Adsorption of $^{(152+154)}$Eu from Radioactive Waste Solution Using Modified Clay Polymer

M. Abdel Geleel[1], M.S. Sayed[2], and H.A. Omar[3]
[1]National Center for Nuclear Safety and Radiation Control, Cairo, [2]Radiation Protection Department, Hot Laboratory Center, [3]Radiation Protection Department, Nuclear Research Center, Atomic Energy Authority, Egypt
Magdass7@hotmail.com

Abstract: Removal of $^{(152+154)}$ Eu from it's liquid radioactive wastes using Aswan clay (C), Aswan clay/Polyacrylonitrile (C/P) and Polyacrylonitrile (PAN) was investigated. Factors affecting the polymer preparation as weight/ratio of clay to polymer, initiator percent (benzoyl peroxide) and temperature were tested. Characterization of the prepared matrices as surface area, swelling properties, FTIR and thermal properties were studied. The effect of pH, contact time, grain size, weight of the sorbent material and concentration of the initial adsorbent on the uptake percent of $^{(152+154)}$Eu from liquid radioactive waste were studied. The data followed the pseudo-first-order kinetic model. The equilibrium sorption data were described by the Langmiur and Freundlich isotherm models. The highest value of Langmiur maximum uptake Q_{max} was found to be 188.68, 155.58 and 70.92 mg.g^{-1} for C, C/P and PAN respectively. The capacity of C/P to adsorb $^{152+154}$Eu was also determined by column technique and found to be 50.66 mg/g. [Journal of American Science 2010;6(7):327-333]. (ISSN: 1545-1003).

Key words: Radioactive wastes/ $^{(152+15)4}$Eu/ Clay/ Polyacrylonitrile/ Adsorption

1. Introduction

Removal of long lived radionuclide from nuclear waste effluent is an important environmental concern in nuclear waste management. Environmental radioactive contamination can be caused by the accidental emissions from any stage of nuclear fuel cycle or fallout from nuclear testing(1). The sorption studies of radio contaminant on various materials were of great importance to evaluate the feasibility of using a particular material for waste treatment and disposal practices(2,3). $^{(152+154)}$Eu is an important nuclear fission products present in the radioactive waste effluents resulting from the reprocessing of the nuclear fuels. It was chosen due to its biotoxicity, long half–life, higher solubility in aqueous systems and the possible recovery from the waste solution(4). In principle, any solid material with a microporous structure can be used as an adsorbent e.g. clays, metal oxides or ash(5-7). Surface area, structure and low cost are some properties necessary to select the adsorbent matrix(8-10). Aswan clay C is available as a large deposits around the Egyptian deserts, this pale brown sedimentary clay consists principally of silica and alumina(11). The most common preparation methods for reactive polymers have included chemical conversion of the existing reactive groups as in the acrylonitrile by coplymerization and grafting (12, 13).

In this work, Aswan clay mixed with polyacrylonitrile is prepared and characterized by FTIR and TGA. The adsorption properties, including effects of pH, time and initial ion concentration on uptake of $^{(152+154)}$Eu were investigated. Batch and column techniques were used as application of the desired matrix to adsorb radioerupium.

2. Materials and Methods

Chemicals and reagents

All reagent used in this work of AR grade chemicals and were used without further purification. Europium was supplied as europium (lll) nitrate from Sigma Aldrich Company, USA. The $^{(152+154)}$Eu was prepared by irradiating europium nitrate in the Second Egyptian Research Reactor, E & R2 at Inshas site. Aswan clay was obtained from natural deposits at upper Egypt. The chemical composition of clay was recommended from Project of Arab Ceramic Company and give the following constituents SiO_2 55%, Al_2O_3 25.8%, Fe_2O_3 2.4% and CaO 1.28%.

Clay / Polymer matrix preparation

Different percents of Aswan clay C as (100, 90, 80,70and 60 %) were added to different percents of PAN as (0, 10, 20, 30 and 40 %) respectively. The best mixtures were chosen at constant weight (0.02 wt %) of benzoyl peroxide as initiator and at 55°C as constant preparation temperature to perform complete polymerization.

