Novel Adsorbent Used for Cesium Removal from Aqueous Solutions

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Cesium (Cs) removal from wastewater becomes an emerging issue after the Fukushima Daiichi Nuclear Power Plant disaster. Cs(I) is an metal ion present in high level radioactive waste and has to be removed for a better disposal in geological formation. The present study investigates the adsorption process of Cs(I) from aqueous solutions on an novel adsorbent material. The novelty of this material is that the solid support, magnesium silicate, is doped with a new extractant, thiourea dissolved in ethyl alcohol. In order to establish the adsorption capacities of the adsorbent material, it was used in the removal process of metal ions. Kinetically, the adsorption process of this metal ion has 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 model. The new doped material proves to be favourable as adsorbent material in the removal of Cs(I) from polluted water.

Keywords: cesium, novel absorbent, adsorption, magnesium silicate, thiourea

After the sever accident at Fukushima, Japan in 2011 where a large volume of radioactive wastewater was discharged, the treatment of wastewater containing radionuclides has become very important [1-3]. Radioactive Cs (^{137}Cs) is special concern due to its high radioactivity and long half-life (~30 years), which is much longer than another isotopes [4-6]. Radioactive materials have major impacts on human health and environment because of their use in medicine, agriculture, industry and scientific research [4, 7]. Methods to remove radionuclides from surface water and groundwater included in the Best Available Technologies (BATs) and in the Small System Compliance Technologies (SSCTs) by US EPA are: coagulation, sand filtration, sedimentation, co-precipitation, ion exchange, liquid-liquid extraction [8], reverse osmosis, separation by extraction with ether crown [9], electrolysis [6], as well as adsorption [8]. Researches on getting new material absorbent have focused on doping an inorganic support, magnesium silicate, with thiourea an environmental friendly and accessible extractant. As materials with adsorbent properties, in literature, are known ion exchanger [10], polymers [11], complexing agents such as EDTA [1], activated carbon [2], sensors and catalysts [11], and inorganic supports such as silica [5] and magnesium silicate [12]. Low mechanical strength, poor resistance to acid and irradiation and low adsorption capacity are the disadvantages that materials used as adsorbents can present [10]. The improvement of the materials through selective doping with different groups has attracted more attention [13-15].

The goal of this paper is the functionalization of magnesium silicate with nitrogen and sulfur groups using as extractant thiourea in order to eliminate cesium from aqueous solutions by adsorption. Thiourea is mentioned in literature as ligand used in the extraction of metals [16].

Experimental part

Materials and methods

For obtaining the adsorbent material 0.1 g thiourea (Fulk AG, Switzerland) was dissolved in 25 mL ethyl alcohol 99.2% (produced by SC PAM Corporation SRL) and put in contact with 5 g magnesium silicate (Merck, Germany, 0.150-0.250 mm) for 24 h. The samples were then dried for another 24 h at 323K in a drying stove.

The obtained material was then tested in the adsorption of Cs(I) from aqueous solutions.

The optimum parameters of the adsorption of Cs(I) were established. For the contact time, 25 mL of a 10 mg/L Cs(I) solution were mixed with 0.1 g doped material for 30, 60, 90, 120 min . The temperature was studied at 298 K, 308 K, and 318 K by mixing 0.1 g doped material with 25 mL Cs(I) solution of the concentration 10 mg/L. After that, the initial concentration was varied. 25 mL of Cs(I) solution with the concentrations 10, 50, 100, 150, and 200 mg/L were mixed for 60 min at 298 K. All samples were mixed in a Julabo SW23 mechanical shaker bath at 200 rot/min, filtrated and analysed by inductively coupled plasma mass spectrometer ICP-MS Bruker aurora M90. The metal solutions were prepared by proper dilution form a 1000 mg/L stock solution.

Results and discussions

Adsorption studies

Influence of the initial concentration

The initial concentration was varied in order to establish the equilibrium capacity and the equilibrium concentration. Figure 1 show the adsorption isotherm of the adsorption process of Cs(I) onto magnesium silicate doped with thiourea. The adsorption capacity increases with increase of the initial concentration. The adsorption capacity reached a constant value of about 2.10 mg/L Cs(I) matching an equilibrium concentration of 100 mg/L.

Kinetic studies

The experimental data were shaped by the first-pseudo order and the second-pseudo order models. Figure 2 presents the variation of the adsorption capacity in time for the removal of Cs(I), the adsorption capacity increased for 60 min when it reached the equilibrium.

