

# Equilibrium and Thermodynamic Studies of Cesium Adsorption on Montmorillonite Clay

Som Shankar Dubey\*

Department of Chemistry, Deen Dayal Upadhyaya Gorakhpur University, Gorakhpur, Uttar Pradesh 273009, India

**Abstract:** Removal of cesium from synthetic aqueous solution through adsorption on montmorillonite, under batch equilibrium experimental condition at different values of pH and four temperatures (303, 313, 323, 333 K) was investigated. For this propose the suitability of the Freundlich adsorption model for equilibrium data were investigated. The parameters in the adopted adsorption isotherm models were determined. The study of equilibrium isotherm shows that the best model for analysis of experimental data is freundlich 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 montmorillonite. Optimum conditions for adsorption were determined as T=323 K, pH=9, montmorillonite dose=1.5 g and contact time of 24 hr. The negative value of the Gibbs free energy  $\Delta G$  demonstrates the spontaneous nature of cesium adsorption onto montmorillonite.

**Keywords:** Equilibrium, Thermodynamic studies, Montmorillonite

## I. INTRODUCTION

Sorption of radionuclides on natural solids strongly affects the behavior and transport of radionuclides in the environment and complicates their description by mathematical models. Hence, the sorption has been extensively studied and modeled. Most of the studies dealt with rather simple systems (minerals and solutions) where the sorption can be better interpreted and described. However, real environmental systems are usually complex and the data and knowledge obtained with simple systems cannot be easily used for environmental conditions. Description of sorption on complex natural solids, solely on the basis of known properties of their components, is very difficult, due to complicated mutual interaction of the components, surface coating and similar effects. A more passable way is probably to take such a complex solid as a whole, to characterize it and to develop a suitable method for describing its sorption properties for a given radionuclide<sup>1</sup>. Cerium being a radiotoxic element, affects the environment adversely and due to this reason, it is very important from environmental pollution and management point of view. Due to toxicity on human beings makes it desirable of its removal from effluent water for clean environment<sup>2-4</sup>. During the last few decades a large number of metal oxides have been explored for their use in adsorption and for various separations of analytical and radiochemical importance<sup>5-8</sup>. The interest in these materials has grown mainly due to their extra stability towards ionizing radiations and higher temperatures in comparison to their organic counterparts<sup>9-11</sup>. The adsorption process has been found to be useful and popular due to its low maintenance costs, high efficiency and ease of operation. Adsorption of toxic metal ions on soil<sup>12-14</sup>, silica gel<sup>15</sup> and activated carbon<sup>16-17</sup> has been described under various related parameters. The effect of various parameters such as concentration, temperature had been examined. The adsorption isotherms during the process have also been discussed and thermodynamic parameters deduced to help in understanding the uptake process.

## II. EXPERIMENTAL

### Sorption Measurements

Cesium (I) as its sulphate salt was used and stock solution ( $1.0 \text{ mol dm}^{-3}$ ) of metal ion was prepared in double distilled water. The solution was further standardized via the standard method of Flaschka<sup>18</sup> and then diluted to obtain desired experimental concentrations ( $10^{-3}$ – $10^{-6} \text{ mol dm}^{-3}$ ). The radioactive cesium ( $^{134}\text{Cs}$ ,  $t_{1/2} = 2.06 \text{ y}$ ) as its respective sulphate in dilute  $\text{H}_2\text{SO}_4$  ( $ca 166.5 \times 10^6 \text{ Bq}$ ) was obtained from the Board of Radiation and Isotope Technology (BRIT), Mumbai (India). A very small amount of this radionuclide was used to label the adsorptive solutions to obtain a measurable radioactivity of minute aliquots of withdrawn samples from bulk. The sorption experiments were performed by stirring, at regular intervals, and equilibrating 0.1000 g of clay with  $10.0 \text{ cm}^3$  of labeled adsorptive solution. The equilibrated solution was centrifuged for phase separation and then supernatant solution was analyzed for its  $\square$ -activity measurements using an end-window GM-counter (Nucleonix, Hyderabad, India). Radioactivities of some samples were also checked for their gamma-activity using a Multi Channel Analyzer (Nucleonix,

Hyderabad, India). Procedures for estimation of the amount adsorbed and evaluation of other parameters were identical to those given earlier<sup>19</sup>.

