Use of magnesium silicate functionalized with thiourea for Sr(II) and Tl(I) removal from polluted water

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Abstract

An appropriate management of high level radioactive waste and removal of radiotoxic elements is important for the development and safety of the nuclear energy system. Sr(II) is a metal ion present in high level radioactive waste and has to be removed for a better disposal in geological formation. Another toxic metal is Tl(I). It is used in numerous industries and its toxicity for the human body is higher than conventional heavy metals. This study investigates the adsorption process of Sr(II) and Tl(I) from aqueous solutions on an adsorbent material. The adsorption proprieties of the solid support were improved through functionalization, using the dry method. The novelty of this material is that the solid support – magnesium silicate – is functionalized with a new extractant, thiourea dissolved in ethyl alcohol. The obtained material was the subject of an energy dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM). In order to establish the adsorption capacities of the adsorbent material, it was used in the removal process metallic ions. Results show a good performance for the Tl(I) ion, with an adsorption capacity of 4.2 mg/g. Kinetically, the adsorption process of these metal ions have the best fit for the pseudo-second-order kinetic model. The removal process through adsorption is endothermic and spontaneous due to the thermodynamic studies. Equilibrium studies were also carried out for the Langmuir, Freundlich and Sips models. The new functionalized material proves to be favourable as an adsorbent material in the removal of Sr(II), Tl(I) from polluted water.
Keywords: thiourea, magnesium silicate, strontium, thallium, water pollution.

1   Introduction

Radioactive materials are widely used in medicine, industry, agriculture and scientific research, presenting a major impact on human health and the environment [1, 2]. It is known that problems can appear without explanation just by the contact of radioactive elements with skin and hair [1]. The most common radioactive elements are ^{201}Tl and ^{90}Sr, which affected especially the East Japan Earthquake and the East region of Romania [2, 3]. In the case of nuclear accidents, contamination of crops, soil, air, surface waters [4], groundwater, drinking water [2], and wastewater from industrial areas appear [1, 5]. The best available technologies (BATs) and the small system compliance technologies (SSCTs) by US EPA for radionuclides removal from surface water and groundwater include: liquid-liquid extraction [5–7], separation by extraction with ether crown [5, 8, 9], ion exchange, reverse osmosis, coagulation, sedimentation, sand filtration, co-precipitation, electrolysis [2], as well as adsorption [10]. The following materials with adsorbent properties are known in literature: ion exchangers [11], polymers [12], complexing agents such as EDTA [1], activated carbon [2], sensors and catalysts [11], and inorganic supports such as silica [5] and magnesium silicate [13]. These materials used as adsorbents presents a number of disadvantages, such as low mechanical strength, low adsorption capacity and poor resistance to acid and irradiation [11]. Recently, the improvement of such materials through selective functionalization with different groups has attracted more attention [14–16]. The present work was intended to remove strontium and thallium from aqueous solutions by adsorption.

The goal of this paper is the functionalization of magnesium silicate with nitrogen and sulphur groups using thiourea as an extractant, to eliminate strontium and thallium from aqueous solutions by adsorption. Thiourea is mentioned in literature as ligand and it is used in the extraction of metals [17].

2   Material and methods

2.1 Functionalization and characterisation of the solid support

Magnesium silicate was used as a solid support and was functionalized with thiourea. The functionalization was made using the dry method. 5 g of magnesium silicate (Merck, Germany, 0.150–0.250 mm) were mixed with 0.1 g thiourea (Fulk AG, Switzerland) dissolved in 25 mL ethyl alcohol 99.2% (produced by SC PAM Corporation SRL) and left in contact for 24 hours. After that, the samples were dried at 323 K for 24 hours. The obtained adsorbent material was characterized by energy dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM), using an apparatus Quanta FEG 250.

