

Removal of cesium and strontium using natural attapulgite: evaluation of adsorption isotherm and thermodynamic data

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Received: 24 June 2016 / Published online: 17 August 2016
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Abstract Natural attapulgite was used for removal of cesium and strontium ions from aqueous media by using a batch technique. It was found that cesium and strontium exhibits a physical adsorption mechanism onto the natural attapulgite with a good adsorption efficiency. The adsorption thermodynamic parameters of cesium and strontium referred to an exothermic nature for strontium ion and an endothermic nature for cesium ion and spontaneity of the adsorption process. Dubinin–Radushkevich isotherm model were the best fitted the adsorption equilibrium data of cesium and strontium ions. E_a values showed that the interaction among cesium and strontium ions and the adsorbent are a physical adsorption.

Keywords Adsorption · Cesium · Strontium · Aqueous media · Adsorption isotherms · Thermodynamic

Introduction

With the rapid development of nuclear energy, fission products especially ^{137}Cs , ^{90}Sr , and ^{239}Pu are generated from nuclear weapon testing and nuclear reactor technology, and enter the eco-system as a serious environmental issue. ^{137}Cs and ^{90}Sr have a long half-life ($t_{1/2}$) of about 30

and 29 years, respectively [1, 2]. Both radionuclides are considered as the most hazardous radioactive fission products because of their high radiotoxicities [3].

Furthermore, radioactive cesium as an excellent gamma source used for some applications such as surgical instrument disinfection, radiotherapy and food sterilization [4]. Radioactive strontium, very strong pure β -emitter, chemically resembles calcium and strongly deposits within the living organisms, mainly in the bones as a source of long term radiation [1, 3].

Therefore, the removal of cesium and strontium in even trace amount from aqueous media should be considered for protection of eco-system [5, 6]. Adsorption process is one of the most important separation processes for hazardous elements and prevents to use of the toxic and carcinogenic solvents during separation process [4, 5, 7, 8].

In the past decade, clay minerals have been investigated as an adsorbent to removal of water pollutants from aqueous media [9, 10]. In recent years, natural and man-made clay minerals become attractive materials again for water purification and radioactive waste management. Attapulgite is a widely used mineral clay composed of hydrated magnesium aluminium silicate mineral and has large specific surface area. Magnesium ions as an exchangeable cation in attapulgite can easily exchange with heavy metal ions and radionuclides [11–13].

The goal of this work was to investigate the adsorption behaviour of cesium and strontium onto natural attapulgite to understand the interaction between cesium/strontium and attapulgite to develop a treatment system for waste disposal areas. Therefore, adsorption data of cesium and strontium were fitted to adsorption isotherm models. The thermodynamic parameters such as free energy (ΔG°), enthalpy of adsorption (ΔH°) and entropy (ΔS°) were calculated separately for cesium and strontium.

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Experimental

Materials and methods

All the reagents used in this work were of analytical reagent grade and were obtained from chemical commercial suppliers.

Natural attapulgite obtained from Amcol Mineral and Mining Company was used as an adsorbent for adsorption experiments. Natural attapulgite was grinded and placed in a drying oven at 105 °C for 4 h. The mineral composition of dried attapulgite sample was analysed by X-ray fluorescence technique (XRF) (Panalytical Axios Advanced Model WDXRF) and shown in Table 1.

Cation exchange capacity (CEC) was determined using methylene blue method which is much faster and is still widely used method than others. Attapulgite suspension was prepared in ratio 6 % solid/liquid. 3 ml of attapulgite suspension was placed in a beaker and 10 mL of distilled water, 0.5 mL of 5 N H₂SO₄ and 15 mL of 3 % H₂O₂ was added and stirred for 10 min on magnetic stirrer. 0.01 M of methylene blue was added with titration method and the mixture was stirred. Cation exchange capacity (CEC) was calculated using the equation below:

$$\text{CEC} = \left(\frac{N \times V}{m} \right) \times 100 \quad (1)$$

where N is normality of methylene blue, V is methylene blue volume dissipated in titration (mL), m is amount of dried attapulgite (g). Cation exchange capacity (CEC) of the attapulgite was 7.032 meq per 100 g.