Characterization of the matrices

The specific surface areas of the studied matrices were determined using Nova SA instrument 3200. Swelling measurements were done by calculating the water uptake of a known weight of the prepared matrices. It was measured by immersing the samples in distilled water for at least two days. After wiping with a cleaning tissue, the samples were weighted as quickly as possible. This procedure was repeated three times until satisfactory reproducibility was achieved. The water uptake onto dry samples was calculated according to:

$$\text{Water uptake (\%)} = [(W_w - W_o)/ W_o] \times 100$$

Where: W_o, W_w are the weights of the dry and wet prepared samples, respectively.

A Fourier transform infrared (FTIR) spectrometer from Perkin Elmer 1600 was used to analyze the matrices in the wave number range 600 – 4000 cm^{-1}. Differential thermal analysis DTA and thermogravimetric analysis TGA were carried out by using TA 50 Shimadzu, Japan . Temperature was cycled at a constant rate of 10 ^oC/min from ambient temperature to 800 ^oC under nitrogen atmosphere.

Sorption kinetic measurements

Batch experiments with 315-500 µm were used to investigate parametric effects of the initial metal on the sorption process. Radio-europium samples were prepared by dissolving a known quantity of labeled Eu as stock solution. The kinetic behavior of Eu^{3+} on different matrices (C,C/P and PAN) were done by shaking the desired weight with 20 ml of 10^{-4}M of labeled europium (as LLW) in a polyethelyene vessels at speed 500 rpm in a thermoststic shaker for one hour at room temperature 25 ± 1^oC . Then a fixed value (2 ml) of the aliquot was pipetted out for determination of the amount of unsorbed radioeuropium. The activity of $^{(152+154)}Eu$ was determined radiometrically using NaI (Tl) scintillation detector. Sorption percentage (E %) of radioions removed from LLW were calculated from:

$$U\,\% = (A_i - A_e)/A_e \times 100$$

Where Ai and A_e are the activity of $^{(152+154)}Eu$ in solution initially and after equilibrium respectively.

The fixed bed column experiment was performed using a glass column of 1 cm diameter and 10cm long. 3gm of C/P matrix was transferred into the column with the aid of distilled water and adjusted at pH 7. The radioactive waste solution was then passed through the column with rate 1 ml/min. The effluent was collected in fractions (50 ml) for radioactive analysis.

3. Results and Discussion

Characterization of the studied matrices

The measured surface area of C, C/P and PAN were 281.59, 263.92 and 215.68 m^2g^{-1} respectively. Fig. (1) shows the swelling degree as a function of time and reach a certain limit after 60 min.. The maximum swelling degree reached by clay due to the presence of humic acid(14).

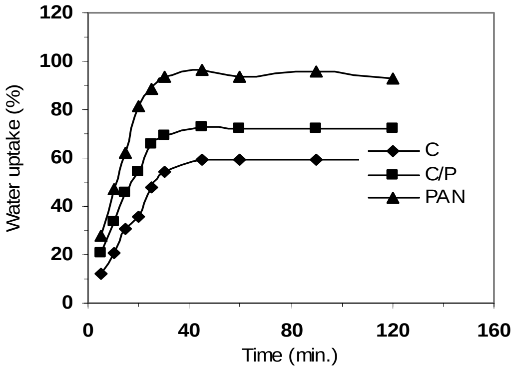

Fig.(1) Swelling behaviour of Aswan Clay (C), Aswan Clay/Polyacrylonitryle(C/p) and Polyacrylonitryl (PAN)

Understanding the mechanism of Eu^{+3} uptakes by C, PAN and C/P, infrared technique was used to evaluate the mechanism involved. Fig.(2) shows the IR spectra of the studied matrices, the main adsorption bands of C occurs at 3650, 1700 and 960 cm^{-1} due to the – OH stretching of the bonded OH groups of water molecule with intermolecular hydrogen bond(15). Vibration bands at 1100, 900 and 650 cm^{-1} due to SiO_2 and Al_2O_3 presents as a main constituent of clay. The main adsorption bands pf PAN cleared at 2900, 1600, 1500 and 800 cm^{-1} due to C=C, C=N, N-O and amine oxide respectively (16). IR spectrum of C/P shows more functional groups added to clay capable for forming more adsorption bonds.

