



Efficient Removal of Ce(III) and Eu(III) Ions from Aqueous Solutions by Local Clay -A Radiotracer Study

SOM SHANKAR DUBEY*, BATTULA SREENIVASA RAO,
B.S.A. ANDREWS and B.VENKATA KIRAN

Department of Chemistry, GITAM Institute of Technology
GITAM University, Visakhapatnam-530045, India
somshankarbhu@yahoo.co.in

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Abstract: Radiotracer technique has been used to study the removal behavior of Ce(III) and Eu(III) ions from aqueous solutions by local clay. Adsorptive concentration (10^{-4} – 10^{-6} mol dm⁻³), pH (*ca* 2.0-9.0) and temperature (303-333 K) were examined for assessing optimal conditions for removal of these ions. The adsorption phenomenon was highly dependent on the amount of the adsorbent concentrations. The uptake of ions, which fitted well for Freundlich isotherm, increased with increase in the temperature and no significant desorption took place in the studied temperature range. The energy of adsorption process for the both cations indicates that the adsorption phenomenon is of chemisorption type. The rate kinetics of the adsorption followed the first order rate kinetics.

Keywords: Ce(III), Eu(III), Clay, Adsorption, Freundlich isotherm, Desorption.

Introduction

Sorption of radionuclide on natural solids strongly affects the behavior and transport of radionuclide in the environment and complicates their description by mathematical models. Therefore, 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 radionuclide¹. Cerium and europium, being a

very toxic heavy element, affects the environment adversely and due to this reason, it is very important from environmental pollution and management point of view. Due to their toxicity to human beings, they must be removed from effluent water for clean environment²⁻⁴.

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 importance⁵⁻⁸. The interest in these materials has grown mainly due to their extra stability towards ionizing radiations and higher temperatures in comparison to their organic counterparts⁹⁻¹¹. 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 soil¹²⁻¹⁴, silica gel¹⁵ and activated carbon¹⁶⁻¹⁷ 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.

Experimental

Cerium(III) and Europium(III) as its sulphate salt was used and stock solution (1.0 mol dm^{-3}) of metal ion was prepared in double distilled water. The solution was further standardized via the standard method of Flaschka¹⁸ and then diluted to obtain desired experimental concentrations (10^{-3} – $10^{-6} \text{ mol dm}^{-3}$). The radioactive cerium (^{141}Ce , $t_{1/2} = 43 \text{ d}$) as its respective sulphate in dilute H_2SO_4 (*ca* $166.5 \times 10^6 \text{ Bq}$) and Europium (^{148}Eu , $t_{1/2} = 54.5 \text{ d}$) 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 cm^3 of labeled adsorptive solution. The equilibrated solution was centrifuged for phase separation and then supernatant solution was analyzed for its β -activity measurements using an end-window GM-counter (Nucleonix, Hyderabad, India). Radio activities of some samples were also checked for their γ -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 earlier¹⁹.

Results and Discussion

Effect of shaking time

The shaking time ranging from 10 minutes to 48 hours was employed for achieving the equilibrium (Figure 1). More than 99% of Eu(III) and 95% of Ce(III) was adsorbed after 10 minutes of shaking. The uptake of Ce(III) was a slow process and it took 16 hours for sorption of more than 99% Ce(III). It is apparent that in the beginning the sorption was achieved by ion-exchange followed by precipitation of hydrolyzed species slowly, but in case of Eu(III) the precipitation of $\text{Eu}(\text{OH})_3$ was rapid and bypassed the formation of chain of these species. For comparison 1 h shaking time was selected in the both cases for further experiments.