2.2 Adsorption experiments on the functionalized material

In the adsorption experiments, the influence of some parameters (contact time, temperature, initial concentration of metal solution) on the adsorption of Sr(II) and

Tl(I) on the functionalized material was analysed. A 1000 mg/L stock solution of every metal was used to produce solutions of different concentration by appropriate dilution. To investigate the influence of the contact time and the temperature on the adsorption process, 0.1 g of functionalized magnesium silicate was mixed with 25 mL metal solution of 10 mg/L concentration for 30, 60, 90 and 120 minutes, at three different temperatures (298 K, 308 K, and 318 K). To study the influence of the initial concentration on the adsorption capacity, 0.1 g of functionalized material was mixed with 25 mL metal solution with the concentrations 10, 50, 100, 150, and 200 mg/L, for one hour. The samples were mixed in a Julabo SW23 mechanical shaker bath at 200 rot/min. All samples were filtered and the metal concentration was analysed by the inductively coupled plasma mass spectrometer ICP-MS Bruker aurora M90.

3 Results and discussions

3.1 Characterisation of the functionalized material

In other to verify if the functionalization of the solid support, magnesium silicate, with the extractant, thiourea, was successful, the obtained adsorbent material analysed by energy dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM) (fig. 1).
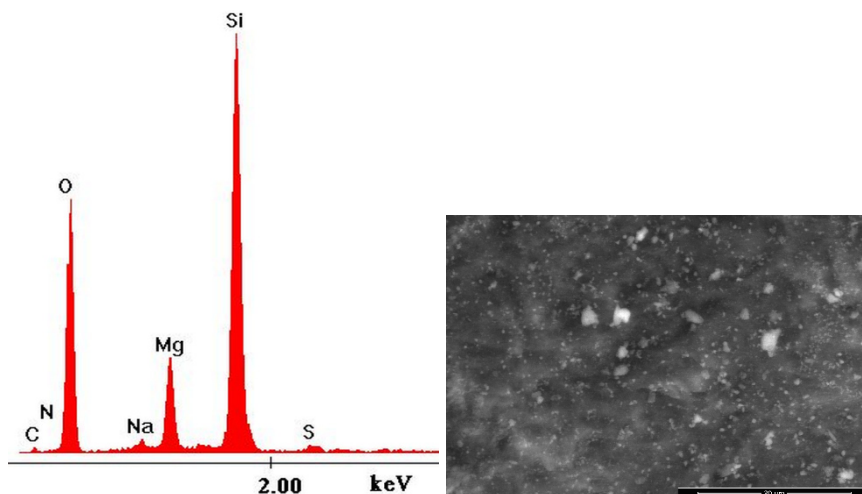

Figure 1:   Characterisation of the functionalized material (a) EDX spectrum (b) SEM image.

The EDX spectrum of the functionalized magnesium silicate reveals peaks such as Mg, O, Si, that are characteristic for the solid support, but also peaks such as S, N that are characteristic for thiourea, used as an extractant. The SEM image reveals white spots on the surface of the solid support that can be associated as being the extractant.

3.2 Metal adsorption

3.2.1 Influence of the initial concentration

Fig. 2 presents the adsorption isotherm of the functionalized material. It describes the amount of metal ions absorbed on the surface of the material versus the amount in the liquid phase at equilibrium. Increasing the initial concentration of the metal solution, the adsorption capacity increases until reaching a constant value. The equilibrium adsorption capacity is 2.10 mg/g for Sr(II) and 4.30 mg/g for Tl(I) at an equilibrium concentration of 100 mg/L.
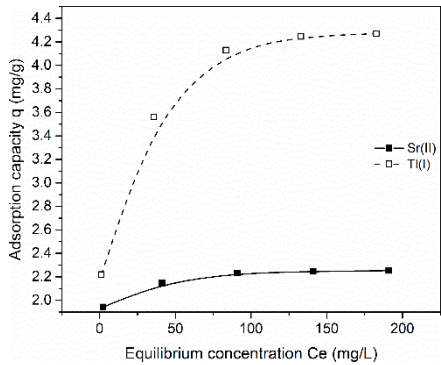

Figure 2:   Adsorption isotherm of the functionalized material.