Fig.(3) shows the DTA thermograms of the studied matrices. It was observed that a very small endothermic peak at 75-80 ^oC for C and C/P due to the dehydration process occurred by the libration of water molecules present in the samples (17). On continues heating up to 400 ^oC an exothermic peak was observed for PAN and C/P samples due to gasification and decomposition of the polymer(18). Table (1) shows the thermogravimetric analysis of the studied matrices at different temperature intervals. It was observed that continues weight loss for PAN and C/P with heating while C was approximately thermally stable up to 350^oC. From 350 – 550 ^oC a remarkable weight loss was observed for both PAN and C/P due to their thermal degradation(19).

Table (1) Thermogravimetric analysis of C, PAN and C/P

sample °C	C	PAN	C/P
Ambint-350	0.4	8	3
350 – 550	1	75	30
550 – 800	8	100	40

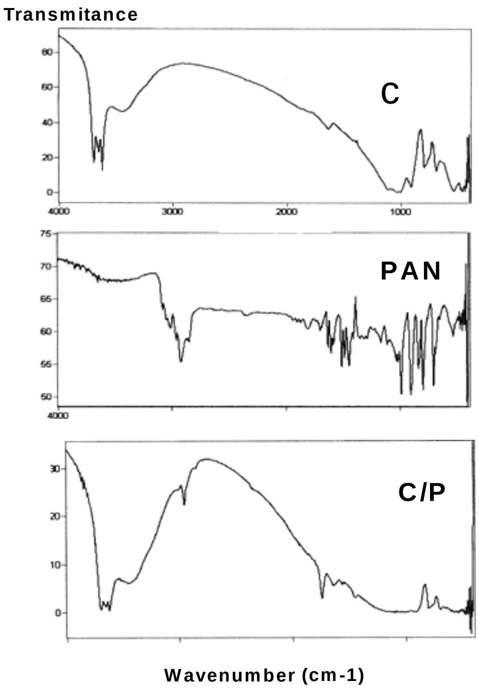

Fig. (2): IR spectra of C, PAN and C/P

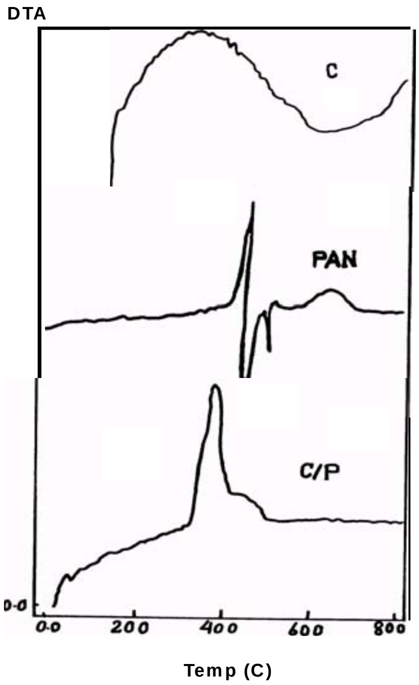

Fig.(3): DTA thermograms of C, PAN and C/P

Adsorption capacity of the studied matrices

Effect of pH

In Fig.(4), the uptake percent of Eu^{3+} by the studied matrices versus initial solution pH has been plotted. As can be seen europium ion uptake increases with increasing solution initial pH. At acidic initial pH <2, the uptake of Eu^{3+} ion was inhibited. This may be attributed to the increase of hydrogen ion concentration at this low pH which make repelling of Eu^{3+} ions from the surface of the adsorbrd matrices. At alkaline initial pH > 7, the uptake of Eu^{3+} ion was decreased due to starting of precipitation of Eu^{3+}. The highest uptake percent was observed at pH 7 (20).

