for the sorption system have been determined. Each adsorbent were subjected to thermal treatment from 600 °C to 900 °C and were investigated by XRD, FTIR, DTA/TGA, SEM and BET surface area methods.

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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]. The management and disposal of such waste is, therefore, an issue relevant to almost all countries. 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. New materials and processes are under consideration and development in various countries [2]. In the past decade inorganic ion-exchange materials have

emerged as an increasingly important replacement or complement for conventional organic ion-exchange resins, particularly in liquid radioactive waste treatment and spent fuel reprocessing applications [3–6]. A variety of inorganic ion-exchangers and adsorbents have been reported: zeolites, ammonium molybdophosphate, magnetite, sodium titanate, titanium phosphate, titanium silicate, zirconium phosphate, hydrated alumina, silica, bentonites, mordenite, hydrous titanium oxide, mixed oxide of titania–silica, zirconium oxide and others [7–12]. Inorganic ion exchangers often have the advantage a much greater selectivity than organic resins for certain radiologically important species, such as the fission products ^{137}Cs and ^{90}Sr , which have relatively long half-life of approximately 30 years. Radiostrontium is considered one of the most hazardous pollutants because of its ability to accumulation in human bones [13]. Due to the high adsorption capacity, irradiation resistance, thermal and chemical stability, inorganic exchangers have found wide application in the treatment of aqueous nuclear wastes. These inorganic materials may also have advantages with respect to immobilization and final disposal when compared to organic ion-exchangers. The ions to be removed are generally present in low concentrations and are associated with an assortment of other cations. The ion-exchange process is very effective at transferring the radioactive content of a large volume of liquid into a small volume of solid. Therefore, the removal of ^{137}Cs and ^{90}Sr in order to convert the majority of the high-level waste into low-level waste, which is more economical to dispose of, is of a great

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concern [12]. 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 form, strontium tends to form complexes with complexing agents (oxalic acid, oxalates, etc.) often present in liquid waste solutions. Strontium uptake is known to be highly affected by the presence of competing ions, especially calcium and the limits for strontium concentrations are lower than for cesium [14]. Because of the diversity of the chemical and radiochemical composition of the liquid radioactive wastes depending on their source, no universal adsorbent material can be considered. Therefore new type of adsorbent materials is needed to be developed. The adsorption is also a surface phenomenon. The surface properties of the adsorbents (specific surface area, pore size, etc.) depend seriously on the initial materials from which are produced and the method used. The rapid development of sorption technologies in liquid radioactive waste management and the utilization of column in adsorption and/or ion-exchange operations involve inevitably produce adsorbents in a column-usable form with high mechanical strength.

In the present study source sols of zirconium and zirconium-titanium (with 1:1 molar ratio) were prepared by the ammonia addition method starting from ZrOCl_2 and TiCl_4 solutions and source sols were gelled in a gelation column containing two phases (methyl isobutyl ketone and ammonia) as sphere forming and gelling medium allowing to direct preparation of ZrO_2 and $\text{ZrO}_2\text{-TiO}_2$ mixed gel spheres suitable for column operation. The adsorption behaviours of each adsorbent towards strontium were optimized by using the central composite design (CCD) method for the possible application to its removal from radioactive waste solutions. The adsorbents were characterized by BET specific surface area, SEM, XRD, and DTA/TGA thermal analysis methods.

2. Experimental

2.1. Reagents

The initial materials titanium (IV) chloride (98%, $d = 1.73 \text{ g mL}^{-1}$) was purchased from BDH Chemicals Ltd. (AnalaR grade) and zirconium (IV) oxide chloride octahydrate was purchased from Merck.

Strontium nitrate was purchased from Merck and was used to prepare Sr(II) stock solutions (1000 mg L^{-1} , in 2% HNO_3). In all experiments natural isotope of strontium (^{88}Sr) was used instead of ^{90}Sr for economical reason and operation facility.

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

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

2.2. Preparation of ZrO_2 and $\text{ZrO}_2\text{-TiO}_2$ microspheres

ZrO_2 and $\text{ZrO}_2\text{-TiO}_2$ microspheres were produced according to the flow sheet given in Fig. 1.

2.2.1. Sol preparation

Source sols of ZrO_2 were prepared by dropwise addition of 30 mL of 8 M NH_4OH solution into the 200 mL of 0.5 M ZrOCl_2 solution at 70°C under pH control and reflux, in a sol preparation system consisting from an oil bath, a three-necked reaction flask, a thermostatically controlled magnetic stirrer, a dosimat (Metrohm 665) for ammonia injection and a titroprocessor (Metrohm 686) for controlling the operation of dosimat according to the pH monitored.

Source sols of $\text{ZrO}_2\text{-TiO}_2$ were prepared by dropwise addition of 34 mL of 8 M NH_4OH solution into the 200 mL of a mixture of

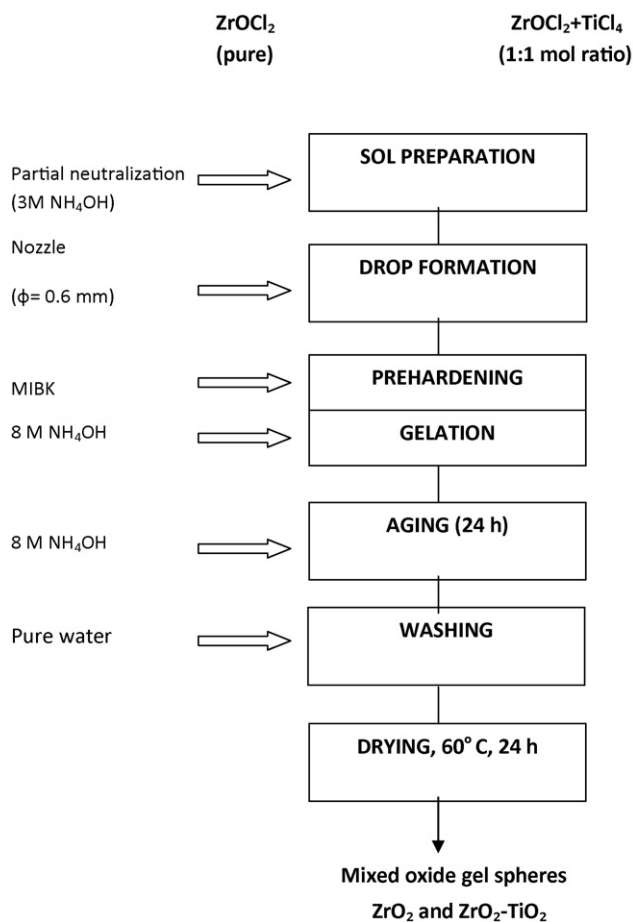


Fig. 1. Process flowsheet.