### III. RESULTS & DISCUSSION

#### Effect of shaking time

The shaking time ranging from 10 minutes to 48 hours was employed for achieving the equilibrium (Fig. 1). More than 95% of Cs (I) was adsorbed after 10 minutes of shaking. The uptake of Cs (I) was a slow process and it took 16 hours for sorption of more than 99% Cs (I). It is apparent that in the beginning the sorption was achieved by ion-exchange followed by precipitation of hydrolyzed species slowly. For comparison 1 hour shaking time was selected in the further experiments.

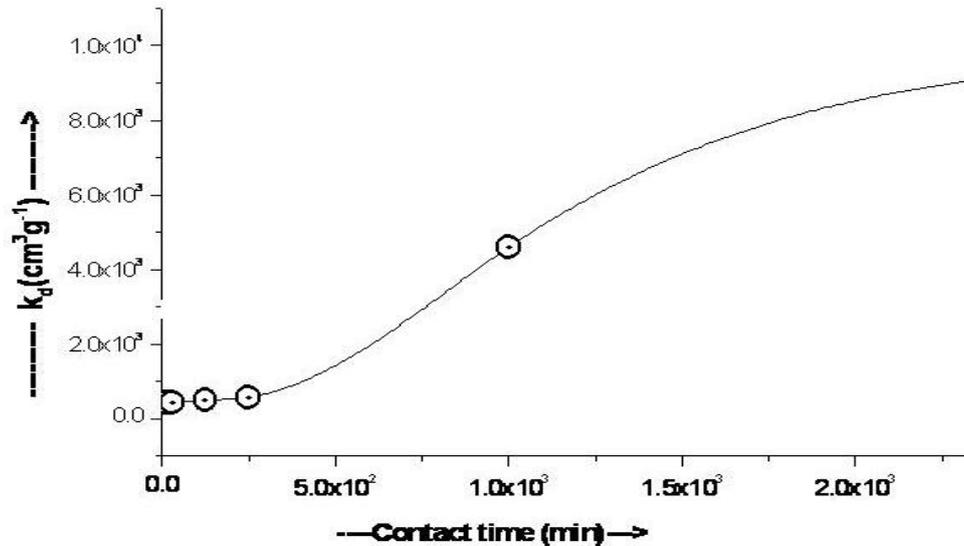


Figure 1: Effect of shaking time on the sorption of Cs(I)

#### Effect of adsorbent concentration

The adsorption of both cerium and europium was studied as function of adsorbent concentration from 10  $\text{g dm}^{-3}$  to 100  $\text{g dm}^{-3}$ . The result is plotted in Fig. 2. In case of cesium,  $K_d$  increased with adsorbent concentration  $K_d$  first increased and then showed a slight decline. This was due to complete and early removal of Cs (I) ions by lesser weight of clay.