Swelling capacity of the attapulgite in water was determined using a rapid and simple method. 6 g of natural attapulgite was placed in a graduated cylinder and read the volume. 90 mL of the distilled water was added to the graduated cylinder and wait for 24 h. Last volume was recorded. Swelling capacity of the attapulgite was calculated using the equation in below:

$$\% \text{ Swelling capacity} = \frac{V_i - V}{V} \times 100 \quad (2)$$

where V is initial volume (mL), V_i is final volume of the suspension. Swelling capacity of the attapulgite was found as 11 %.

Adsorption–desorption experiments to calculate the specific surface area (BET) was carried out using a nitrogen gas sorption system at 10^{−4} Pa and 150 °C with Quantachrome Instruments Autosorb 1-Ultracycrometer 1000 equipments. Specific surface area of the natural attapulgite sample was estimated as 198 m² g^{−1} using multipoint BET methods. Density of the samples was determined as 2.55 g cm^{−3} by using Archimedes principle.

The adsorption of cesium and strontium on natural attapulgite were implemented by a batch technique. Cesium nitrate and strontium nitrate (Merck) was used for adsorption experiments. Solutions of cesium and strontium were prepared by dissolving known quantities of cesium nitrate and strontium nitrate in distilled water. For pH adjustment of cesium and strontium solutions, the buffers of pH 4 and 8 were used for the calibration of pH meter. Solutions of HNO₃ and Na₂CO₃–NaHCO₃ were added for pH adjustment.

0.1 g of the attapulgite was equilibrated with 25 mL of the cesium and strontium solutions of known concentration in a flask at ambient temperature in a thermostated shaker water bath for a known period of time. After equilibration, solid and solution phases were separated by filtration using Whatman No. 42 filter paper. The cesium and strontium concentrations in solution were determined by ICP-OES (Perkin Elmer). The results are the average of at least duplicate independent measurements. Adsorption efficiency (%) were calculated using mass balance equation as follows:

$$\text{Adsorption yield (\%)} = \left[\frac{C_i - C_f}{C_i} \right] \times 100 \quad (3)$$

where C_i is the concentration of the initial cesium or strontium solution (mg mL^{−1}), C_f is the concentration of the cesium or strontium solution in equilibrium (mg mL^{−1}).

Table 1 Mineral composition of natural attapulgite

Metal oxides	Chemical composition (%)	Metal oxides	Chemical composition (%)
SiO ₂	75.90	Cr ₂ O ₃	0.021
MgO	2.231	MnO	0.045
Al ₂ O ₃	12.24	Fe ₂ O ₃	3.990
Na ₂ O	0.440	ZrO ₂	0.018
P ₂ O ₅	0.042	BaO	0.055
SO ₃	0.361	Cl	0.024
CaO	1.960	K ₂ O	2.014
TiO ₂	0.566	Total	99.909

All experiments were carried out in duplicate. Uncertainties connected with results were different. Total uncertainties in all experimental parameters changed between 5 to 10 %. Total uncertainties never exceeded 10 % for each replicate.

Adsorption isotherms

Various adsorption isotherm models namely Langmuir, Freundlich and Dubinin–Radushkevich (D–R) were used to describe the interaction between concentration of cesium and strontium in solution and attapulgite at ambient temperature. Linear regression was used to determine the best-fitting isotherm amongst the adsorption isotherm models by judging the correlation coefficients.

Thermodynamic parameters

Thermodynamic parameters comprised Gibbs energy change (ΔG°), enthalpy change (ΔH°) and Entropy change (ΔS°) were estimated to exhibit types and mechanisms adsorption process. Thermodynamic parameters on the sorption of cesium and strontium ions onto natural attapulgite were calculated in different temperature from 293 to 333 K.

Kinetic models

Based on the effect of the contact time on cesium and strontium adsorption, different kinetic models including the pseudo first-order, the pseudo second-order and Elovich models were used to fit the adsorption data for accurately describing the adsorption process. Kinetic experiments at preset time intervals (from 5 to 360 min) were carried out at ambient temperature.

Results and discussion

Effect of parameters on Cs and Sr ions sorption onto attapulgite

To understand the cesium and strontium adsorption behaviours, the effectual parameters were investigated under varying conditions in initial activity concentration of cesium and strontium, pH of the adsorptive solution, contact time and temperature.

