Equilibrium and Thermodynamic Studies of Cesium Adsorption on Natural Vermiculite and Optimization of Operation Conditions

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ABSTRACT: *Removal of cesium from synthetic aqueous solution through adsorption on vermiculite, under batch equilibrium experimental condition at six initial values of pH (3, 4, 6, 9, 11 and 12) and five temperatures (25, 50, 75, 85 and 95 °C) has been investigated. It is necessary to propose a suitable model for a better understanding of the mechanism of cesium adsorption on vermiculite. For this propose the suitability of the Langmiur, Freundlich and Redlich-Peterson (R-P) adsorption models for equilibrium data were investigated. The parameters in the adopted adsorption isotherm models were determined by Eviews software. The study of equilibrium isotherm shows that the best model for analysis of experimental data is Redlich-Peterson model with correlation coefficient higher than 0.99(both for temperature and pH). The results showed that increasing of pH and temperature increased the adsorption ability of vermiculite. Optimum conditions for adsorption were determined as T=75 °C, pH=9, vermiculite dose=1.5 g and contact time of 24 hr. Finally the thermodynamic constants of adsorption phenomena, $\Delta H°$ and $\Delta S°$ were found to be 2.672 kJ/mol and 0.563 kJ/mol K in the range of 25-95 °C respectively. The negative value of the Gibbs free energy ΔG demonstrates the spontaneous nature of cesium adsorption onto vermiculite.*

KEY WORDS: *Adsorption, Vermiculite, Cesium, Equilibrium.*

INTRODUCTION

The contamination of waters by industrial effluents rich in radionuclide has received much attention in the last decades. The waste water purification system most usually employed by industries is the precipitating technique. However, in many cases this treatment does not allow reaching the legal limits imposed for radioactive wastewaters and even generates a large amount of sludge difficulty to handle. More effective purification systems, such as ion-exchange columns, are often more expensive and, hence, unsuitable for these industries [1]. For these reasons, in recent years, many researchers studied the behavior of natural organic or inorganic materials having high adsorption capacity and which are particularly abundant and inexpensive in order to use

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them as low-cost effective sorbents for the removal of radionuclide from various effluents [2].

Cesium is an important radionuclide for several reasons: it exhibits almost unlimited solubility; its inventory in radioactive waste is significant and is extremely long-lived. Furthermore, because of its chemical similarity to K, cesium is readily assimilated by terrestrial and aquatic organisms. Clay minerals are known to adsorb cesium very well and there are many studies concerning in particular the adsorption of cesium on clay minerals, especially illite, smectite and vermiculite. [3-6].

Vermiculite is a clay mineral with 2:1 crystalline structures with high cation exchange capacity, which is a consequence of surface and interlayer ion exchange processes, as well as isomorphic substitution. Such properties, associated to high surface area, have made this material the target of several adsorption studies aiming for a better understanding of environmental process in soils and waters [7-9].

The characteristics of adsorption behavior are generally inferred in terms of both adsorption kinetics and equilibrium isotherms. They are also important tools to understand the adsorption mechanism, vis. the theoretical evaluation and interpretation of thermodynamic parameters [10, 11].

Equilibrium isotherms

Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of sorbent, at a fixed temperature and pH [10].

What the adsorption isotherm describes is the relationship between the solute concentration q (1/g adsorbent) in the equilibrium adsorbent and the solute concentration C in the case of certain temperature and pH [12]. The amount of metal ion sorbed on the vermiculite, q_e was computed by the following equation:

$$q_e = \frac{\upsilon}{m}(C_0 - C_e) \tag{1}$$

Where C_0 and $C_e$are the initial concentration and the equilibrium concentration of the ions in the liquid phase, respectively. Also v and m are the volume of the solution and weight of the resin particles, respectively.