Effect of adsorbent concentration

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

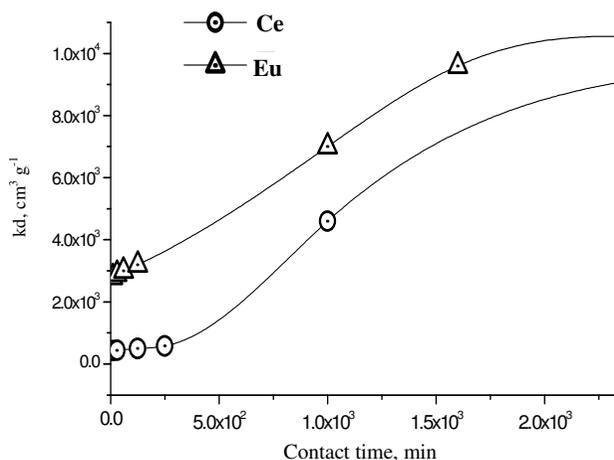


Figure 1. Effect of shaking time on the sorption of Ce and Eu

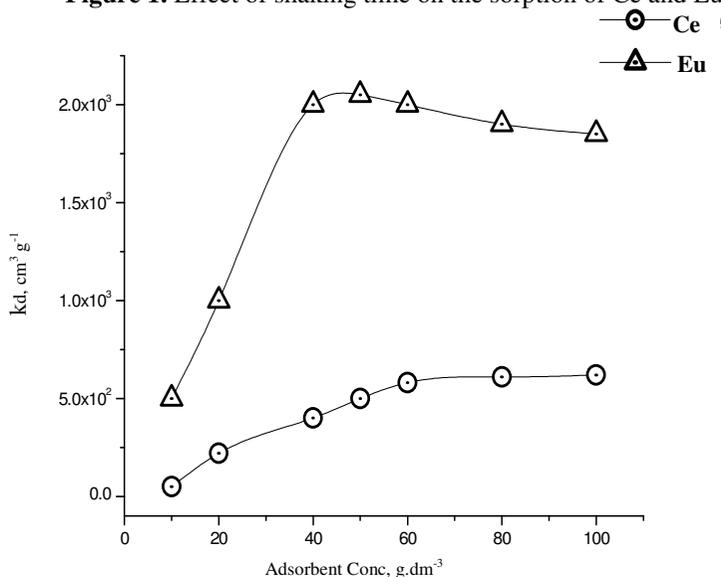


Figure 2. Variation of K_d of Ce and Eu with adsorbent concentration

Effect of metal ion concentration

Concentration effect for the adsorption of Ce(III) and Eu(III) on Clay was carried out by varying the adsorptive concentrations at 303 K and results of the uptake of Ce(III) and Eu(III) ions are shown in Figure 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 (Ce-Clay and Eu-Clay) 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 Ce(III) the concentration was varied between 3.37×10^{-6} to 3.33×10^{-4} mol dm^{-3} and for Eu(III) it was varied from 3.59×10^{-6} to 3.33×10^{-3} mol dm^{-3} . 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 adsorbents²⁰.

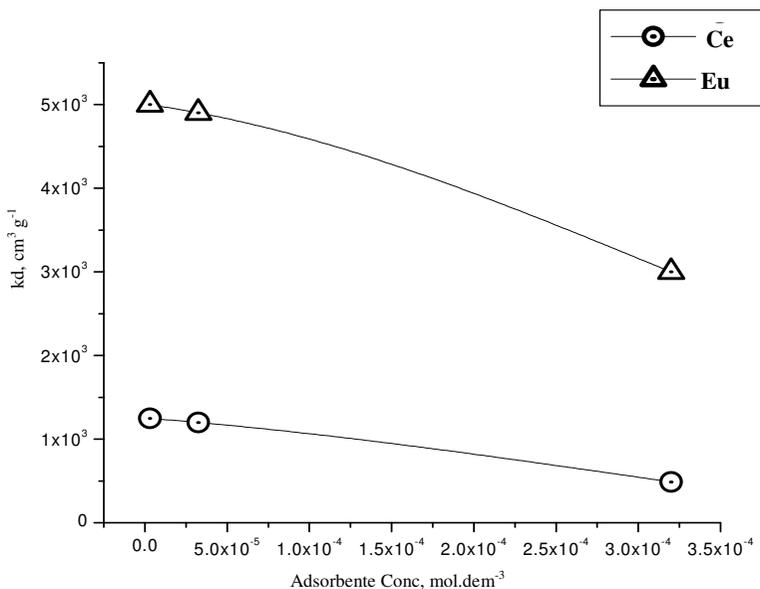


Figure 3. Variation of K_d with change in adsorbate concentration

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.

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

Here a_e and C_e are the amounts adsorbed (mol g^{-1}) at equilibrium and equilibrium bulk concentration (mol dm^{-3}) 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 $\log a_e$ vs. $\log C_e$ and straight lines were found for both the systems. These linear plots confirm about the monolayer coverage of ions at the surface of both adsorbents²¹. The value of $1/n$ and K were 0.953 and $2.81 \times 10^{-2} \text{ mol g}^{-1}$ (for Ce-Clay) and 0.842 and $4.46 \times 10^{-2} \text{ mol g}^{-1}$ (for Eu-Clay) system, respectively. 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 sites²⁰. 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 $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ at pH 7.52 (for Ce-Clay and Eu-Clay) systems. 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 sites²² 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:

$$\log (a_e - a_t) = \log a_e - k_1 \cdot t/2.303 \quad (2)$$

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 and 2. 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 Ce(III) ions on local clay

Temperature, K	Rate Constant $\text{min}^{-1} \times 10^2$	Energy of activation, kJ mol^{-1}	Enthalpy change kJ mol^{-1}	Entropy, $\text{kJ K}^{-1} \text{mol}^{-1} \times 10^2$
303	11.56			
313	12.34	9.11±0.04	17.72±0.04	8.64±0.03
323	12.97			
333	14.13			