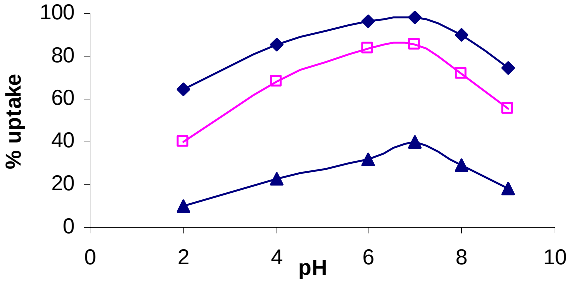

Fig.(4): Effect of pH values on the uptake of Eu^{3+} by C, C/P and PAN

Effect of contact time:

For an initial metal concentration around 1x 10^{-4} $molL^{-1}$, the results revealed that the uptake percent of Eu^{3+} ion at initial pH 7 by the studied matrices as a function of contact time seems to occur in two steps, Fig.(5). The first step increases rapidly within the first 30 minutes of contact, produce (90, 65 and 35%) adsorption for (C, C/P and PAN) respectively. The second step, produce the uptake of Eu^{3+} ion to about (95, 85 and 40 %) for (C, C/P and PAN) respectively, and attained equilibrium by the end of contact time period of 120 minutes. The rapid uptake of Eu^{3+} ions by either (C, C/P and PAN) may be due to adsorption or exchange of ions with some ions on the surfaces of the matrices(21). It should be noted that the diffusion of metal ions onto the clay lattice or polymer surface is a time dependant. Therefore, pseudo equilibrium is attained when the contact time is lengthened. Various models such as first–order, pseudo–first–order and pseudo–second order have been used to describe the kinetics of adsorption (22). The pseudo-first-order rate equation is the most widely used for the adsorption of a solute from a liquid solution. The rate constant of Eu^{3+} adsorption on (C, C/P and PAN) were determined using the pseudo-first-order rate equation (Lagergren rate equation) shown below:

$$\text{Log}\,(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303}\,t$$

Where K_{ad} is the Lagergren rate constant and q_e and q_t are the amount of $Eu3^{+}$ ion sorbed (mg/g) at equilibrium and at time t, respectively. The straight line plot of $\text{Log}\,(q_e - q_t)$ versus t for different matrices cleared in Fig. (6) indicate the applicability of the above equation to Eu^{3+} ion uptake on the studied matrices. The values of K_{ad} for uptake of Eu^{3+} ion on C and C/P were 0.068 min^{-1} and 0.0407 min^{-1} respectively.

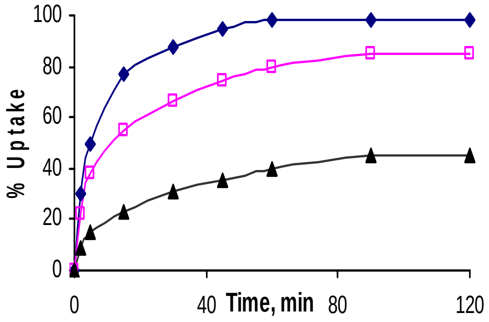

Fig. (5): Effect of shaking time on the uptake of Eu^{3+} by C, C/P and PAN

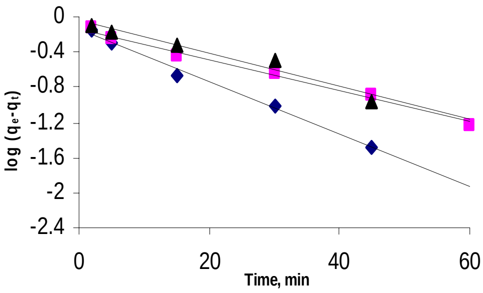

Fig. (6): Lagergren plot for uptake of Eu^{3+} on C, C/p, PAN

Effect of Sorbent Weight

The uptake of $^{(152+154)}Eu$ using (C, C/P and PAN) as a function of sorbent weight is shown in Fig. (7). Sorbent weight was varied from 0.02 gm to 0.2 gm. It is clear that, with increase of the sorbent weight the Eu^{3+} sorption percent increases and reached a constant optimum value in all cases (C, C/P and PAN). This increase is possibly due to the ease of exchange of the Eu^{3+} ion with the easily removed ions on the surface of the sorbent matrix.