3.2.2 Kinetic studies

The adsorption process was carried out at different contact times and at different temperatures, in order to determine the kinetic model and the activation energy. Fig. 3 shows the influence of the contact time on the adsorption of the studied metal ions. The adsorption capacity increases with the increase of contact time.
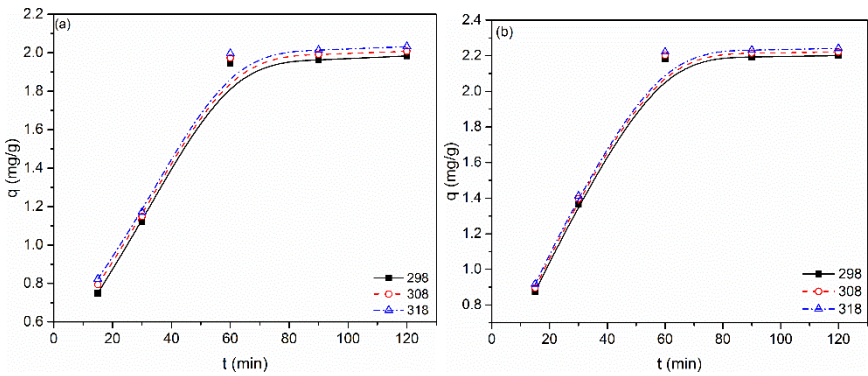

Figure 3:   Influence of the contact time on the adsorption of (a) Sr(II) and (b) Tl(I) on the functionalized material.

For both metal ions, there is a major increase of the adsorption capacity in the first 60 minutes, after which the process shows no significant changes.

Therefore, the pseudo-first order model by Lagergren [18] and the pseudo-second order model by Ho and McKay [19], were used to fit the experimental data. By plotting $\ln(q_e-q_t)$ against t, the rate constant k_1 and the correlation coefficient can be calculated for the pseudo-first order, as well as the rate constant k_2 and the correlation coefficient for the pseudo-second order, by plotting t/q_t against t. The plots of the two kinetic models used are shown in figs 4 and 5, respectively.
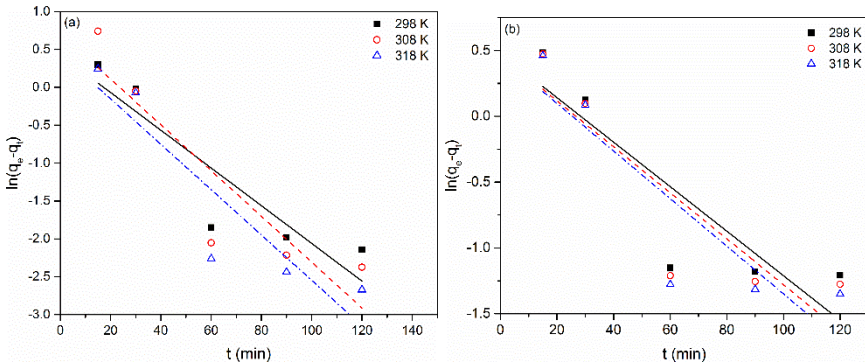

Figure 4: Pseudo-first order kinetic plot for the adsorption of (a) Sr(II) and (b) Tl(I).
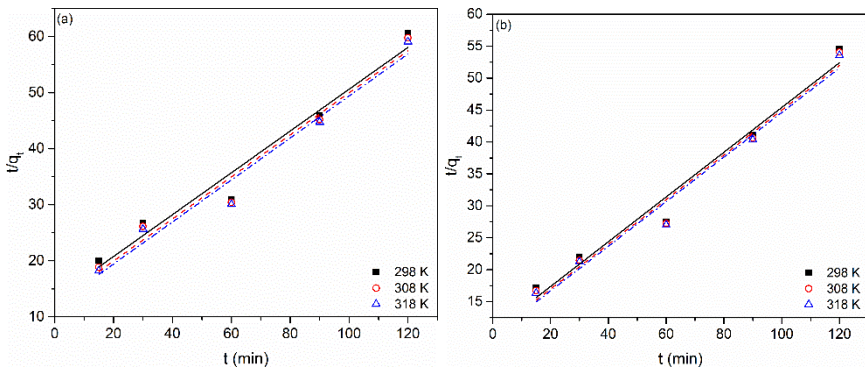

Figure 5: Pseudo-second order kinetic plot for the adsorption of (a) Sr(II) and (b) Tl(I).