The quantitative explanation for adsorption experimental data can be expressed using different mathematical models, of which Langmuir model and Freundlich model are most widely considered as the base for studying adsorption process and they are most commonly used to describe the adsorption characteristics of adsorbent used in water and wastewater [13]. The Redlich-Peterson equation is a combination of Langmuir and Freundlich models

Langmuir isotherm

This model is obtained under the ideal assumption of a totally homogenous adsorption surface and it may be represented as follows:

$$q_e = \frac{q_0 k_{ad} C_e}{1 + k_{ad} C_e} \tag{2}$$

The Langmuir constants q_0 and k_{ad} are related to the adsorption capacity and the energy of adsorption, respectively.

Freundlich isotherm

This model is suitable for a highly heterogeneous surface as well as multilayer sorption and is expressed by the following equation:

$$q_e = k_f C_e^{1/n} \tag{3}$$

n and k_f are the Freundlich constants.

The fit of data to Freundlich isotherm indicates the heterogeneity of the sorbent surface. The magnitude of the exponent 1/n gives an indication of the adequacy and capacity of the adsorbent/adsorbate system [14].

Redlich - Peterson isotherm

Such an isotherm is a combination of two previous models [15] which is defined as follows:

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{\beta}} \tag{4}$$

Where α_R and K_R are the constants of Redlich-Peterson and β is the exponent of equation which lies between 0 and 1. When $\beta=1$, this equation changes to Langmuir isotherm and when $\beta=0$, it changes to Henry equation which is defined as follows:

$$q_e = \frac{K_R C_e}{1 + \alpha_R} \tag{5}$$

Table 1: Characterization of vermiculite.

OXIDES	PCT
SiO_2	34.04
Al_2O_3	17.85
Fe_2O_3	10.97
TiO_2	6.63
MgO	14.99
CaO	N.D.
K_2O	6.17
Na_2O	0.36
H_2O	8.75
TOTAL	99.67

The present work deals with a series of experiments to assess the optimum conditions of vermiculite for the removal of cesium from aqueous solutions. The amounts adsorbed at equilibrium sorption were measured at different pHs and temperatures. The adsorption isotherms at varying solution temperatures and pHs were measured, and suitable model equations were tried to fit the experimental data

MATERIALS AND METHODS

Adsorbent

The vermiculite sample was supplied by the company, Gilan Mica .The vermiculite mine is located in Amlash, Gilan Province, Iran. The original vermiculite sample was characterized by X-ray diffraction patterns. Vermiculite with a mean size of 1 mm was used in the entire study. The chemical composition of such vermiculite in weight percentage is presented in table 1.

Pre-treatment of vermiculite

Vermiculite samples were thoroughly washed with distillated water to remove all adhering dirt and then, were oven-dried at 70 °C, till achieving constant weight. The dried vermiculite was used without any physical or chemical pre-treatment.

Solutions

The divalent cation cesium was in chloride form (Merck) as reagent grade was used without previous purification. The range in concentrations of Cs prepared from stock solution varied between 2×10^{-5} and 8×10^{-5} mol.L^{-1}.

ADSORPTION EXPERIMENTS

Batch adsorption experiments were carried out by allowing an accurately weighted amount of vermiculite to reach equilibrium with Cs solutions of various initial concentrations between 2×10^{-5} and 8×10^{-5} mol.L^{-1}. For evaluating the influence of pH, the suspension pH was adjusted to 3, 4, 6, 9, 11 and 12 by adding KOH and HNO_3. The effect of temperature on adsorption process was also checked by adjusting the temperature of shaking machine on 25, 50, 75, 85 and 95 °C. Known weights of vermiculite (1.5 g) were added to 100 mL solution. The bottles were shaken in a temperature-controlled shaker at a constant speed of 180 rpm.

Preliminary experiments showed that adsorption equilibrium was reached within 24 hr. At the end of the equilibrium period the contents of the bottles were filtered. The uptake of cesium was calculated from the measured values of its concentration before and after equilibration. The results are expressed as % Adsorption.

$$\%\ \text{Adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (6)$$

Where, C_0 and C_e are the cesium concentration before and after equilibrium.