The first-pseudo order model and the second-pseudo order model [17] are given in equations (1) and (2).

$$\ln(q_e - q_t) = \ln q_t - k_1 t \qquad (1)$$

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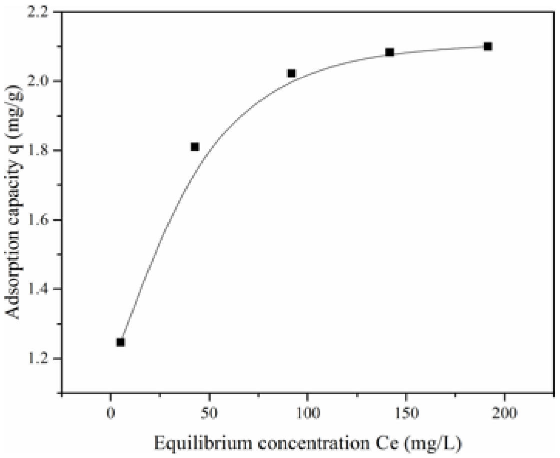

Fig.1. Adsorption isotherm

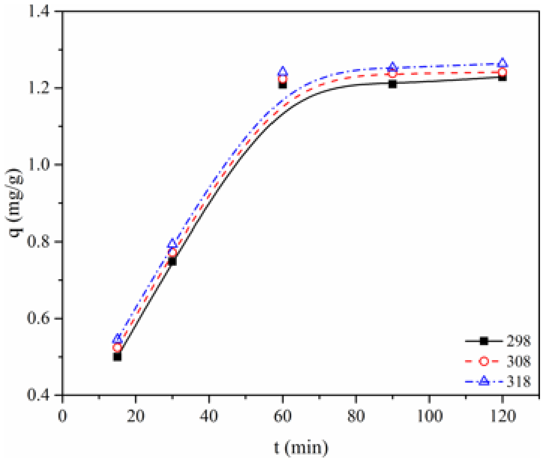

Fig. 2. Influence of the contact time on the adsorption of Cs(I)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

where q_e is the adsorption capacities at equilibrium (mg/g), q_t is the adsorption capacities at time t (mg/g), t is the contact time (min), k_1 is the pseudo-first-order adsorption rate constant (min^{-1}) and k_2 the pseudo-second-order adsorption rate constant (g/mg . min).

Figure 3 represents the pseudo-first order model. Using the slope and intercept of the linear representation of $\ln(q_e - q_t)$ against t, the rate constant k_1 and the regression coefficient R^2 can be calculated.

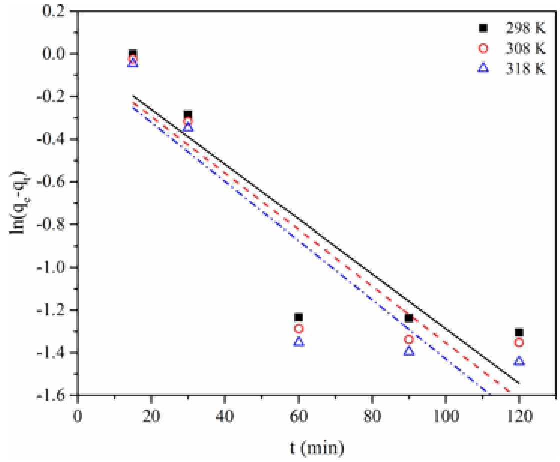

Fig. 3. Pseudo-first order kinetic plot

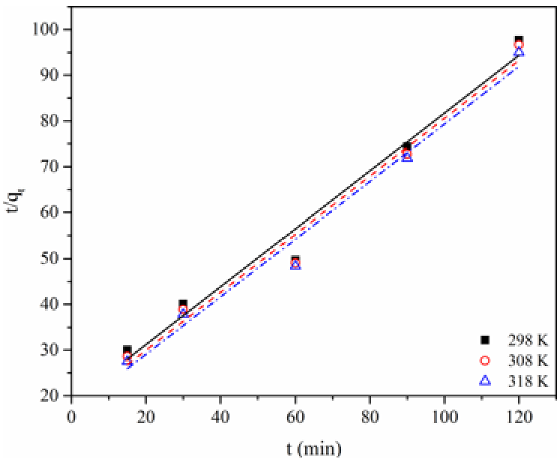

Fig. 4. Pseudo-second order kinetic plot

Figure 4 represents the pseudo-second order model. Representing linear t/q_t against t, the rate constant k_2 and the regression coefficient R^2 can be obtained.