The effect of initial concentration from 5 to 60 $\mu\text{g mL}^{-1}$ on cesium and strontium adsorption was investigated at 30 °C. Figure 1 shows the effect of initial concentration of cesium and strontium ions on the adsorbent. As shown in Fig. 1, when the initial activity concentration was increased in range from 5 to 60 $\mu\text{g mL}^{-1}$, adsorption of

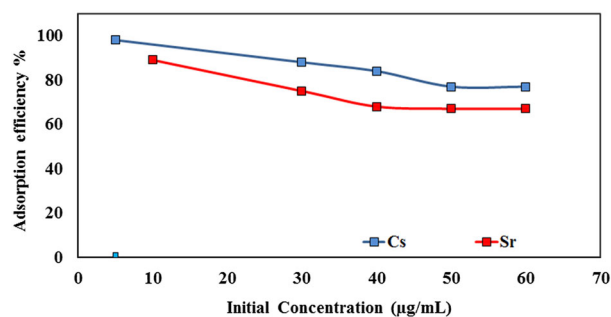


Fig. 1 Effect of initial concentration on cesium and strontium adsorption

cesium and strontium ions onto the natural attapulgite decreased. The adsorbent and ions attained equilibrium at 50 $\mu\text{g mL}^{-1}$ as 77 % for cesium and at 40 $\mu\text{g mL}^{-1}$ for strontium.

On the basis of these results, effect of pH on the cesium and strontium adsorption capacities was studied in the range from pH 2 to 10. Figure 2 shows the influence of pH on the cesium and strontium adsorption onto the attapulgite. With the increase of pH, the cesium and strontium adsorption efficiencies increased until pH 4. After pH 4, adsorption efficiencies of both ions remained steady as about 78 % for cesium ions and as about 67 % for strontium ions. When the pH was higher than 8, the adsorption efficiencies of cesium and strontium ions decreased with an increasing the pH. The results reveals that the adsorbent can be used to remove of both ions from waste solution in a wide range of pH from 4 to 8 with a quite high efficiency.

The effect of contact time on the adsorption of cesium and strontium ions onto natural attapulgite was investigated to understand the kinetic modelling of both ions for using to design of a low cost wastewater treatment system. The variation of adsorption efficiencies for both ions with contact time was given in Fig. 3. The adsorption efficiency of cesium and strontium ions onto natural attapulgite slightly increased with an increasing the contact time and reached an equilibrium within 15 min. for cesium ions and 30 min. for strontium ions.

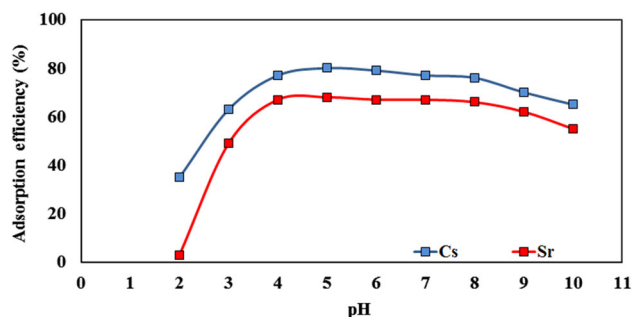


Fig. 2 Effect of pH on the cesium and strontium adsorption capacities

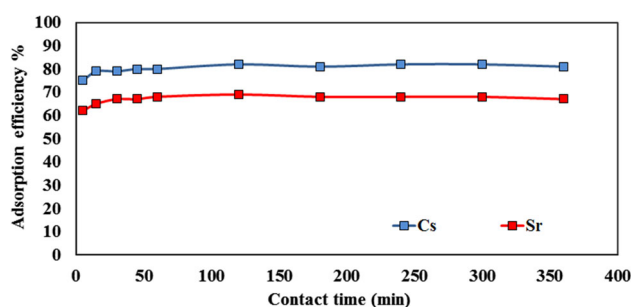


Fig. 3 Variation of adsorption efficiency of cesium and strontium ions with contact time

In order to determine thermodynamic parameters of cesium and strontium adsorption behaviours, influence of temperature on the adsorption of both ions on the adsorbent was studied at different temperatures (from 293 to 333 K) under optimized conditions. As shown in Fig. 4, the adsorption efficiency for cesium ions slightly decreased from 80 to 76 % with rise of temperature from 293 to 333 K. On the other hand, the adsorption efficiency for strontium ions was obtained regularly stable as 68 %.