0.25 M ZrOCl_2 and 0.25 M TiCl_4 solutions at 70°C under pH control and reflux, in the previously described sol preparation system.

2.2.2. Gelation

Gelation was carried out in the apparatus shown in Fig. 2. A stainless steel nozzle with an inner diameter of 0.60 mm was used for sol drops formation. The nozzle was adapted into a vibration system giving permission to inner passage of sols which are dispersed into droplets. The sol drop system was horizontally 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 methyl isobutyl ketone (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 24 h to improve their mechanical characteristics. The aged spheres were washed by demineralised water and dried at 333 K.

2.3. Experimental design and optimization of parameters

In assessing the effects of multiple parameters on adsorption efficiency, the use of an adequate experimental design is particularly important. To study the interactions of two or more variables, response surface methodology (RSM) has proved to be a useful tool [15]. It is a collection of mathematical and statistical techniques for designing experiments, building numerical models, evaluating the effects of variables and searching for the optimum combinations of factors. Experimental design methodology involves changing all variables from one experiment to the next simultaneously. The

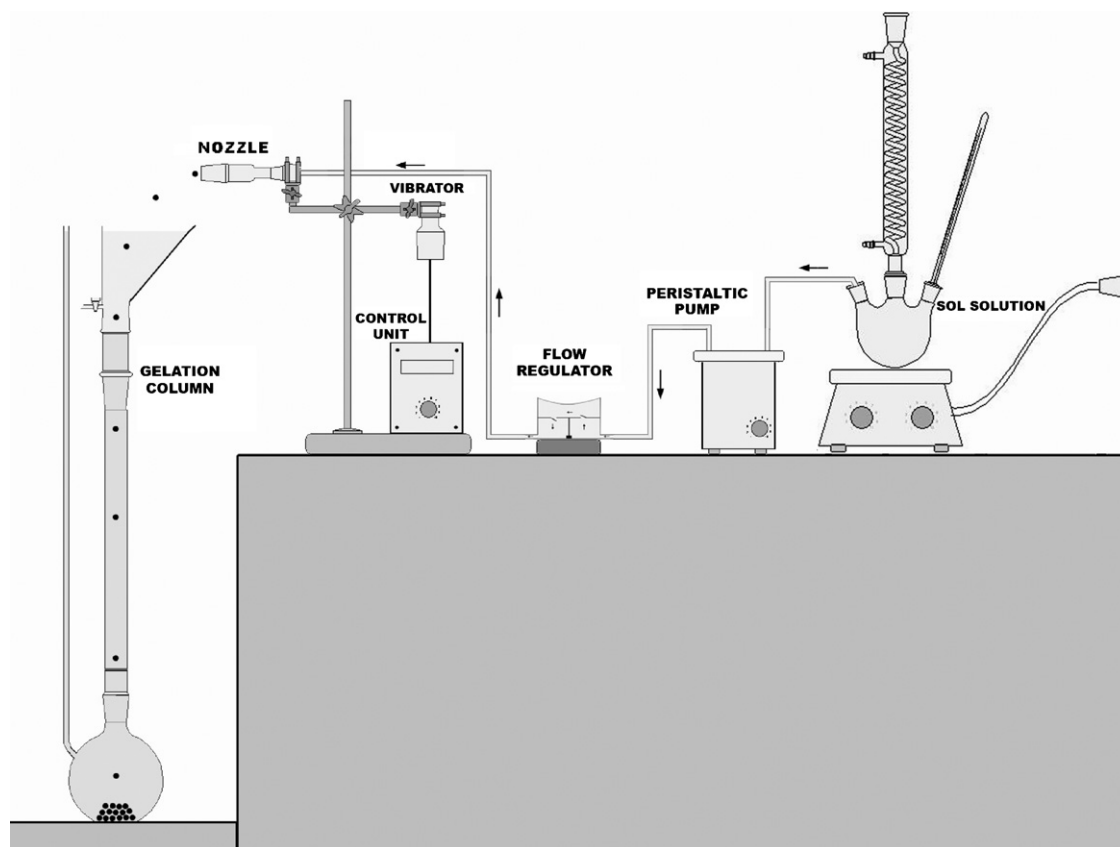


Fig. 2. Sol-gel preparation apparatus.

reason for this is that variables can influence each other, and the ideal value for one of them can depend on the values of the others. This interaction between variables is a frequent phenomenon [16] and therefore, in this study statistical experimental design was employed in place of the traditional “one-factor-at-a-time” experiments. In order to determine the optimum conditions for synthesized ZrO_2 , ZrO_2 - TiO_2 mixed oxide spheres, Central Composite Design (CCD) has been used. The CCD is an effective design that is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points [17]. According to the CCD, the optimization of Sr^{2+} removal was carried out by four chosen independent process variables (pH (X_1), temperature (X_2), initial Sr^{2+} concentration (X_3) and shaking time (X_4)) with seven replicates at centre points, thus a total of 31 experiments were employed in this study. The effects of independent variables on metal sorption of sorbents were examined by batch tests. Batch sorption behaviors of $Sr(II)$ ions on the ZrO_2 , ZrO_2 - TiO_2 mixed oxide spheres were conducted by adding 0.1 g sorbent in 30 mL of liquid phase. Following the $Sr(II)$ adsorption, the samples were filtered with blue ribbon filter paper, then $Sr(II)$ concentrations were measured by Perkin Elmer Optima 2000DV ICP-OES. Shaking experiments were done in a temperature controlled environment at 150 RPM using a GFL 1086 water bath shaker equipped with microprocessor thermostat.

The ranges and the levels of the variables (high, low, centre and star points) investigated in the work are given in Table 1.

The design matrix for four variables is varied at five levels ($-\alpha$, -1 , 0 , $+1$, $+\alpha$). The full model equation with linear and quadratic terms for predicting the optimal response was given in Eq. (1).

$$y_i = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \quad (1)$$

Table 1

Experimental range and levels of independent process variables for strontium removal.