RESULTS AND DISCUSSION

Determination of optimum operating conditions optimum dosage

The effect of the adsorbent dosage on the adsorption of C_S on vermiculite is shown in Fig. 1. Vermiculite dosage was varied between 0.5 and 2.5 g/100 mL for C_S concentration of 4×10^{-5} and equilibrated for 24 hr. It can be revealed from Fig. 1. That the removal of cesium increase with increase in vermiculite dosage. The removal of C_S at vermiculite dosage greater than 1.5 g/100 mL remains almost constant. Thus the equilibrium concentration is considered to be 1.5 g/100 mL (93 % Adsorption) for vermiculite.

Optimum contact time

Fig. 2 presents the plot of C_S removal versus contact time for vermiculite in initial concentrations between 2×10^{-5} and 8×10^{-5} mol.L^{-1} at 25 °C. It is revealed that

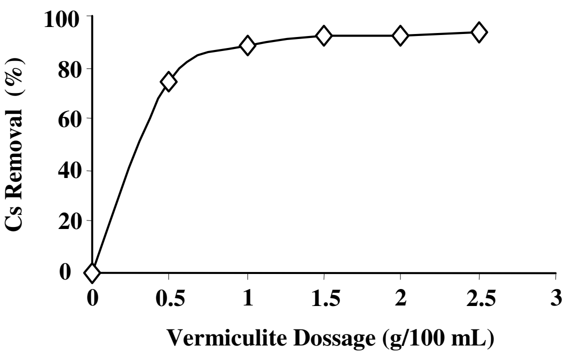

Fig. 1: Effect of vermiculite dosage on Cs removal (T=298 K; contact time=24 hr; C0 = 4×10-5 mol L^{-1}).

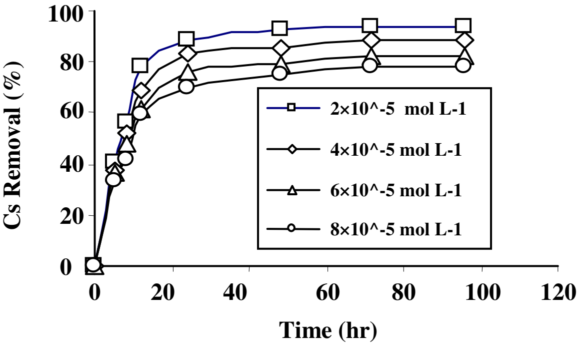

Fig. 2: Removal of Cs vs. contact time (T=298 K; vermiculite dosage=1.5 g/100 mL).

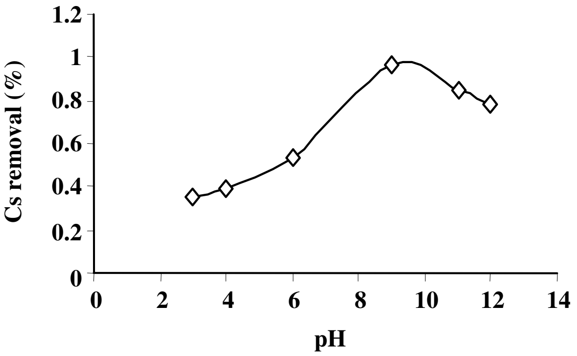

Fig. 3: Removal of Cs vs. pH (T=25 °C; vermiculite dosage=1.5 g/100 mL).

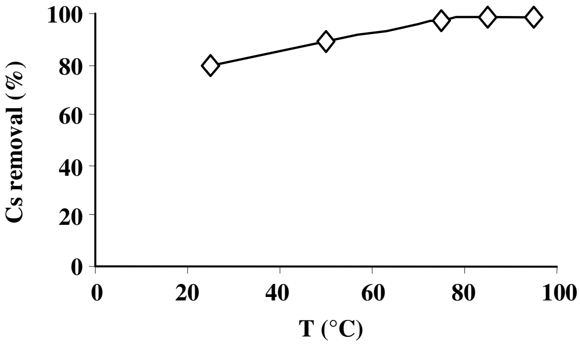

Fig. 4: Removal of Cs vs. Temprature (pH 9; vermiculite dosage=1.5 g/100 mL).

there was no considerable change for C_S removal after 24 hr of contact time for different initial concentrations.