Thermodynamic parameters

To evaluate the spontaneity and the heat change of the cesium and strontium adsorption processes, thermodynamic parameters (ΔH° , ΔS° and ΔG°) were estimated the equations in below [14–17]:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

where K_d is the thermodynamic stability constant, ΔS° is standard entropy ($\text{J mol}^{-1} \text{K}^{-1}$), ΔH° is standard enthalpy (kJ mol^{-1}), T is the absolute temperature (K) and R is the gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$). Table 2 shows thermodynamic parameters for cesium and strontium adsorption onto natural attapulgite.

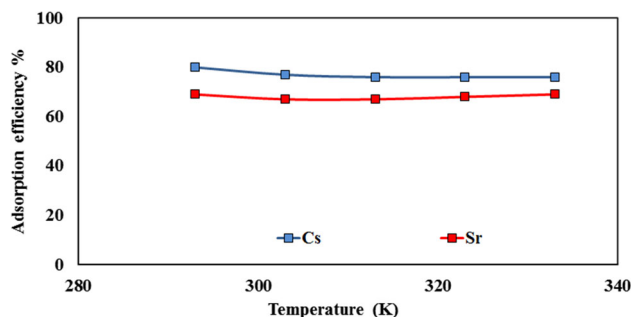


Fig. 4 Influence of temperature on the adsorption of cesium and strontium on the attapulgite

Activation energy was calculated using Arrhenius equation that expressed by the following equation [18, 19]:

$$\ln k_1 = \ln A - \frac{E_a}{RT} \quad (6)$$

where k_1 is the rate constant for the reaction, A is a proportionality constant that varies from one reaction to another, E_a is the activation energy for the reaction, R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$) and T is the temperature in kelvin.

The positive value of enthalpy indicates that the interaction between cesium and adsorbent is an endothermic reaction which consumes energy. On the other hand, the adsorbent and strontium interaction gave a negative enthalpy value which indicates an exothermic nature. Enthalpy value shows the type of solid/ion interaction. If the enthalpy value is lower than 40 kJ mol^{-1} , the type of adsorption is physical process [13, 20, 21]. The enthalpy values for cesium and strontium were found as lower than 40 kJ mol^{-1} . Entropy values for cesium and strontium were obtained as positive which indicates increasing randomness at the solid/liquid interface. The negative values of Gibbs free energy suggest spontaneous nature of the adsorption and required energy to carry out the reaction [22, 23]. Gibbs free energy values for cesium and strontium has a spontaneous and physisorption nature of the adsorption reaction.

The activation energy plays a key role to get information on whether interaction between solid and ions is physical or chemical. If the magnitude of the activation energy has $4\text{--}40 \text{ kJ mol}^{-1}$, the adsorption is a chemisorption process. When the activation energy is lower than 4 kJ mol^{-1} , the interaction between solid and ions accepts as adsorption [24]. The value of activation energies were calculated using Eq. 6 to be 4.39 and $-1.81 \text{ kJ mol}^{-1}$ for cesium and strontium, respectively. These values indicate that the reaction between strontium and the adsorbent leads by physical adsorption mechanism. Although activation energy value is in lower limit for cesium adsorption, physical adsorption mechanism could be accepted for cesium adsorption.

Adsorption isotherm

To study the adsorption isotherms of cesium and strontium ions onto attapulgite, different sorption isotherm models, namely Langmuir, Freundlich and D–R which were described in detailed in our previous studies [25–27], were examined for the experimental sorption equilibrium data. To provide sufficient physicochemical information about mechanism properties and to describe sorption capacities of attapulgite for cesium and strontium ions, the adsorption data was fitted the sorption isotherm models.