Independent variable		$-\alpha$	-1	0	1	α
pH	X_1	2	4	6	8	10
Temperature ($^{\circ}C$)	X_2	20	30	40	50	60
Sr concentration ($mg L^{-1}$)	X_3	10	30	50	70	90
Shaking time (min)	X_4	30	120	210	300	390

In the equation, b_0 signifies the term of intercept. The terms are coded as b_i linear effects, b_{ii} second-order effects, b_{ij} dual interaction between investigating parameters. For the current model investigated in this study the second-order polynomial equation can be presented as,

$$y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{44} X_4^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{14} X_1 X_4 + b_{23} X_2 X_3 + b_{24} X_2 X_4 + b_{34} X_3 X_4$$

2.4. Isotherm studies

The investigation of adsorption isotherm was conducted by batch process. 30 mL of strontium nitrate solution at different concentrations (20–200 ppm) were prepared and the pH values of these solutions were adjusted to 9 with 1 M NaOH. 0.10 g of the zirconium dioxide microspheres were added to each sample. The samples were treated in a thermostatically controlled shaker at $303 \pm 1 K$ for 6 h. The supernates were filtered and the concentrations of strontium were determined by ICP-OES. The quantity of adsorbed strontium on the zirconium dioxide microspheres was

Table 2
Central Composite Design model for Sr adsorption with ZrO₂ and ZrO₂-TiO₂.

No.	pH	Temp. (°C)	Sr conc. (mg L ⁻¹)	Shaking time (min)	ZrO ₂		ZrO ₂ -TiO ₂	
					Sr removal efficiency (%) Act.	Sr removal efficiency (%) Pred.	Sr removal efficiency (%) Act.	Sr removal efficiency (%) Pred.
1	1	1	1	1	44.30	45.74	43.68	33.11
2	1	1	1	-1	38.19	35.61	40.61	34.81
3	1	1	-1	1	85.31	77.75	79.46	80.51
4	1	1	-1	-1	77.77	73.35	74.37	76.91
5	1	-1	1	1	39.49	36.94	43.33	49.10
6	1	-1	1	-1	31.00	31.95	54.47	53.82
7	1	-1	-1	1	56.46	56.83	92.00	75.78
8	1	-1	-1	-1	61.10	57.56	85.33	75.20
9	-1	1	1	1	9.68	7.16	5.14	5.35
10	-1	1	1	-1	8.16	3.14	-2.21	2.42
11	-1	1	-1	1	14.25	8.65	42.56	31.62
12	-1	1	-1	-1	13.86	10.35	39.07	23.39
13	-1	-1	1	1	10.34	10.12	30.15	16.01
14	-1	-1	1	-1	9.74	11.24	27.06	16.09
15	-1	-1	-1	1	2.97	-0.51	25.68	21.56
16	-1	-1	-1	-1	12.41	6.33	17.38	16.35
17	α	0	0	0	98.96	102.55	98.04	104.29
18	-α	0	0	0	5.63	12.74	2.41	17.67
19	0	α	0	0	13.45	22.98	14.87	21.39
20	0	-α	0	0	8.98	10.15	15.34	30.33
21	0	0	α	0	11.39	10.54	11.73	16.73
22	0	0	-α	0	26.08	37.64	47.87	64.38
23	0	0	0	α	16.69	21.40	13.64	27.37
24	0	0	0	-α	12.12	18.11	16.07	23.86
25	0	0	0	0	12.32	13.43	15.62	14.79
26	0	0	0	0	16.86	13.43	16.12	14.79
27	0	0	0	0	14.58	13.43	10.62	14.79
28	0	0	0	0	12.30	13.43	15.05	14.79
29	0	0	0	0	11.48	13.43	16.10	14.79
30	0	0	0	0	13.83	13.43	15.41	14.79
31	0	0	0	0	12.66	13.43	14.59	14.79

calculated as the difference between initial and final concentration at equilibrium. The results are then analyzed in terms of Langmuir, Freundlich and Dubinin–Radushkevich isotherms. The similar experiments were realized also for ZrO₂-TiO₂ microspheres by keeping constant the experimental conditions.

2.5. Thermodynamic parameters

The experiments were carried out at 293, 303, and 313 K for both adsorbents. The other parameters were kept constant. In all experiments, 30 mL of 100 ppm strontium nitrate solution was shaken with 0.100 g microspheres at pH 9 for 2 h. The strontium concentration was determined by ICP-OES. The distribution coefficients (K_D) were calculated from the following equation:

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

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:

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

3. Results and discussion

3.1. Strontium adsorption experiments with ZrO₂ and ZrO₂-TiO₂ microspheres

CCD consists of 16 factorial points, 9 star points (1 at centre) and 6 replicate points. Coded experimental data points used in Central Composite Design and predicted and actual responses are given in Table 2.

3.1.1. Adsorption with ZrO₂

The relationship between independent variables and response was drawn by second-order polynomial equation. The regression equation coefficients were calculated and data was fitted to a second-order polynomial equation for the removal of Sr²⁺ ions with synthesized ZrO₂ mixed oxide spheres.

$$y = 13.4329 + 22.4529X_1 + 3.2063X_2 - 6.7754X_3 + 0.8212X_4 + 11.0533X_1^2 + 0.7833X_2^2 + 2.6633X_3^2 + 1.5808X_4^2 + 2.9394X_1X_2 - 7.6306X_1X_3 + 1.5269X_1X_4 - 3.0306X_2X_3 + 1.2844X_2X_4 + 1.4294X_3X_4$$

On the basis of second-order polynomial equation of response surface methodology, the effect of independent variables: pH, temperature, initial Sr²⁺ concentration and contact time on the adsorption of Sr²⁺ were analyzed. Table 3 shows the regression analyses of independent variables.

The efficiency values obtained as a result of 31 experiments determined at the Central Composite Design conditions were compared with the calculated efficiency values from the applied model.

Table 3
Analysis of variance (ANOVA) for the regression model for Sr²⁺ uptake capacity of ZrO₂.

Sources of variation	Sum of squares	DF	Mean square	F-value	Prob. > F
Regression	18345.82	14	1310.42	34.94	0.0000
Residual	600.13	16	37.51		
Total	18945.96	30			

$R^2 = 0.97$, adjusted $R^2 = 0.94$, multiple $R^2 = 0.98$.

