Removal of Radioisotopes from Waste Solutions by Activated Carbon

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ABSTRACT
Removal of some radioisotopes namely $^{(152)}$*Eu and* ^{65}*Zn from radioactive solutions by activated carbon using both batch and column techniques has been performed. Experimental studies were conducted to evaluate and optimize the various process variables i.e., equilibrium time, carbon dose, solution pH. Sorption data have been interpreted in terms of both Freündlich and Langmuir isotherms. The fixed-bed results indicate the high capacity of the activated carbon for the removal of europium and zinc ions. The data suggest the possible use of activated carbon for the removal of these cations from radioactive waste solutions.*

Key Words: Activated carbon, Radioisotopes, Removal, Fixed bed, Simulated Waste.

1. INTRODUCTION

Liquid organic radioactive wastes typically include lubricating and hydraulic fluids from reactor operations, solvents and diluents from fuel reprocessing, scintillation fluids from analytical laboratories, dry-cleaning solvents and miscellaneous organic solvents from decontamination and decommissioning activities [1]. Aqueous radioactive wastes represent the main volume to be treated. The processes used, most extensively for the treatment of aqueous radioactive wastes, are based on chemical precipitation [2-4]; solvent extraction; ion exchange and adsorption. Many agricultural byproducts of cellulosic origin are available at very little cost and have been successfully utilized for metal ions adsorption since its cell wall is made of lignin, cellulose, hemicellulose, crude protein [5].

Activated carbons are used extensively as adsorbents of different compounds and have high removal capacity [6]. The objective of this research was to conduct a study of the sorption phenomenon of zinc and europium radioactive isotopes from aqueous solutions by commercial activated carbon after oxidation with 8M HNO_3 to improve its surface characters and enhance the uptake process.

2. EXPERIMENTAL

2.1. Tracers:

Radioactive isotopes of ^{152}Eu and ^{65}Zn were prepared by irradiation of highest purity grade metal oxides at the Iran Research Reactor at Tehran. Suitable weight (100 – 200 mg) of each target was wrapped separately in a high purity grade aluminum foil and placed in separate irradiation cans. Aqueous radioactive stock solutions were prepared by dissolving the irradiated metal oxides samples in concentrated HCl. The obtained acidic radioactive solutions of $EuCl_3$ or $ZnCl_2$ were neutralized by repeated evaporation/dissolution cycles using distilled water. The stock solutions were stored and diluted for each use [7].

2.2. Sorbent material:

Activated carbon used in this study was a commercial one provided by the AEOI. Commercial activated carbon was immersed in 8M HNO_3 for 24 h to increase the oxygen functional groups on the surface and improve the uptake process.

2.3. Sorption measurements:

The sorption of radioisotopes by activated carbon was carried out using a batch technique where 0.5g of carbon was contacted with 10 ml solution of 10^{-4}M radioisotope metal chloride. The amount carbon and the volume of aqueous solution in all sorption measurements were kept constant except where otherwise specified. In all cases, the pH of the solutions was adjusted using solutions of ammonium hydroxide and hydrochloric acid. The vials were shaken in a thermostat shaker bath at 25 °C. After different shaking periods, the radioactivities of the solutions were measured using a single channel analyzer supplied with a well-type NaI(TL) detector.

Three replicates were prepared in each case. In all cases, the activity was determined as a mean value after subtracting the background.

$$\text{Percentage uptake}: U(\%) = \frac{C_f - C_o}{C_f} \qquad \text{"eq. 1"}$$

2.4. Sorption isotherm studies:

The effect of carrier concentration on the adsorption of radioisotopes was studied under the optimized conditions of 90 min shaking time and v/m = 20 (v=10 ml and m= 0.5 g) at different concentrations, ranging from 10^{-2} to 10^{-4}M, of stock radioisotopes and sorption isotherm equations were applied.