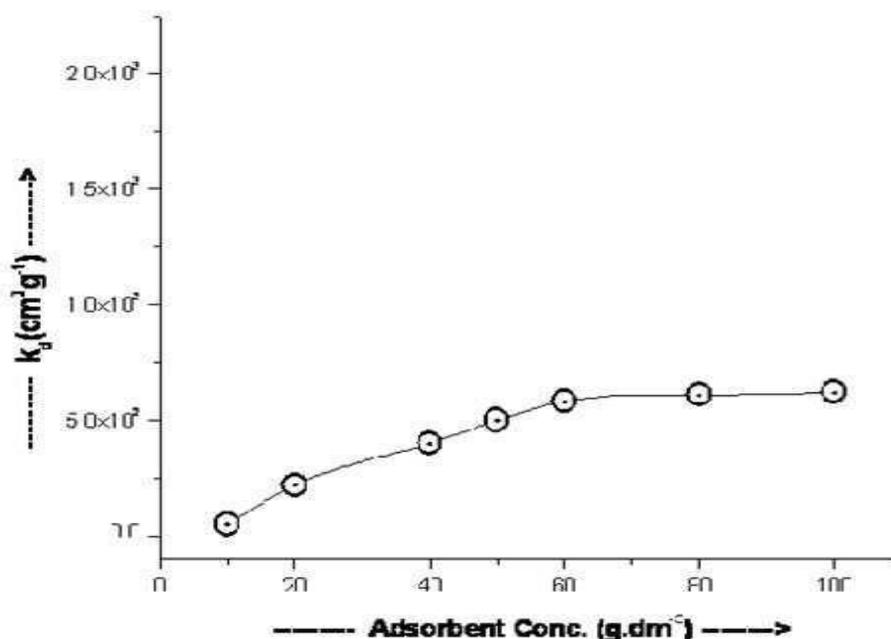


Figure 2: Variation of  $K_d$  of Cs(I) with adsorbent concentration

**Effect of metal ion concentration**

Concentration effect for the adsorption of Cs (I) on Clay was carried out by varying the adsorptive concentrations at 303 K and results of the uptake of Cs (I) ions are shown in Fig. 3. It is observed that initially a fast uptake of metal ions occurred, which became slower with the lapse of time and an apparent equilibria between the two phases achieved within *ca* 10 min of contact time. No further uptake was observed even after 48 h of contact. Moreover, the smooth and continuous curves leading to saturation for the uptake of the ions over clay infer about the adsorption of metal ions occurring in a single step and not accompanied by any complexity. For Cs (I) the concentration was varied between  $3.47 \times 10^{-6}$  to  $3.23 \times 10^{-4}$  mol dm<sup>-3</sup>. This increase in the adsorption is explicable on the basis of the fact that a relatively smaller number of adsorptive species would be available at higher dilution for deposition on an equal number of surface sites of adsorbents<sup>20</sup>.

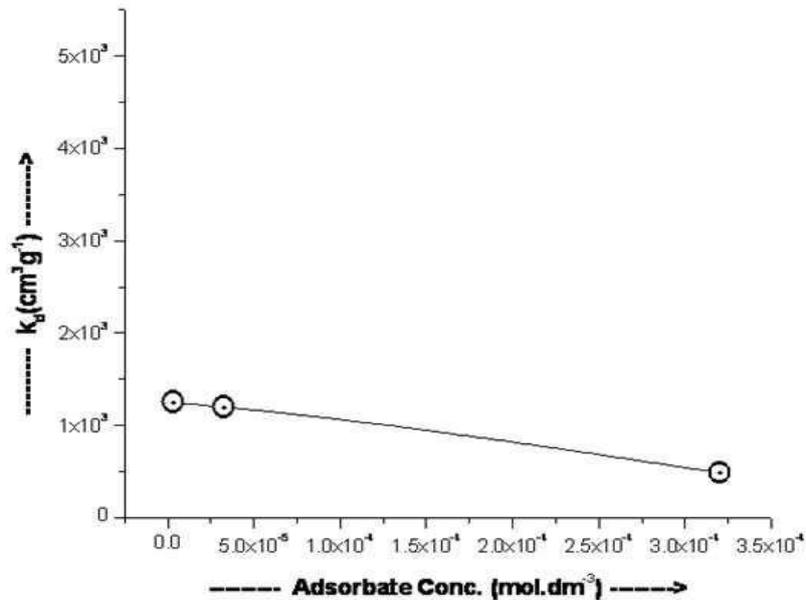


Figure 3: Variation of K<sub>d</sub> with change in adsorbate concentration

**Equilibrium modeling**

The concentration dependence data were further utilized in equilibrium modeling of the removal process by using the Freundlich and Langmuir equations. It has been observed that the concentration data fitted well by Freundlich equation (1) rather than the Langmuir equation.