Table 4
Correlation coefficients and *t* values in the strontium adsorption with ZrO₂.

	Coefficients	Standard error	<i>t</i>	<i>P</i>
Intercept	13.43	2.31	5.80	2.69E-05
X ₁	22.45	1.25	17.96	4.99E-12
X ₂	3.21	1.25	2.56	2.08E-02
X ₃	-6.77	1.25	-5.42	5.68E-05
X ₄	0.82	1.25	0.66	5.20E-01
X ₁ X ₁	11.05	1.15	9.65	4.49E-08
X ₂ X ₂	0.78	1.15	0.68	5.04E-01
X ₃ X ₃	2.66	1.15	2.32	3.36E-02
X ₄ X ₄	1.58	1.15	1.38	1.86E-01
X ₁ X ₂	2.94	1.53	1.92	7.29E-02
X ₁ X ₃	-7.63	1.53	-4.98	1.35E-04
X ₁ X ₄	1.53	1.53	1.00	3.34E-01
X ₂ X ₃	-3.03	1.53	-1.98	6.52E-02
X ₂ X ₄	1.28	1.53	0.84	4.14E-01
X ₃ X ₄	1.43	1.53	0.93	3.64E-01

Table 2 shows that the calculated values are in good agreement with which are determined experimentally. The value of R^2 was found 0.97 (Table 3) for strontium adsorption on ZrO₂. Probability *F*-value ($F < 0.05$) and high value of R^2 indicate that the model fits the experimental data well.

The coefficients of independent variables and *P* values according to the investigated parameters (pH, temperature, Sr concentration and shaking time) are given in Table 4. pH ($P = 4.99 \times 10^{-12}$), temperature ($P = 2.08 \times 10^{-2}$) and strontium concentration ($P = 5.68 \times 10^{-5}$) parameters were found statistically significant. The positive values of coefficients belong to pH ($X_1 = 22.45$) and temperature ($X_2 = 3.21$) indicate that pH and temperature have a positive effect on the adsorption of Sr²⁺ from aqueous solution by synthesized ZrO₂ spheres. It means the adsorption of Sr²⁺ increases as pH and temperature increase. Adsorption

increases with increasing pH, in all temperature ranges. At lower pH conditions, Sr(II) uptake was decreased due to increasing positive charge of the sorbent surface. The sorbent surface is mostly protonated at lower pHs. The metal ions which are expected to be adsorbed are also positively charged, thus the adsorption is not favoured. On the contrary, as the pH increases, the adsorbent surface becomes more negatively charged and therefore the adsorption of positively charged species is more favourable. However, initial Sr²⁺ concentration ($X_3 = -6.77$) has a negative effect on adsorption. It means the adsorption of Sr²⁺ decreases with the increasing initial Sr²⁺ concentration. Although shaking time is statistically non-significant ($P > 0.05$), it has a positive cumulative effect on adsorption of Sr²⁺ from aqueous solution.

Interactions between independent variables are shown in 3D surface plot (Fig. 3). Fig. 3 shows interaction between two independent variables pH (X_1) and initial Sr²⁺ concentration (X_3) with another variables being at fixed levels. From the plot, the maximum strontium adsorption was observed in a pH range of 9–10 and between 10 and 50 mg L⁻¹ strontium concentrations.

3.1.2. Adsorption with ZrO₂-TiO₂

The relationship between independent variables and response was drawn by second-order polynomial equation. The regression equation coefficients were calculated and data was fitted to a second-order polynomial equation for the removal of Sr²⁺ ions with synthesized ZrO₂-TiO₂ mixed oxide spheres.

$$y = 14.7871 + 21.6533X_1 - 2.2358X_2 - 11.9125X_3 + 0.8775X_4 + 11.5484X_1^2 + 2.7684X_2^2 + 6.4422X_3^2 + 2.7059X_4^2 - 1.3313X_1X_2 - 5.2825X_1X_3 - 1.1588X_1X_4 - 5.1787X_2X_3 + 0.7550X_2X_4 - 1.3237X_3X_4$$

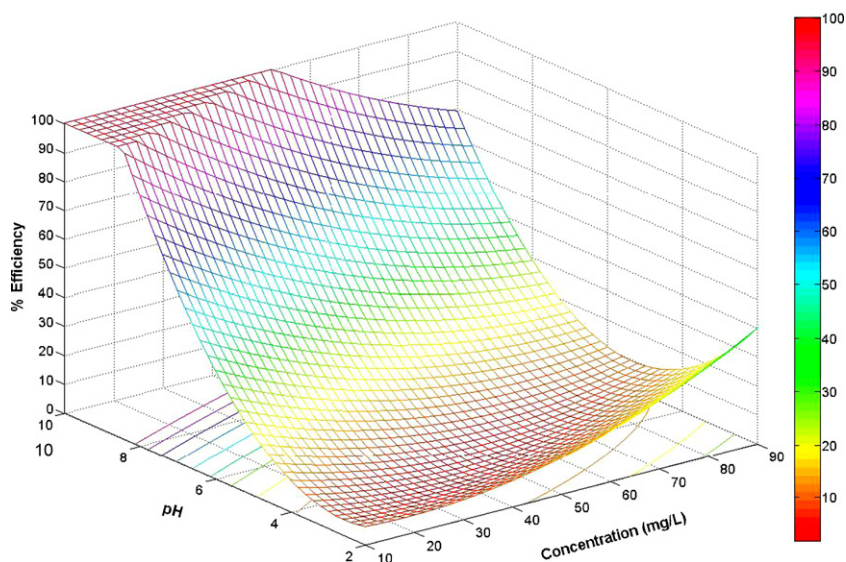


Fig. 3. Surface response for Sr adsorption on ZrO₂ depending pH and concentration.

Table 5
Analysis of variance (ANOVA) for the regression model for Sr²⁺ uptake capacity of ZrO₂-TiO₂.

Sources of variation	Sum of squares	DF	Mean square	F-value	Prob. > F
Regression	20414.06	14	1458.15	9.78	0.0000
Residual	2385.93	16	149.12		
Total	22800	30			

$R^2 = 0.90$, adjusted $R^2 = 0.80$, multiple $R^2 = 0.95$.

On the basis of second-order polynomial equation of response surface methodology, the effect of independent variables: pH, temperature, initial Sr²⁺ concentration and contact time on the adsorption of Sr²⁺ were analyzed. Table 5 shows the regression analyses of independent variables.