Table 1 summarizes the kinetic parameters for the adsorption of Cs(I) on magnesium silicate doped with thiourea.

The pseudo-second order model fits better the experimental data. The correlation coefficient R^2 for the pseudo-second order model is closer to 1, suggesting a better linearization of the data. The increase of the adsorption rate with the temperature suggests a

Table 1
KINETIC PARAMETERS OF THE ADSORPTION PROCESS

Pseudo-first order				
T (K)	**$q_{e,exp}$ (mg/g)**	**k_1 (min^{-1})**	**$q_{e,calc}$ (mg/g)**	**R^2**
298	1.20	$1.28 \cdot 10^{-2}$	0.996	0.7191
308	1.22	$1.32 \cdot 10^{-2}$	0.970	0.7147
318	1.24	$1.38 \cdot 10^{-2}$	0.956	0.7277
Pseudo-second order				
T (K)	**$q_{e,exp}$ (mg/g)**	**k_2 (g/mg·min)**	**$q_{e,calc}$ (mg/g)**	**R^2**
298	1.20	$2.14 \cdot 10^{-2}$	1.583	0.9694
308	1.22	$2.31 \cdot 10^{-2}$	1.580	0.9721
318	1.24	$2.39 \cdot 10^{-2}$	1.590	0.9758

endothermic adsorption process. Forwards, using the rate constant k_2, the activation energy of the adsorption of Cs(I) was determine using the Arrhenius equation (3).

$$\ln k_2 = \ln A - \frac{E}{RT} \qquad (3)$$

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 slop of the plot $\ln k_2$ against 1/T presented in figure 5.

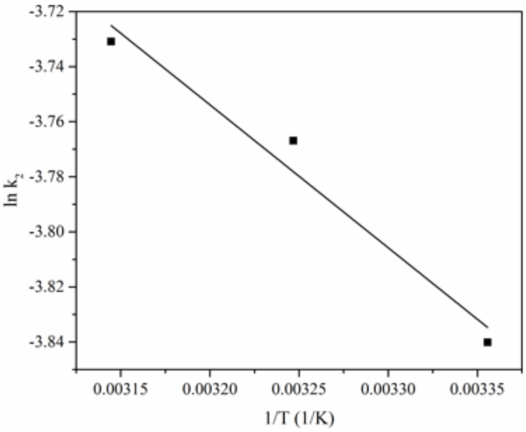

Fig. 5. Arrhenius plot for the adsorption process

The obtained activation energy value 4.31 kJ/mol is positive and smaller than 8.4 kJ/mol defining an endothermic process and a physic-sorption of Cs(I) onto magnesium silicate doped with thiourea.

Thermodynamic studies

For the adsorption of Cs(I) onto magnesium silicate doped with thiourea, thermodynamic studies were carried out. Equation (4) defines the equilibrium constant K_d:

$$K_d = \frac{q_e}{C_e} \qquad (4)$$

where: q_e is the equilibrium adsorption capacity (mg/g) and C_e the equilibrium concentration (mg/L).

The van't Hoff equation is defined by equation(5):

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (5)$$

where: R is the ideal gas constant and T is the absolute temperature (K).

Plotting $\ln K_d$ versus 1/T (fig. 6), the standard entropy ΔS^0 and the standard enthalpy ΔH^0 were calculated. The free Gibbs energy ΔG^0 was calculated using the Gibbs-Helmholtz equation (6). The thermodynamic parameters are given in table 2.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (6)$$

Due to the positive value of ΔH^0 and smaller than 8 kJ/mol, the adsorption process of Cs(I) onto magnesium silicate doped with thiourea is endothermic and a physic-sorption. The small negative value of ΔS^0 shows a small decreased disorder of the system.

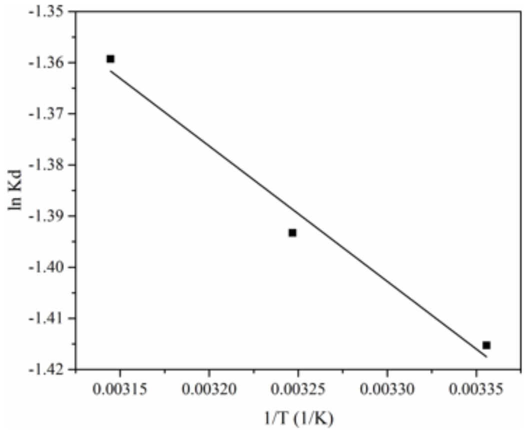

Fig. 6. $\ln K_d$ vs. 1/T for the adsorption of Cs(I) on the functionalized material

Equilibrium studies

The Langmuir, Freundlich and Sips non-linear isotherm models were used to fit the experimental data.