$$\log a_e = \frac{1}{n} \log C_e + \log K \text{ ---- (1)}$$

Here *a<sub>e</sub>* and *C<sub>e</sub>* are the amounts adsorbed (mol g<sup>-1</sup>) at equilibrium and equilibrium bulk concentration (mol dm<sup>-3</sup>) respectively and 1/*n* and *K* are the Freundlich constants which correspond to adsorption intensity and adsorption capacity, respectively. In order to find out these constants a plot has been drawn between log *a<sub>e</sub>* vs log *C<sub>e</sub>* and straight lines were found for both the systems. These linear plots confirm about the monolayer coverage of ions at the surface of both adsorbents<sup>21</sup>. The value of 1/*n* and *K* were 0.951 and  $2.83 \times 10^{-2}$  mol g<sup>-1</sup>. The fractional values of 1/*n* (0 < 1/*n* < 1) obtained for both the systems are considered to be due to the heterogeneous surface structure of adsorbents with an exponential distribution of surface active sites<sup>20</sup>. The higher numerical values of *K* for both the systems again confirm the significant affinity of ions for clay.

**Effect of temperature**

The effect of solution temperature varying from 303 to 333 K in steps of 10 K on adsorption of ions clay has been investigated; the initial concentration of ions being kept at  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup> at pH 7.62. The increase in adsorption of metal ions may be either due to acceleration of slow adsorption steps or due to creation of some new active sites<sup>22</sup> or to transport against a concentration gradient, and/or diffusion controlled transport across the energy barrier.

A kinetic study for the uptake of ions over clays has also been worked out, which follows the first order rate law obeying Lagergren equation:

$$\log (a_e - a_t) = \log a_e - k_1 \cdot t / 2.303 \text{ ----(2)}$$

where  $a_e$  and  $a_t$  are the amounts adsorbed at equilibrium and at contact time intervals  $t$  and  $k_1$  is the adsorption rate constant. The values of adsorption rate constants at different temperatures have been estimated from the slopes of straight lines obtained from  $\log(a_e - a_t)$  vs time and the values are listed in Table 1. These values for both systems increase with the increase in temperature, which is in conformity to expectations as adsorption increases with the increase in temperature for non-physical type adsorption.

Table-1: Thermodynamic parameter for adsorption of Cs (I) ions on montmorillonite clay.

Temperature (K)	Rate Constant ( $\text{min}^{-1}$ ) $\times 10^2$	Energy of activation ( $\text{kJ mol}^{-1}$ )	Enthalpy change ( $\text{kJ mol}^{-1}$ )	Entropy ( $\text{kJ K}^{-1} \text{mol}^{-1}$ ) $\times 10^2$
303	12.56	10.13±0.04	17.72±0.04	9.64±0.03
313	13.34			
323	13.97			
333	15.13			

The Arrhenius plots of  $\log k_1$  vs  $1/T$  gave the activation energy for the adsorption process of Cs (I) on clay as  $10.13 \pm 0.04 \text{ kJ mol}^{-1}$ . These low values of activation energy indicates that the process of uptake can occur even under normal conditions of temperature and pressure and also indicate about the strong force of attraction operating during the adsorption.

The change in standard enthalpy  $\Delta H^0$  during the adsorption process has been evaluated using van't Hoff equation (3);

$$\log K_D = \frac{H^0}{2.303 RT} + \text{Constant} \quad (3)$$

where  $K_D$ ,  $\Delta H^0$ ,  $R$  and  $T$  have their usual meaning. The values of  $\Delta H^0$  (at 303K) found from the slopes of straight lines obtained by plotting  $\log K_D$  vs  $1/T$  are found to be  $16.72 \pm 0.04 \text{ kJ mol}^{-1}$ . The positive value of  $\Delta H^0$  confirms the endothermic nature of the adsorption process<sup>22</sup> and the numerical value indicates an ion exchange type mechanism<sup>23</sup> for the uptake.