Table 2 Thermodynamic parameters for adsorption of cesium and strontium ions onto the adsorbent

	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)				
			293 K	303 K	313 K	323 K	333 K
Cs ⁺	4.39	41.98	-16.69	-17.11	-17.53	-17.95	-18.37
Sr ²⁺	-1.81	57.98	-18.79	-19.37	-19.95	-20.53	-21.11

Table 3 Values of Langmuir, Freundlich and D–R constants

	Ion	Q_m (mg g ⁻¹)	k_L (mg L ⁻¹)	R^2
Langmuir	Cs ⁺	9.091	0.723	0.9677
	Sr ²⁺	8.110	0.236	0.9640
		k_F (mg g ⁻¹)	n_F	R^2
Freundlich	Cs ⁺	2.159	2.22	0.9890
	Sr ²⁺	1.936	2.38	0.8637
		X_m (mg)	β (kJ mol ⁻¹)	R^2
D–R	Cs ⁺	7.6865	0.7244	0.9949
	Sr ²⁺	7.9818	0.3543	0.9967

Q_m and k_L Langmuir’s constants related to the capacity and energy of the adsorption, k_F the adsorption capacity of adsorbent, n_F a dimensionless constant related to adsorption intensity, X_m the maximum sorption capacity, β the activity coefficient related to mean sorption energy

Table 3 shows the regression coefficients and the constant values for all isotherm models. Regression coefficients indicated that the Freundlich ($R^2 = 0.99$) and D–R ($R^2 = 0.99$) isotherm models well fitted the cesium adsorption data and only D–R ($R^2 > 0.99$) isotherm model well fitted the strontium adsorption data onto the attapulgite at ambient temperature.

Freundlich isotherm models describe multiple layer molecular adsorption process on surface of attapulgite. The factor “1/n” indicates that adsorption is favourable for the ions. If values of 1/n smaller than 0.5, it shows that adsorbate is easily adsorbed; if values of 1/n larger than 2, it indicates that the adsorbate is hardly adsorbed [14, 24, 28]. For cesium adsorption onto the adsorbent, the 1/n value was determined as 0.45. This result indicates that the adsorption process was favourable for cesium ions. Adsorption capacity was found as 2.16 and 1.94 $\mu\text{g g}^{-1}$ at ambient temperature for the removal of cesium and strontium ions, respectively.

The regression coefficients were well fitted the D–R isotherm models ($R^2 > 0.99$) for both ions with a good adsorption capacity given by X_m values. Mean sorption energy (E) value reveals that the adsorption process is physical or chemical or ion exchange. The adsorption process accepts as a physical adsorption if E is in the range 1–8 kJ mol⁻¹. E which is in the range 8–16 kJ mol⁻¹,

indicates that ion exchange process is dominant. If the process is chemical adsorption, E should be in the range 16–40 kJ mol⁻¹ [14, 28]. For this study, E values were found as 0.83 kJ mol⁻¹ for cesium ions and 1.19 kJ mol⁻¹ for strontium ions. The results show that the adsorption process is a physical adsorption for both ions.

Conclusions

This research study has demonstrated the adsorption mechanism of cesium and strontium ions onto the natural attapulgite as a function of effectual parameters such as initial concentration, pH, contact time and temperature. Based on the experimental results of this study, it is observed that the natural attapulgite which is an economic and environmental benefits, has a potentially good adsorbent capacity to remove the cesium and strontium ions from aqueous solution.

The results show that adsorption mechanisms of cesium and strontium onto the adsorbent is highly dependent on pH and initial concentration of solution. The results reveals that the attapulgite can be used to remove of cesium and strontium ions from waste solution in a wide range of pH from 4 to 8 with a quite high efficiency in a short time. Removal of cesium and strontium were slightly affected by increasing temperature. This result reveals that physical adsorption leads the adsorption mechanism of both ions.

Various isotherm models were properly applied to experimental data of both ions. Freundlich isotherm model was well fitted for only cesium adsorption data, while D–R isotherm model was well utilized for cesium and strontium adsorption data. It can be considered that adsorption mechanism leads multilayer coverage on the adsorbent surface and in micro pores of the adsorbent.

Adsorption enthalpy changes indicated an exothermic process for strontium and an endothermic process for cesium. Adsorption process for both ions was increasing randomness at the solid/liquid interface.

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