Equation (7) was used to calculate the adsorption capacity.

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (7)$$

where: C_0 is the initial concentration of metals (mg/L), C_e is the equilibrium concentration of metal in solution (mg/L), V is the volume of the metal solution (L) and m is the amount of functionalized support (g).

The Langmuir non-linear isotherm [18] is defined by equation 8:

$$q_e = \frac{q_L K_L C_e}{1 + K_L C_e} \qquad (8)$$

where: q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration of metal in solution (mg/L), K_L is the Langmuir constant and q_L is the Langmuir maximum adsorption capacity (mg/g).

The Freundlich non-linear isotherm [19] is defined by equation 9:

$$q_e = K_F C_e^{1/n_F} \qquad (9)$$

where: K_F and n_F are the characteristic constants.

The Sips non-linear isotherm [20] is defined by equation 10:

$$q_e = \frac{q_S K_S C_e^{1/n_S}}{1 + K_S C_e^{1/n_S}} \qquad (10)$$

where: q_S is the maximum adsorption capacity (mg/g), K_S is a constant and n_S is the heterogeneity factor.

The isotherm parameters are shown in table 3. Figure 7presents the adsorption isotherm of Cs(I) onto the doped material.

From the value of the correlation coefficient obtained for the Langmuir, Freundlich and Sips isotherm models, it can be concluded that the experimental data for Cs(I) adsorption best fit to the Sips isotherm model R^2=0.99287. The Sips model accrues from both Freundlich and Langmuir model. It has Freundlich characteristics at low

Table 2
THERMODYNAMIC PARAMETERS OF THE ADSORPTION PROCESS

ΔH^0 (kJ/mol)	ΔS^0 (J/mol·K)	ΔG^0 (kJ/mol)			R^2
		298 K	308 K	318 K	
2.20	-0.0044	3.51	3.55	3.60	0.9601

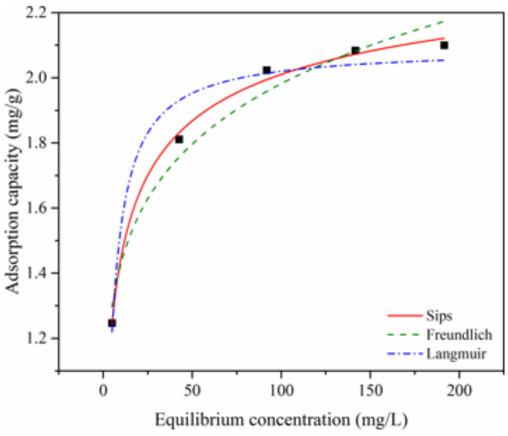

Fig. 7. Adsorption isotherm of Cs(I) on the doped support

Table 3

PARAMETERS OF LANGMUIR, FREUNDLICH AND SIPS ISOTHERM OF THE ADSORPTION OF THE METAL IONS

Langmuir			
$q_{m,exp}$ (mg/g)	**K_L (L/mg)**	**q_L (mg/g)**	**R^2**
1.20	0.27977	2.0922	0.95028
Sips			
K_S	**q_S (mg/g)**	**$1/n_S$**	**R^2**
0.46091	2.50404	0.47309	0.99287
Freundlich			
K_F (mg/g)	**$1/n_F$**	**R^2**	
1.03182	0.14173	0.96116	

adsorbent concentration and Langmuir characteristics at high adsorbent concentration. A monolayer adsorption onto a homogeneous surface is described by Langmuir model and adsorption onto heterogeneous adsorbent surface is described by Freundlich model. The small values of the parameters $1/n_F$ and $1/n_S$ describe a raised heterogeneity of the adsorbent material, a favorable Cs(I) adsorption and a convex isotherm.

Conclusions

A novel adsorbent material by doping magnesium silicate with thiourea for the adsorption of Cs(I) ions from polluted waters, was developed in this study. The influence of contact time, temperature and initial concentration were studied. The studied material has high selectivity for Cs(I) compared to other materials, achieving a adsorption capacity of 2.1 mg/g. Therefore, it can be used for removal Cs(I) ions from aqueous solutions.

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