Table 2. Thermodynamic parameter for adsorption of Eu(III) ions on local clay

Temperature, K	Rate Constant $\text{min}^{-1} \times 10^2$	Energy of activation, kJ mol^{-1}	Enthalpy change, kJ mol^{-1}	Entropy, $\text{kJ K}^{-1} \text{mol}^{-1} \times 10^2$
303	9.46			
313	10.24	10.46±0.08	10.06±0.03	7.46±0.04
323	10.87			
333	12.03			

The Arrhenius plots of $\log k_1$ vs. $1/T$ gave the activation energies for the adsorption process of Ce(III) on clay as 9.11±0.04 and on Eu on clay as 10.46±0.08 kJ mol^{-1} . These low values of activation energies for both the systems 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 ΔH^0 during the adsorption process has been evaluated using Van't Hoff equation (3);

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

Where K_D , ΔH^0 , R and T have their usual meaning. The values of ΔH^0 (at 303K) found from the slopes of straight lines obtained by plotting $\log K_D$ vs. $1/T$ are found to be 17.72 ±0.04 kJ mol^{-1} for Ce-Clay and 10.06±0.03 kJ mol^{-1} for Eu-Clay systems respectively. The positive value of ΔH^0 confirms the endothermic nature of the adsorption process²² and the numerical value indicates an ion exchange type mechanism²³ for the uptake.

Desorption study

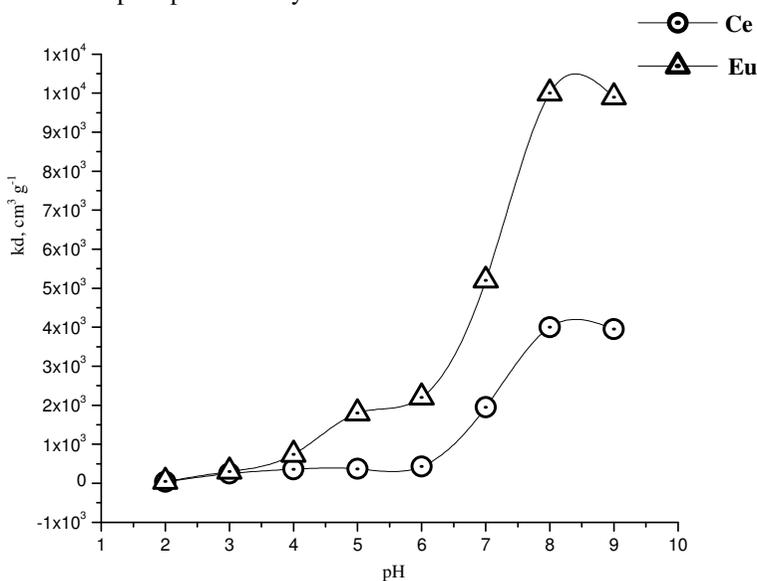
Clay with preadsorbed Ce(III) and Eu(III) was washed with double distilled water to ensure the removal of adhering species and subsequently the adsorbent was dried in an electric oven at 383K. The desorption of preadsorbed ions on these solid was studied in Ce(III) and Eu(III) solution ($1.0 \times 10^{-5} \text{ mol dm}^{-3}$) at different temperatures (*i.e.*, 303 to 333 K). The very low values of percentage desorption at different temperatures (*cf* Table 3) 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 3. Effect of time on the desorption of Cerium and Europium using 0.01 mol dm^{-3} CaCl_2 and water as desorbent

Fission Product	Time of Desorption, h	% Desorption 0.01 mol dm^{-3}	
		CaCl_2	Plain Water
Ce	1	1.04	0.51
	4	1.09	0.33
	24	1.11	0.46
Eu	1	0.57	0.42
	4	0.76	0.31
	24	0.82	0.30

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 $1.0 \times 10^{-5} \text{ mol dm}^{-3}$. Cerium(III) and Europium(III) occurs with its stable +3 oxidation state and exists with its various forms on varying the pH range 2-9 of solution (Figure 4). The sorption increased with pH in the both cases with relatively greater effect on Eu(III). Above pH 7 the uptake of the cations was almost complete. At lower pH lesser adsorption was due to completion of hydrogen ions with Eu(III) and Ce(III) for exchange sites. At higher pH hydrolyzed species are formed and are precipitated as hydroxides.

**Figure 4.** Effect of pH on the sorption of Ce and Eu

Conclusion

Clay was found to be effective in rapid and efficient removal of micro concentrations of Ce(III) and Eu(III) toxic ions from aqueous solutions. The adsorption process follows Freundlich isotherm with endothermic/irreversible nature.

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