Optimum pH

One of the most important parameters in the adsorption process is initial pH of solution. For each metal ion, there is a specific pH value at which the maximum adsorption of that ion takes place. This pH takes place in basic region (i.e. at high pH values) for the cationic metals; it takes place as an exceptional case at the low pH values for the anionic metals.

The adsorption of cesium on to vermiculite is dependent on the pH of the solution, which affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbent species [16-18]. Solutions with values of pH (3, 4, 6, 9, 11 and 12) and same concentration (4×10^{-5} mol/L), containing 1.5 g of vermiculite were prepared and placed into shaking machine by adjusting the temperature at 25 °C. Change of % Cs removal as a function of pH is given in Fig. 3. This curve shows that increase in the initial pH of the solution from 3 to 9 caused increasing in the percentage of Cs ions adsorption.

Adsorption of Cs ions was about 95 % at pH of 9, and it decreased to 84 %, 70 % and lower values with the increasing pH values. This may be explained by the influence of solution pH on the surface charge distribution which is strongly related with the metal ions removal. At pH 9, due to the excess amount of OH^- ions within the medium, the active site on the vermiculite is negatively charged.

This causes a strong attraction between these sites and positively charged Cs ions. Therefore pH of 9 is the optimum pH of solution.

Optimum temperature

The other effective parameter is temperature of adsorption process. Effect of temperature on adsorption capacity of vermiculite was investigated at 4×10^{-5} mol/L initial concentration by using 1.5 g of vermiculite at the temperatures of 25, 50, 75, 85 and 95 °C. the results at this experiment are given in Fig. 4.

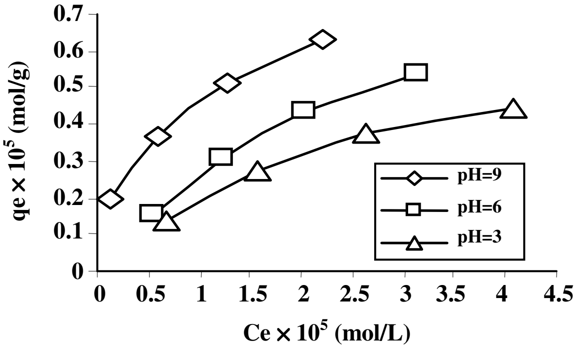

Fig. 5: Effect of initial pH on equilibrium adsorption on vermiculite(T=298 K).

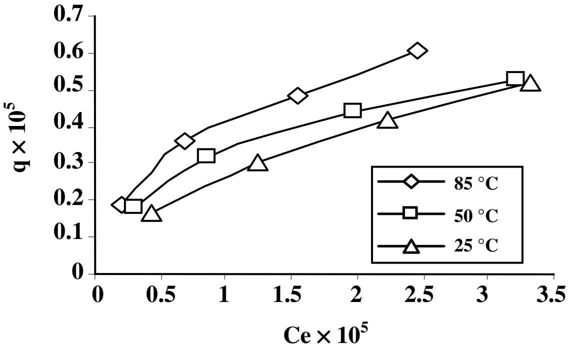

Fig. 6: Effect of initial temperature on equilibrium adsorption on vermiculite (pH=9).

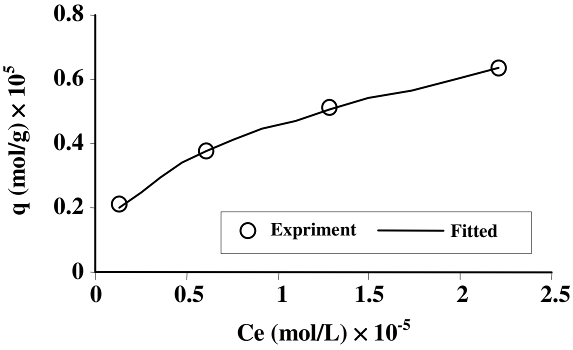

Fig. 7: Comparing an experimental isotherm curve and its corresponding Redlich-Peterson profile at pH 9.