### Desorption study

Clay with preadsorbed Cs (I) was washed with double distilled water to ensure the removal of adhering species and subsequently the adsorbent was dried in an electric oven at 383K. The desorption of preadsorbed ions on the solid was studied in Cs (I) solution ( $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ) at different temperatures (i.e., 303 to 333 K). The very low values of percentage desorption at different temperatures (cf Table 2) indicates that the desorption process is almost independent of temperature. Thus a low value of desorption, unaffected by increase of temperature shows that the process of adsorption for ions is irreversible in nature. It also indicates that a major part of ion were probably bound to the clay surface through strong interaction and converted to a final stable adsorption phase.

Table-2: Effect of time on the desorption of Cesium using  $0.01 \text{ mol dm}^{-3} \text{ CaCl}_2$  and Water as desorbent

Adsorbate	Time of desorption (h)	% Desorption	
		$0.01 \text{ mol dm}^{-3} \text{ CaCl}_2$	Plain Water
Cs(I)	1	2.04	0.55
	4	2.09	0.35
	24	2.11	0.48

### Effect of pH

In order to find out the mechanism involved at the solid/solution interface, the study has been extended for the adsorption of ions on the surface clay as a function of adsorptive pH at a constant temperature (303 K) and using metal ion solution of  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ . Cesium (I) varying the pH range 2-9 of solution (fig. 4). The sorption increased with pH in the present case above pH 7 the uptake of the cations was almost complete. At lower pH lesser adsorption was due to completion of hydrogen ions with Cs (I) for exchange sites. At higher pH hydrolyzed species are formed and are precipitated as hydroxides.

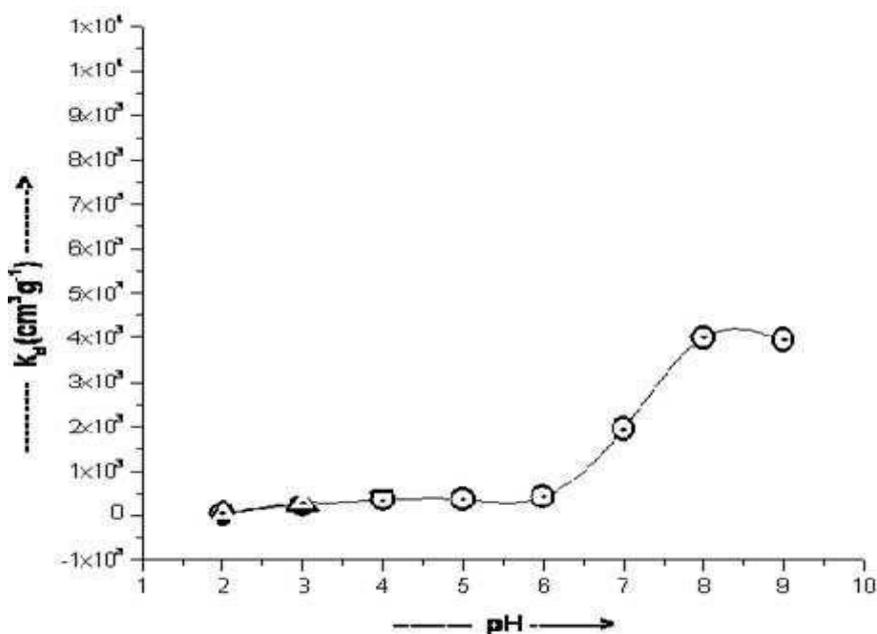


Figure-4: Effect of pH on the sorption of Cs(I)

#### IV. CONCLUSION

Montmorillonite clay was found to be effective in rapid and efficient removal of micro concentrations of Cs (I) ions from aqueous solutions. The adsorption process follows Freundlich isotherm with endothermic/irreversible nature.

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