The efficiency values obtained as a result of 31 experiments determined at the Central Composite Design conditions were compared with the calculated efficiency values from the applied model. Table 2 shows that the calculated values are in good agreement with which are determined experimentally. The value of R^2 was found 0.90 (Table 5) for strontium adsorption on ZrO₂-TiO₂. Probability F -value ($F < 0.05$) and high value of R^2 indicate that the model fits the experimental data well.

The coefficients of independent variables and P values according to the investigated parameters (pH, temperature, Sr concentration and shaking time) are given in Table 6. pH ($P = 1.87 \times 10^{-7}$) and strontium concentration ($P = 2.05 \times 10^{-4}$) parameters were found statistically significant. The positive value of coefficient belong to pH ($X_1 = 21.65$) indicates that pH has a positive effect on adsorption of Sr²⁺ from aqueous solution by synthesized ZrO₂-TiO₂ spheres. It means the adsorption of Sr²⁺ increases as pH increases. As mentioned on ZrO₂, lower pH conditions imply lower Sr(II) uptake because of increasing positive charge of the sorbent surface. On the other hand, as the pH increases, the adsorbent surface becomes more negatively charged and therefore the adsorption of positively charged species is more favourable. Nevertheless, initial Sr²⁺ concentration ($X_3 = -11.91$) has a negative effect on adsorption. It means the adsorption of Sr²⁺ decreases with the increasing initial Sr²⁺ concentrations. Although, temperature and shaking time are statistically non-significant ($P > 0.05$), temperature has a negative cumulative effect and shaking time has a positive cumulative effect on adsorption of Sr²⁺ from aqueous solution.

Table 6
Correlation coefficients and t values in the strontium adsorption with ZrO₂-TiO₂.

	Coefficients	Standard error	t	P
Intercept	14.79	4.62	3.20	5.53E-03
X_1	21.65	2.49	8.69	1.87E-07
X_2	-2.24	2.49	-0.90	3.83E-01
X_3	-11.91	2.49	-4.78	2.05E-04
X_4	0.88	2.49	0.35	7.29E-01
X_1X_1	11.55	2.28	5.06	1.17E-04
X_2X_2	2.77	2.28	1.21	2.43E-01
X_3X_3	6.44	2.28	2.82	1.23E-02
X_4X_4	2.71	2.28	1.18	2.53E-01
X_1X_2	-1.33	3.05	-0.44	6.68E-01
X_1X_3	-5.28	3.05	-1.73	1.03E-01
X_1X_4	-1.16	3.05	-0.38	7.09E-01
X_2X_3	-5.18	3.05	-1.70	1.09E-01
X_2X_4	0.76	3.05	0.25	8.08E-01
X_3X_4	-1.32	3.05	-0.43	6.71E-01

Interactions between independent variables are shown in 3D surface plot (Fig. 4). Fig. 4 shows interaction between two independent variables pH (X_1) and initial Sr²⁺ concentration (X_3) with another variables being at fixed levels. From the plot, the maximum strontium adsorption was observed in a pH range of 9–10 and between 10 and 50 mg L⁻¹ strontium concentrations.

3.2. Isotherm studies

Figs. 5 and 6 show the relationship between the quantity of strontium adsorbed per unit mass of the zirconium dioxide microspheres and the equilibrium concentrations at pH 9.

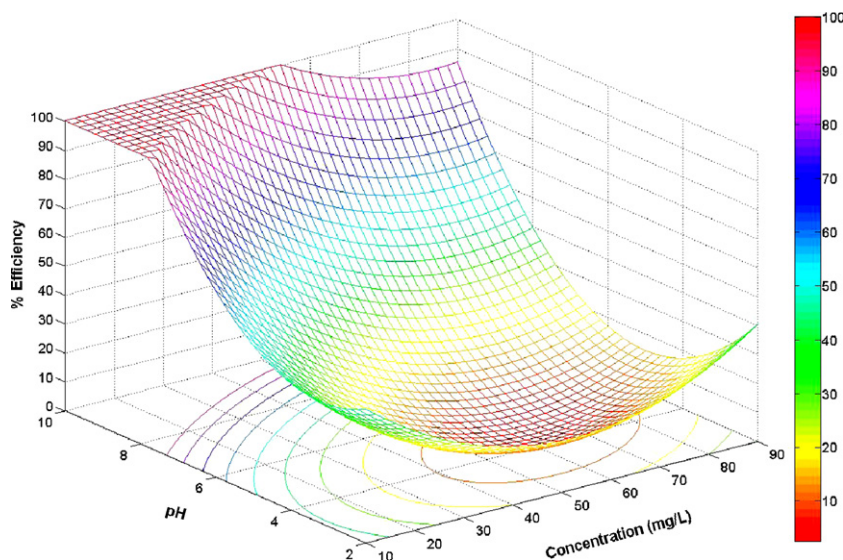


Fig. 4. Surface response for Sr adsorption on ZrO₂-TiO₂ depending pH and concentration.

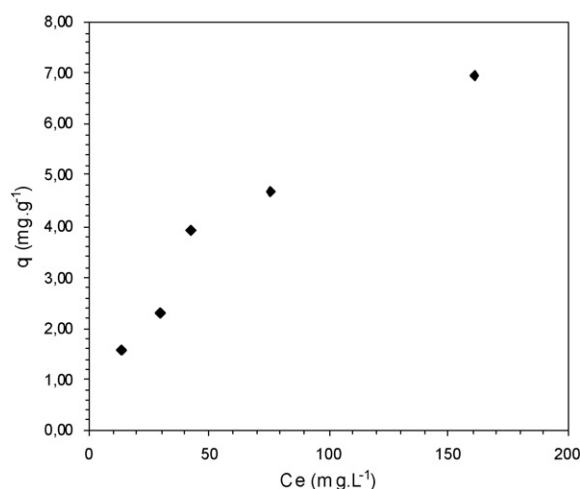


Fig. 5. Adsorption isotherm of Sr on ZrO₂ microspheres: 0.10 g adsorbent in 30 mL solution, pH 9, shaking time 6 h, temperature = 303 K.

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

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

where x/m is the amount of strontium ions adsorbed per unit weight of ZrO₂ microspheres (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_F and $1/n$ were calculated and their values are given in Table 7.