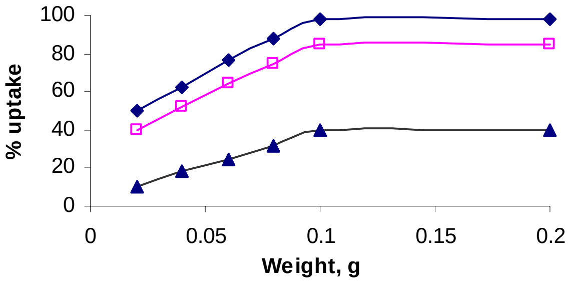

Fig. (7): Effect of dosage on the uptake of Eu^{3+} by C,C /P and PAN

Effect of Particle Sizes

The particle size effect was examined for two different particle sizes; >500 µm and 315-500 µm. Table (2) shows that both particle sizes can be compared with the uptake percent (98, 85 and 45 %) for (C,C/P and PAN) respectively at size 315-500 µm, while uptake percents was (92, 77 and 38 %) for the same matrices at size > 500 µm. So, it's cleared that Eu^{3+} uptake by the studied matrices particle sizes dependant. The smaller particle size matrix have more outer surface for contacting with the Eu^{3+} solution. Therefore, the size 315-500 µm was selected for all further studying

Table (2) Effect of particle size on Eu^{3+} uptake percent by C, C/P and PAN

Particle size	Uptake % C	 C/P	 PAN
315-500 µm	98	85	45
>500 µm	92	77	38

Effect of initial ion concentrations

The uptake of $^{(152+154)}Eu$ using the studied matrices as a function of different concentrations was investigated from $1x10^{-4}$ M to $2x10^{-2}$ M. The maximum uptake of Eu^{3+} about (95, 85 and 45 %) for (C, C/P and PAN) respectively. The Langmuir isotherm has been applied to many adsorption systems including organic(23) and inorganic(24) adsorbates. The batch equilibrium isotherm is fitted by both the Freundlich and Langmuir equations in the form:

$$\text{Log } q_e = \text{Log } K + 1/n \text{ Log } C_s \qquad \text{Freundlich}$$

$$C_s/q_e = 1/K_LQ_o + C_s/Q_o \qquad \text{Langmuir}$$

Where, Q_o (mg/g) is defined as the monolayer adsorbent capacity and K_L is Langmuir constant. C_s is the equilibrium concentration of europium ion in solution (mg/l). K and 1/n in Freundlich equation are constants related to the strength of adsorptive bond and heterogeneity factor respectively. Langmuir isotherm was found to fit only the concentration range of $1x10^{-4}$ to $1x10^{-2}$M of Eu^3. Fig. 9 shows the straight lines obtained for, C, C/P and C/PAN, when C_s/q_e is plotted versus C_s. The values of the constant K_L and Q_o are evaluated from the intercept and slope is represented in Table (3).

Fig. 8 shows the straight lines obtained, for C, C/P and C/PAN, when log q_e is plotted versus log C_s according to Freundlich equation. The values of the constants k and 1/n are evaluated from the intercept and slope and represented in Table (3). The value of 1/n lies between 0 and 1, the more heterogeneous the surface the closer value is to 0. The Freundlich equation was found to fit the data in the whole range of Eu^{3+} concentration(25).