The kinetic parameters obtained for the adsorption of Sr(II), Tl(I) on magnesium silicate functionalized with thiourea are shown in table 1.

According to the obtained kinetic parameters, the adsorption of the studied metal ions Sr(II), Tl(I) on the functionalized material is best fitted to the pseudo-second order kinetic model. Comparing the obtained correlation coefficients for both kinetic models, the difference between the pseudo-first order model

Table 1:   Kinetic parameters of the adsorption on the functionalized material.

Pseudo-first order					
Metal	T (K)	$q_{e,exp}$ (mg/g)	k_1 (min^{-1})	$q_{e,calc}$ (mg/g)	R^2
Sr(II)	298	1.94	$2.49 \cdot 10^{-2}$	1.535	0.7668
	308	1.97	$3.02 \cdot 10^{-2}$	2.041	0.7577
	318	1.99	$2.99 \cdot 10^{-2}$	1.558	0.7806
Tl(I)	298	2.18	$1.69 \cdot 10^{-2}$	1.615	0.7021
	308	2.20	$1.74 \cdot 10^{-2}$	1.593	0.7050
	318	2.22	$1.80 \cdot 10^{-2}$	1.582	0.7077
Pseudo-second order					
Metal	T (K)	$q_{e,exp}$ (mg/g)	k_2 (g/mg·min)	$q_{e,calc}$ (mg/g)	R^2
Sr	298	1.94	$1.04 \cdot 10^{-2}$	2.680	0.9543
	308	1.97	$1.12 \cdot 10^{-2}$	2.665	0.9583
	318	1.99	$1.17 \cdot 10^{-2}$	2.669	0.9610
Tl	298	2.18	$1.18 \cdot 10^{-2}$	2.855	0.9655
	308	2.20	$1.22 \cdot 10^{-2}$	2.856	0.9681
	318	2.22	$1.25 \cdot 10^{-2}$	2.866	0.9698

($R^2 < 0.7806$) and the pseudo-second order model ($R^2 > 0.9543$) is noticeable. The second-order absorption rate increases with the increase of the temperature, meaning that the adsorption process on the functionalized material is endothermic. The activation energy of the adsorption process was calculated using the Arrhenius equation (eqn (1)) and the rate constant k_2 from the pseudo-second order kinetic model.

$$\ln k_2 = \ln A - \frac{E}{RT} \qquad (1)$$

where k_2 is the pseudo-second-order rate constant (g/(min·mg)), A is the Arrhenius constant, which is a temperature independent factor (min·g/mg), E is the activation energy (kJ/mol) and T is the absolute temperature (K).

The activation energy was calculated from the slope of the plot of $\ln k_2$ against 1/T (presented in fig. 6).
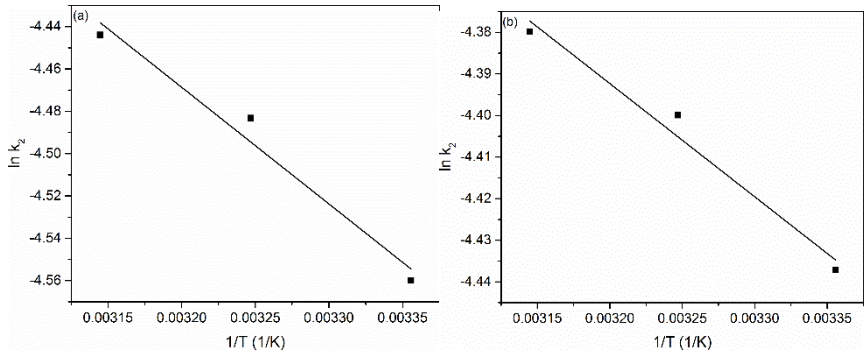

Figure 6:   Arrhenius plot for the adsorption of (a) Sr(II) and (b) Tl(I).