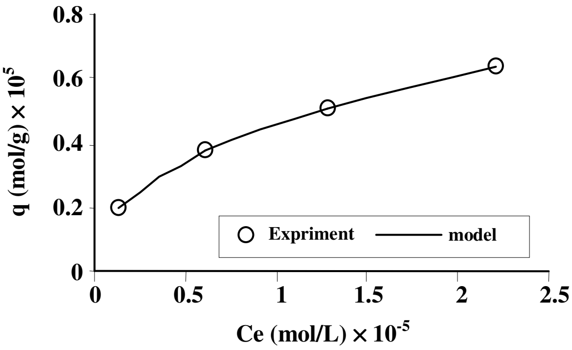

Fig. 8: Comparing an experimental isotherm curve and its corresponding Redlich-Peterson profile at T= 75 °C.

This figure shows that there is a slight increase in equilibrium concentration when temperature is changed from 25 to 75 °C and then the changes were almost constant. Kinetic energies of Cs ions were low at low temperatures. Therefore T=75 °C is the optimum temperature for this adsorption system. It is very difficult and time-consuming process for ions to reach the active sites on the adsorbent. Increase in temperature causes increase in the mobility of the ions.

Equilibrium study

The equilibrium adsorption of C_S ion onto vermiculite at six initial pH solution (3, 4, 6, 9, 11 and 12) and five temperatures (25, 50, 75, 85 and 95 °C) was investigated. In order to optimize the design of sorption system to remove C_S ions from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. In this part, based on the results of optimization studies, three pHs (3, 6, 9) and three temperatures (25, 50, 75 °C) were selected for equilibrium studies. The results were shown in Figs. 5 and 6. These figures show the adsorption isotherms of C_S ions at different pHs and varying solution temperatures respectively. Also the experimental data were fitted with various isotherm models. The adsorption isotherm parameters are calculated with EViews program. (Listed in tables 2, 3).

The correlation coefficients parameters in tables 2 and 3 demonstrate that all of the models are acceptable (R^2>0.9, both in different pHs and temperatures).

Furthermore, the parameters in the Redlich-Peterson model have been found to describe the experimental data very well.

Figs. 7 and 8 show a plot comparing an experimental isotherm curve and its corresponding Redlich-Peterson profile at optimum pH and temperature respectively.

Determination of thermodynamic parameters

The Gibbs free energy change ΔG° indicates the degree of the spontaneity of adsorption process.

Table 2: Isotherm parameters for Cs adsorption on vermiculite at different pH.

Isothermal	pH	Model parameters
Langmuir	3	q=0.768; k_{ad}=1.973; R^2 =0.955; Adjusted R^2=0.933
	6	q=1.075; k_{ad} =0.320; R^2 =0.998; Adjusted R^2=0.997
	9	q=1.741; k_{ad} =0.344; R^2 =0.994; Adjusted R^2=0.992
Freundlich	3	k_f=0.200; n=1.695; R^2 =0.974; Adjusted R^2=0.961
	6	k_f=0.258; n=1.520; R^2 =0.987; Adjusted R^2=0.981
	9	k_f=0.457; n=2.465; R^2 =0.999; Adjusted R^2=0.999
Redlich- Peterson	3	k_r=1.994; α_r=9.473; β=1.555; R^2 =0.999; Adjusted R^2=0.997
	6	k_r=1.960; α_r=6.568; β=1.393; R^2 =0.999; Adjusted R^2=0.999
	9	k_r=0.463; α_r=0.009; β=0.602; R^2 =0.999; Adjusted R^2=0.998

Table 3: Isotherm parameters for Cs adsorption on vermiculite at different temperature.