Langmuir isotherm equation in its linear form is:

$$\frac{C_e}{q} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

where q_m and b are monolayer adsorption capacity and Langmuir constant related to energy of adsorption, respectively.

From the slope and intercept of the linear graph of C_e/q versus C_e , Langmuir constants q_m and b were calculated and their values are given in Table 7.

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 ZrO₂ microspheres (mol/g) and maximum amount of Sr ions on the mixed gel spheres (mol/g), respectively, K a constant related to the

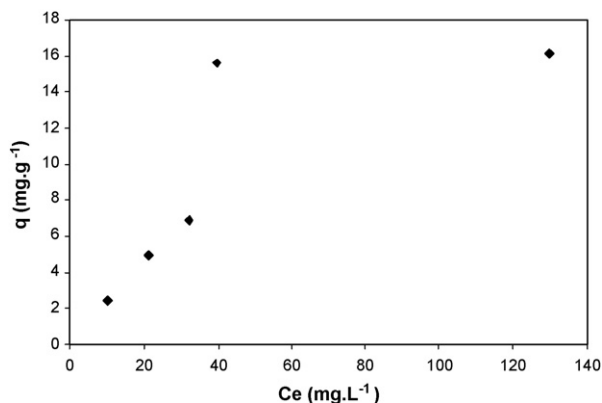


Fig. 6. Adsorption isotherm of Sr on ZrO₂-TiO₂ microspheres: 0.10 g adsorbent in 30 mL solution, pH 9, shaking time 6 h, temperature = 303 K.

Table 7

Langmuir, Freundlich, D–R isotherm parameters for strontium adsorption on the ZrO₂ and ZrO₂-TiO₂ gel spheres.

Parameters	Adsorbents	
	ZrO ₂	ZrO ₂ -TiO ₂
Langmuir isotherm		
q_m (mg g ⁻¹)	10.52	28.01
b (mg L ⁻¹)	0.012	0.012
R^2	0.943	0.717
Freundlich isotherm		
k_F (mol/g)	3.88×10^{-3}	5.94×10^{-3}
$1/n$	0.609	0.760
R^2	0.957	0.813
D–R isotherm		
X_m (mol/g)	4.02×10^{-4}	1.93×10^{-3}
K (mol ² /kJ ²)	0.006	0.008
E (kJ/mol)	8.84	8.01
R^2	0.964	0.841

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 (8.314×10^{-3} kJ mol⁻¹ K⁻¹), T is the 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 7). The mean energy of sorption (E) is the free energy change when one mole 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 values of Langmuir, Freundlich, and D–R isotherm parameters for strontium adsorption on the ZrO₂ and ZrO₂-TiO₂ gel spheres were given in Table 7.

Langmuir constants related to monolayer capacity for strontium adsorption on the ZrO₂ and ZrO₂-TiO₂ gel spheres were found as 10.52 mg/g and 28.01 mg/g, respectively. Although there are other sorbents showing higher adsorption capacity towards strontium in the literature [8,10,18–21], the prepared ZrO₂-TiO₂ sorbent seems to be advantageous with easy preparation by the sol–gel process, spherical shape allowing to be used in column applications, chemical, mechanical and thermal resistance.

The calculated E values for Sr adsorption are 8.84 kJ/mol and 8.01 kJ/mol for ZrO₂ and ZrO₂-TiO₂, respectively. These values are in the range of 8–16 kJ, so sorption is governed by ion exchange for both adsorbents. These low values are in the border of the physical forces which may also affect the sorption mechanism.

3.3. Thermodynamic parameters

The thermodynamic parameters for strontium adsorption onto ZrO₂ and ZrO₂-TiO₂ were given in Tables 8 and 9, respectively. Positive ΔH° values calculated for both sorbent indicate that the sorption processes are endothermic in nature.

Table 8

Thermodynamic parameters for Sr adsorption on ZrO₂ microspheres.

ΔH° (kJ/mol)	ΔS° (kJ mol ⁻¹ K ⁻¹)	ΔG° (kJ/mol)		
		293 K	303 K	313 K
33.86	0.14	-8.70	-10.15	-11.61

Table 9
Thermodynamic parameters for Sr adsorption on ZrO_2 - TiO_2 .

ΔH° (kJ/mol)	ΔS° (kJ mol ⁻¹ K ⁻¹)	ΔG° (kJ/mol)		
		293 K	303 K	313 K
58.51	0.23	-10.18	-12.52	-14.87

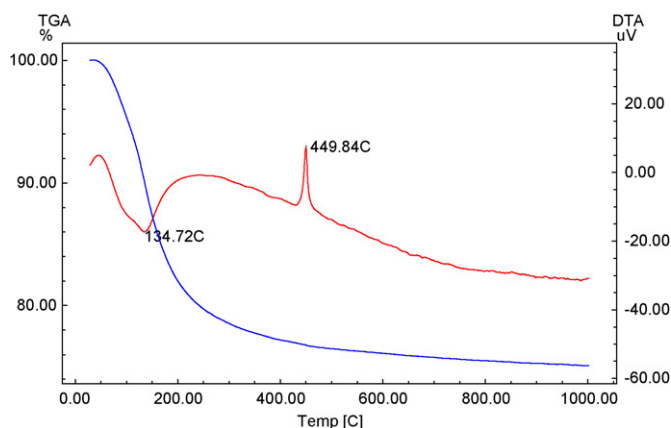


Fig. 7. DTA/TGA curves of ZrO_2 .

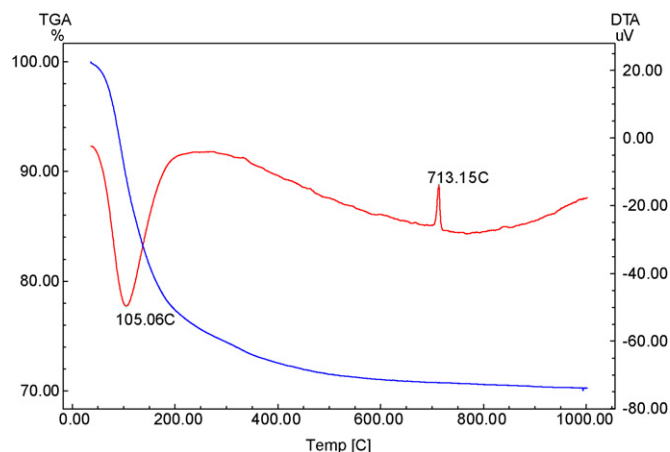


Fig. 8. DTA/TGA curves of ZrO_2 - TiO_2 .