For the two studied metal ions, the obtained activation energy registers positive values, indicating that the adsorption process is endothermic. The values of the activation energy for the studied metal ions are lover than 8.4 kJ/mol (4.58 kJ/mol Sr(II), 2.26 kJ/mol Tl(I)), suggesting that the adsorption process of these metal ions on the functionalized material is physiosorption.

3.2.3 Thermodynamic studies

Thermodynamic studies for the adsorption process of Sr(II) and Tl(I) on the functionalized magnesium silicate were made.

The equilibrium constant K_d as the ratio between the equilibrium adsorption capacity q_e (mg/g) and the equilibrium concentration C_e (mg/L). The standard entropy ΔS^0 and the standard enthalpy ΔH^0 can be calculated from the slope of the plot of lnK_d versus $1/T$ (fig. 7). These values are summarized in table 2.
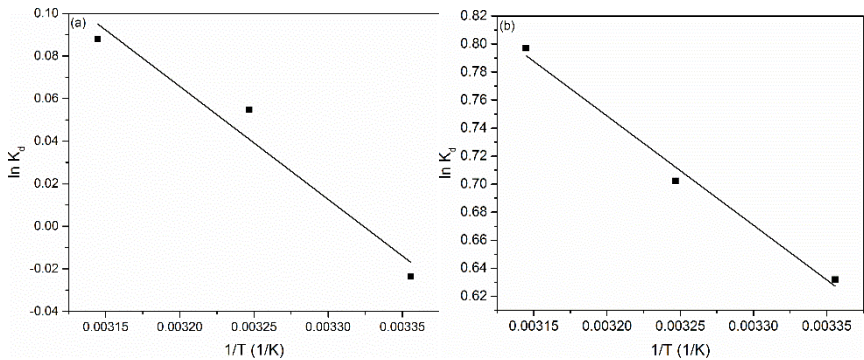

Figure 7: lnK_d vs. $1/T$ for the adsorption of (a) Sr(II) and (b) Tl(I) on the functionalized material.

Table 2:   Thermodynamic parameters of the adsorption of the studied metal ions on the functionalized solid support.

Metal	ΔH^0 (kJ/mol)	ΔS^0 (J/mol·K)	ΔG^0 (kJ/mol)			R^2
			298 K	308 K	318 K	
Sr(II)	4.41	0.014	0.041	-0.10	-0.25	0.9121
Tl(I)	6.48	0.026	-1.55	-1.82	-2.09	0.9792

The relationship between the thermodynamic parameters are given by the Gibbs-Helmholtz equation [20], being able to calculate the Gibbs free energy ΔG^0. The values of the Gibbs free energy for the ions Sr(II) and Tl(I) become more negative with the increasing of the temperature, suggesting that the adsorption on the functionalized material is spontaneous and favoured at higher temperature. The positive values of ΔH^0 indicate that the adsorption process on magnesium silicate

functionalized with thiourea is endothermic. The ΔH^0 values are smaller than 8 kJ/mol, proposing a physiosorption. The positive value of ΔS^0 shows an increased disorder in the system, while a negative value shows a decreased disorder in the system