Isothermal model	Temperature (K)	Model parameters
Langmuir	298	q=0.646; k_{ad} =0.507; R^2 =0.989; Adjusted R^2=0.984 .
	323	q=0.754; k_{ad} =1.140; R^2 =0.992; Adjusted R^2=0.988
	348	q=0.807; k_{ad} =1.377; R^2 =0.983; Adjusted R^2=0.975
Freundlich	298	q=0.266; b=0.556; R^2 =0.999; Adjusted R^2=0.999
	323	q=0.332; b=0.409; R^2 =0.971; Adjusted R^2=0.957
	348	q=0.405; b=0.443; R^2 =0.994; Adjusted R^2=0.991
Redlich- Peterson	298	k_r=0.311; α_r=0.163; β=0.505; R^2 =0.999; Adjusted R^2=0.999
	323	k_r=0.583; α_r=0.648; β=0.928; R^2 =0.992; Adjusted R^2=0.998
	348	k_r=0.501; α_r=0.206; β=0.688; R^2 =0.997; Adjusted R^2=0.992

For significant adsorption to occur, the free energy changes of adsorption ΔG° 0must be negative. The Gibbs free energy change can be calculated by the following equation:

$$\Delta G^\circ = -RT \ln K_{ad} \qquad (7)$$

Where K_{ad}, adsorption equilibrium constant (derived from Langmuir model);T, absolute temperature, K; R,gas constant 8.3144×10^{-3} , kJ/(mol K).

The relation among K_{ad} and thermodynamic parameters ΔH (enthalpy) as well as ΔS (entropy) can be described using Van't Hoff formul.

$$\ln K_{ad} = \Delta S/R - \Delta H/RT \qquad (8)$$

The values of ΔH and ΔS were obtained from the slop and intercept of ln(K_{ad}) versus l/T plot (Fig. 9). ΔH is the positive value, whereby proving that the process of cesium adsorption on vermiculite is endothermic process. In addition, it can be known from calculated value ΔH=2.672 kJ/mol that the above process is physical adsorption rather than chemical adsorption. ΔG is the negative values with the general trend appearing to be the negative growth, whereby proving that the above process is the spontaneous process; and ΔS is the

Table 4: Thermodynamic parameters for adsorption process of cesium onto vermiculite.

Temperature (K)	K_{ad}	ΔG ($kJmol^{-1}$)	ΔH ($kJmol^{-1}$)	ΔS ($kmol^{-1}K^{-1}$)	R^2
298	0.507	-14.1082			
323	1.140	-15.5080	2.672	0.563	0.999
348	1.377	-16.9238			

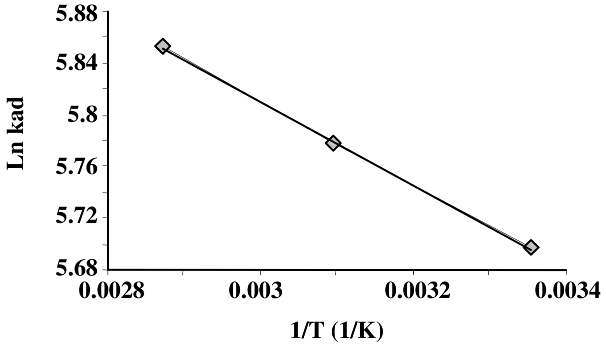

Fig. 9: Van't Hoff straight line.

positive values thus, showing that process is the entropy increasing process. The values of thermo-dynamic parameters are presented in table 4.

CONCLUSIONS

The isotherms for the adsorption of cesium from aqueous solution by vermiculite have been analyzed. Optimum adsorbent dose observed as 1.5 g/100 mL of solution for C_S oncentration of 4×10^{-5}. The equilibrium between vermiculite and cesium was achieved in approximately 24 hr with 93 % removal of cesium. Based on the present investigation, it can be concluded that vermiculite exhibits good sorption properties for cesium ions in aqueous solution. Many experimental factors influence the extent of C_S uptake, such as pH and temperature. Results showed that pH of 9.0 and T = 75 °C are the optimal pH and temperature for adsorption of Cs on vermiculite.

It is necessary, hence, to consider these factors to effectively predict the behavior of this sorbent in purification systems of wastewaters contaminated by C_S.

Redlich-peterson model is the best model among three presented equilibrium models in this study to describe Cs/vermiculite adsorption system, as it has the maximum R^2 value. The negative value of ΔG° indicates the feasibility and spontaneity of the adsorption process. The positive value of ΔH suggests, adsorption on vermiculite is endothermic nature of the adsorption process.

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