ΔG° values were also given in Tables 8 and 9. Decrease in the values of ΔG° with increasing temperature indicates that the sorption processes are spontaneous and preferentially driven towards the products for both sorbent. In addition, the values of ΔS° were found to be positive due to the exchange of metal ions with more mobile ions present on the exchanger which would cause an increase in the entropy during the adsorption process.

3.4. Identification and characterization

ZrO_2 and ZrO_2 - TiO_2 spheres obtained by the sol-gel process were dried in an oven at 333 K for 24 h. Figs. 7 and 8 show the DTA/TGA curves of ZrO_2 and ZrO_2 - TiO_2 spheres, respectively.

DTA analysis of the pure ZrO_2 sample shows an exothermic peak due to amorphous-to-crystalline phase transition at 723 K. This

Table 10
BET surface area, mean pore diameter and total pore volume values of thermally treated ZrO_2 and ZrO_2 - TiO_2 microspheres.

Oxides	80 °C			600 °C			750 °C			900 °C		
	BET surface area (m ² /g)	Mean pore diameter (nm)	Total pore volume (cm ³ /g)	BET surface area (m ² /g)	Mean pore diameter (nm)	Total pore volume (cm ³ /g)	BET surface area (m ² /g)	Mean pore diameter (nm)	Total pore volume (cm ³ /g)	BET surface area (m ² /g)	Mean pore diameter (nm)	Total pore volume (cm ³ /g)
ZrO_2	157.2	2.23	0.0803	27.2	10.26	0.0693	10.3	19.04	0.0482	0.87	40.35	0.0145
ZrO_2 - TiO_2	489.7	2.48	0.3769	218.6	4.20	0.2650	42.5	19.6	0.2004	14.4	56.8	0.1987

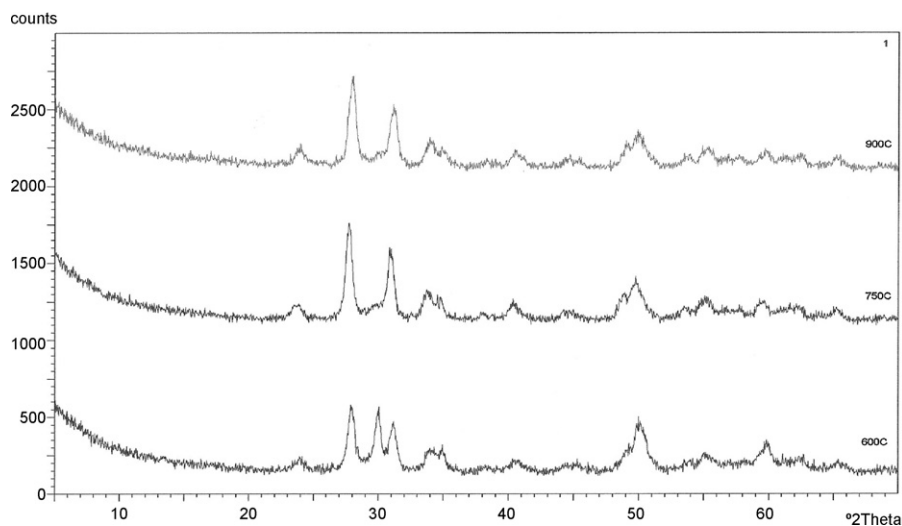


Fig. 9. XRD patterns of ZrO_2 after calcination at 600 °C, 750 °C and 900 °C.

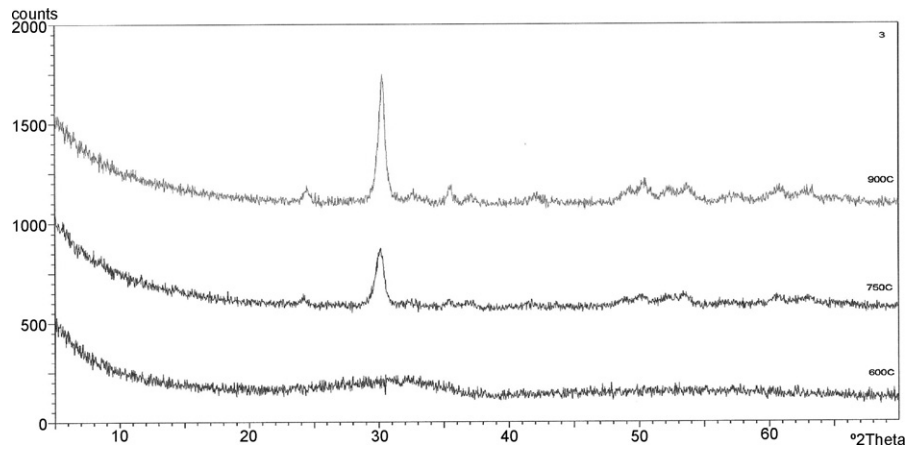


Fig. 10. XRD patterns of ZrO_2-TiO_2 after calcination at 600 °C, 750 °C and 900 °C.

exothermic peak appears at 986 K for ZrO_2-TiO_2 . The endothermic peaks at 681 K and at 651 K for ZrO_2 and ZrO_2-TiO_2 , respectively signify the loss of water. From the TGA, these values were calculated as $2H_2O$ for ZrO_2 and $4H_2O$ for ZrO_2-TiO_2 .

ZrO_2 and ZrO_2-TiO_2 microspheres were heated at 873 K, 1023 K and 1173 K. Then BET specific surface area, porosity, XRD and SEM analyses were realized for each adsorbent fraction.