3.2.4 Equilibrium studies

The experimental data of the adsorption process of the metal ions on the magnesium silicate functionalized with thiourea were fitted to the Langmuir [21], Freundlich [22] and Sips [23] non-linear isotherm models. The Langmuir model implies a monolayer adsorption onto a homogeneous surface; all sites are equivalent and the ability of a molecule to adsorb at a given site independent of the occupation of neighbouring sites [21]. The Freundlich model implies that the absorbent has a heterogeneous surface and a possible multilayer adsorption. All isotherm parameters are summarized in table 3. Fig. 8 shows the adsorption isotherm of the metal ions Sr(II), Tl(I), onto the functionalized material, magnesium silicate with thiourea. According to the obtained correlation coefficient form the Langmuir, Freundlich and Sips isotherm models, the experimental data for all two studied metal ions have the best fit to the Sips isotherm model ($R^2 > 0.9829$). The Sips isotherm model is derived from the Freundlich and Langmuir model. It takes proprieties from both isotherm models, depending on the interval of the adsorbate concentration. The Sips isotherm model can take Langmuir characteristics at high adsorbent concentrations, and Freundlich characteristics at low adsorbent concentrations.
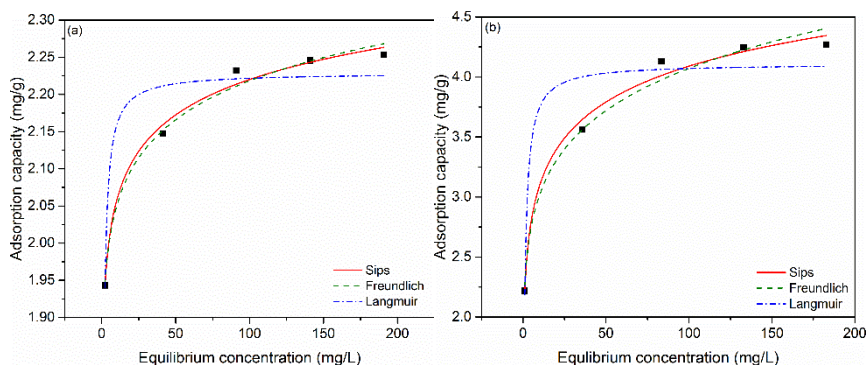

Figure 8: Adsorption isotherm of (a) Sr(II) and (b) Tl(I) on the functionalized support.

The parameters $1/n_F$ and $1/n_S$ are subunitary, indicating a favourable adsorption of the studied metal ions on the functionalized material and a convex isotherm. The values of $1/n_F$ (0.03449 and 0.13033) and the values of $1/n_S$ (0.10609 and 0.24019) signify that the heterogeneity of the adsorbent material is slightly raised.

Table 3:   Parameters of Langmuir, Freundlich and Sips isotherm of the adsorption of the metal ions.

Langmuir			
Metal	**$q_{m,exp}$ (mg/g)**	**K_L (L/mg)**	**q_L (mg/g)**	**R^2**
Sr(II)	1.94	3.02065	2.22908	0.89215
Tl(I)	2.18	1.03143	4.10993	0.88519
Sips			
	K_S	**q_S (mg/g)**	**$1/n_S$**	**R^2**
Sr(II)	1.52042	3.11592	0.10609	0.9829
Tl(I)	0.42923	7.24233	0.24019	0.9818
Freundlich			
	K_F (mg/g)	**$1/n_F$**	**R^2**
Sr(II)	1.89256	0.03449	0.98654
Tl(I)	2.23409	0.13033	0.98078

4   Conclusion

In this study, a new adsorbent material by functionalization of magnesium silicate with thiourea was developed for the adsorption of Sr(II) and Tl(I) ions from polluted waters. The obtained material was characterized by energy dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM). The influence of contact time, temperature and initial concentration were studied. The equilibrium adsorption capacity is 2.10 mg/g for Sr(II) and 4.30 mg/g for Tl(I) at an equilibrium concentration of 100 mg/L. Between the pseudo-first order and pseudo-second order kinetic models, the experimental data had the best fit to the pseudo-second order. From the thermodynamic studies, the adsorption process of Sr(II) and Tl(I) on the magnesium silicate functionalized with thiourea is endothermic and spontaneous. The experimental data were fitted to the non-linear isotherm models Langmuir, Freundlich and Sips. According to the regression coefficients, the best fit for the adsorption process was the Sips model. Therefore, the adsorbent material, magnesium silicate functionalized with thiourea, can be used for Sr(II) and Tl(I) the adsorption from polluted water.

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