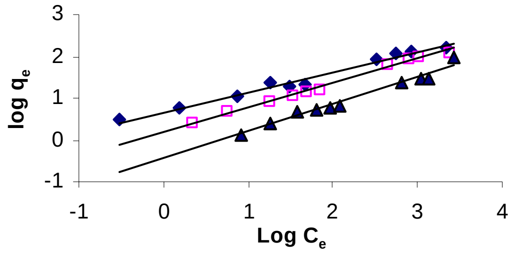

Fig. (8): Freundlich plot of Eu^{3+} sorption by C, C/P, PAN

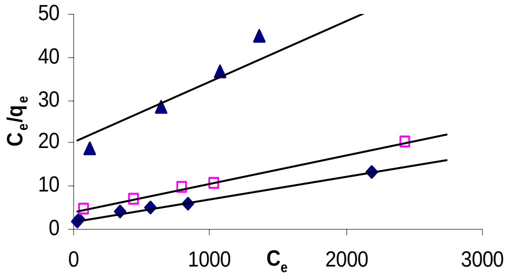

Fig.(9): Langmuir plot of Eu^{3+} by C, C/P, PAN

Table (3):Langmuir and Freundlich isotherm parameters of Eu^{3+} ion sorbed onto C, C/P and C/PAN

Sample	Langmuir Q_o(mg/g)	 K_L(mg/L)	 r^2	Freundlich K	 1/n	 r^2
C	188.68	0.003	0.997	4.62	0.48	0.982
C/P	153.85	0.001	0.999	1.58	0.58	0.992
C/PAN	70.92	0.007	0.938	0.36	0.65	0.977

Column Studies

Fig.(10) shows that 3gm of C/P matrix was used into the column, effluent and influent samples are collected after a regular interval. All the sorption experiments were carried out at the room temperature of 25 ±2 ◦C and initial pH of 7.0. The residual activity of $^{(152+154)}$Eu was determined radiometrically using NaI (Tl) scintillation detector. As the adsorbate solution passes through column, the adsorption zone (where the bulk of adsorption takes place) starts moving out of the column and the effluent activity start rising with time. This is termed as break point. The volume taken for the effluent activity to reach a specific breakthrough of interest is called the break though volume. The effluent activity (*C*) of $^{(152+154)}$Eu reached 50% of the feed solution (C_o). Breakthrough curve were plotted-giving ratio of effluent and feed (influent) activity (C/C_o) and volume, ml, for varying operating conditions.

Breakthrough capacity *Q*0.5 (at 50% or $C/C_o = 0.5$)

The maximum capacity under the condition of the experiment is calculated as 50.66 mg.g^{-1} (26). The column was regenerated using 1M HCl and sorption-desorption studies were carried out for five cycles.

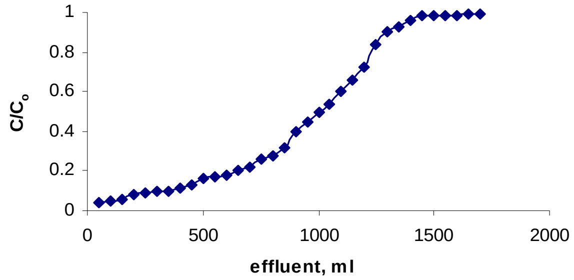

Fig. (10): Breakthrugh curve for Eu^{3+} on C/P

4. Conclusion

It could be generally concluded that the optimum condition of the preparation of clay/polymer ratio was C/P as 80:20, at weight percent of initiator was 0.02 and at temperature 55°C. The uptake percent of Eu^{3+} was 95, 85, 40 for C, C/P and PAN respectively, at pH 7, 120 min and 315-500 µm grain size. The rate constant of Eu^{3+} adsorption on C,C/P and PAN were determined using the pseudo-first-order rate equation (Lagergren rate equation). The Langmiur model is applicable in cases where only one molecular layer of adsorbate is formed at the adsorbent surface. Monolayer adsorption is distinguished by the fact that the amount adsorbed reaches a maximum value at a moderate concentration from 10^{-4} to 10^{-2}, this corresponds to complete coverage of the adsorbent surface by a monolayer of adsorbate. The simple Freundlich isotherm was able to describe the adsorption over all the concentration range used from $1x10^{-4}$ to $2x10^{-2}$ M. In Column tests, $^{(152+154)}$Eu removal by C/P reached about 100% and almost completely recovered with three to four times. Thus C/P matrix can be used to remove $^{(152+154)}$Eu as a heavy radioactive ion from aqueous wastes. Also coating the clay with PAN, avoiding the gel and swelling formation of the Aswan clay used.

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