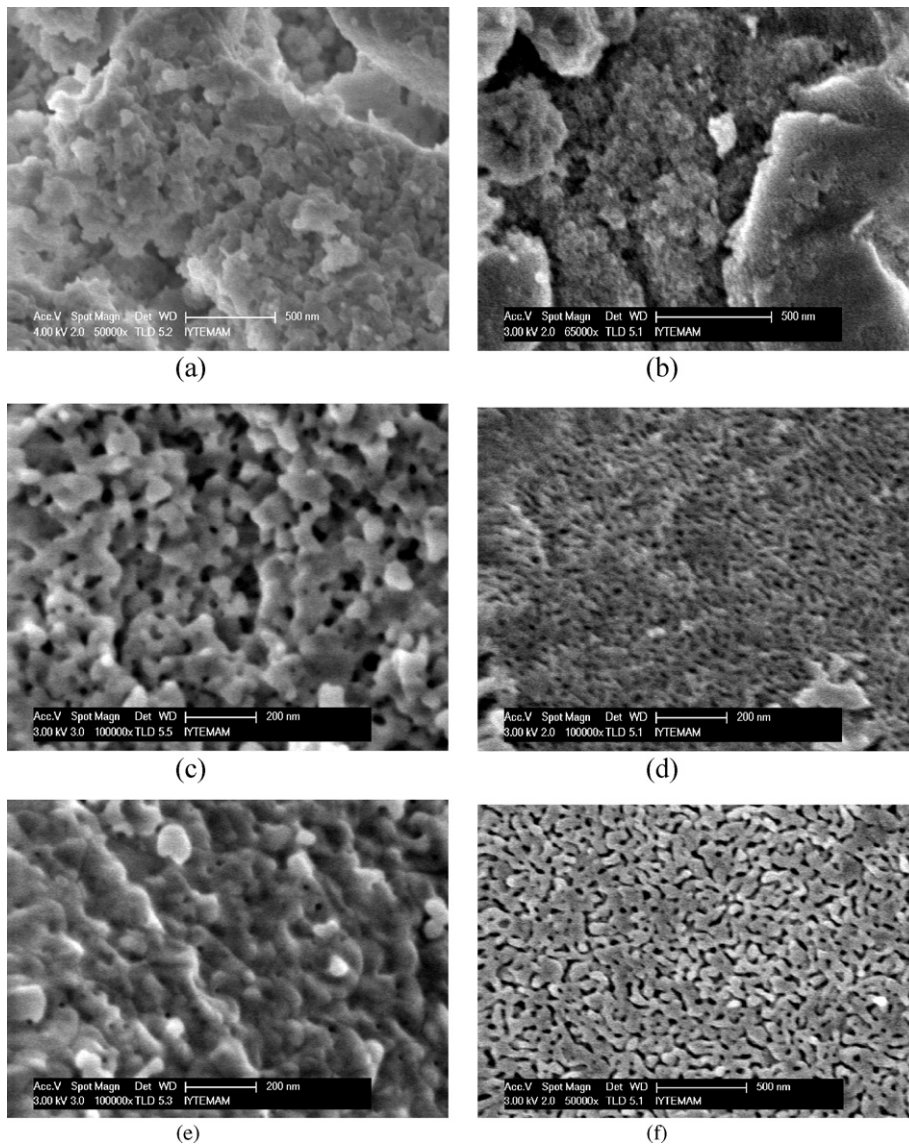


Fig. 11. SEM images of samples: (a) ZrO_2 (600 °C); (b) ZrO_2-TiO_2 (600 °C); (c) ZrO_2 (750 °C); (d) ZrO_2-TiO_2 (750 °C); (e) ZrO_2 (900 °C); (f) ZrO_2-TiO_2 (900 °C).

4. Surface areas

The trend of the surface areas, mean pore diameters and total pore volumes measured for the samples of ZrO_2 and ZrO_2 - TiO_2 after calcination at different temperatures is shown in Table 10. It is clearly seen that the surface area of the mixed oxide is significantly higher than that of the pure ZrO_2 . The surface area of the mixed oxide is more than triple with respect to the pure oxide. This trend can be attributed to the lower degree of crystallisation of the mixed oxides with respect to the pure oxides. The surface areas and total pore volumes decrease with increasing temperature, in contrast the mean pore diameters increase with increasing temperature for both oxides.

Fig. 9 shows XRD patterns of ZrO_2 after calcination at 873 K, 1023 K and 1173 K. From the XRD data at 873 K, a mixture of monoclinic (ICDD no. 37-1484) and tetragonal (ICDD no. 42-1164) phases of zirconium dioxide was observed. At 1023 K and 1173 K, the crystallization was monoclinic. From Fig. 7 the exothermic DTA peak at 723 K corresponds to the crystallization of ZrO_2 . Below this temperature ZrO_2 possess an amorphous structure.

Fig. 10 shows XRD patterns of ZrO_2 - TiO_2 after calcination at 873 K, 1023 K and 1173 K. From the XRD data, it has been shown that the equimolar addition of titania to the pure zirconia modifies progressively the crystallization behaviour of zirconia. In particular the main effect of titania addition is the inhibition of the crystallization of ZrO_2 phases. On the other hand, a similar progressive hindering of the crystallization of the metastable TiO_2 phase anatase by ZrO_2 is found. From the DTA/TGA data in Fig. 8, the sample looks completely amorphous until 986 K. At 1023 K, a mixture of orthorhombic and cubic phases of zirconium dioxide was determined (ICDD nos. 79-1796 and 49-1642). XRD pattern taken after calcination of mixed oxide at 1173 K shows the crystallization of orthorhombic $ZrTiO_4$ (ICDD no. 34-0415). DTA/TGA and XRD data are in good agreement to clarify the crystallization behaviours of mixed oxide.

Fig. 11 comprises SEM images of ZrO_2 and ZrO_2 - TiO_2 microspheres after calcinations at different temperatures. Images clearly demonstrate the difference of pure and mixed oxide surface morphologies and the variation of surface morphology with heat treatment.

5. Conclusion

Microspheres of ZrO_2 and ZrO_2 - TiO_2 with a good spherical character were prepared by the sol-gel process. As a result of our experimental conditions it was observed that the pure and the mixed oxide spheres were both chemically and mechanically stable in a wide pH range (pH 2–10) and under vigorous shaking conditions. The adsorption of strontium is affected by the surface properties of adsorbents. By the addition of equimolar amount of TiO_2 to ZrO_2 it is possible to prepare a binary oxide with considerably higher specific surface area, exhibiting better adsorption properties than the pure ZrO_2 . The overall results indicate that ZrO_2 - TiO_2 mixed gel spheres exhibit better sorption properties than the pure ZrO_2 spheres for efficient removal of Sr(II) from aqueous and radioactive waste solutions. Besides its spherical shape

allowing to be used in column separation processes, its production simplicity, chemical and mechanical stabilities can be considered as important advantages on the other sorbents.

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