3. RESULTS AND DISCUSSION

3.1. Sorbent material:

Characterization and FTIR-spectra of sorbent material are given in table 1 and Fig.1, respectively.

The FTIR transmittance spectra for treated HNO_3-oxidized carbon are shown in Fig.1. The FTIR bands can differentiate into three ranges of spectra: 4000-2000, 2000-1300, 1300-800cm^{-1}. The first is usually assigned to dehydration and aliphatic units, mostly free O-H, hydrogen bonded O-H, absorbed H_2O, symmetric and asymmetric stretching in C-H, -CH_2 or CH_3 bonds. The second range comprises the most important oxygen functionalities characterized by the presence of C-O and N-O containing structures. Absorption within the third range, which appears within 1300-1000 cm^{-1} as a broad band, is currently assigned to various C-O single bonds such as those in ethers, phenols and hydroxyl groups. Shoulder bands at lower wave numbers (830cm^{-1}) might be related to an out-of-plane bending mode in aromatic structures.

In the first and third absorption ranges, only small changes are observed in the spectra of carbon, which might be associated with the varying water contents and eventual changes in, aliphatic to aromatic structures. The most characteristic changes appear particularly within the central range of 1820-1300cm^{-1}. For the HNO_3-oxidized carbon the characteristic vibration of unionized and uncoordinated carboxyl is shown as a strong peak of COO^- stretching at 1720cm^{-1} and a shoulder of OH deformation vibration at 1455cm^{-1}.

3.2. Factors Affecting the Adsorption Process:

3.2.1. Effect of contact time:

Fig.2 shows the variations of percentage adsorption with contact time. The adsorption increases with increasing shaking time and attains equilibrium nearly after 90 min. Therefore, 90 min shaking time was selected for all further studies.

3.2.2. Effect of solution pH:

The removal of metal ions from aqueous solution by adsorption is highly depending on pH of the solution, which affects the surface charge of the adsorbent and the degree of ionization and speciation of adsorbate 13. The percentage adsorption increases with increasing pH up to 4.2 for Eu^{3+} and (6-7) for Zn^{2+}, then starts decreasing with further rise in pH as shown in Fig.3. This may be attributed to the formation of hydroxocomplexes.

3.2.3. Carbon dose:

Effect of adsorbent weight on the sorption process of the investigated radioisotopes was shown in Fig. 4. It was found that the % removal of both radioisotopes increased with increasing the amount of adsorbent up to 0.5 g and stays nearly constant with no significant increase in % removal.

3.3. Isotherm studies

The simple Freündlich isotherm was able to describe the adsorption over all the concentration range used according to the equation:

$$Log\ q_e = log\ A + 1/n\ log\ C_e \qquad "eq\ 2"$$

where, q_e is the amount of Eu^{3+} and Zn^{2+} ions sorbed per unit weight of activated carbon (mg/g) and Ce is the equilibrium concentration of Eu^{3+} and Zn^{2+} ions in solution (mg/l), A and 1/n are constants related to the sorption capacity and intensity of the sorbent, respectively. From Fig.5 the constants A and 1/n were respectively evaluated from the intercept and slope. The values of A, 1/n and r for activated carbon are represented in Table 2. It was found that the slope value ranges between 0 and 1. It can be concluded that the sorption of the investigated elements takes place through the formation of a single monolayer of the sorbed species. The Freundlich equation was found to fit the data in the whole range used of Eu^{3+} and Zn^{2+} concentrations.

The Langmuir isotherm was applied for the sorption equilibrium of activated carbon:

$$Ce/q_e = 1/bQ_o + C_e/Q_o \qquad "eq\ 3"$$

where, C_e is the equilibrium concentration (mg/l), q_e is the amount of sorbed metal per unit weight of sorbent material at equilibrium (mg/g), and Q_o and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. Linear plots of C_e/q_e vs C_e show that the adsorption obeys the Langmuir isotherm model for activated carbon Fig. 6. The correlation coefficients, Qo and b were determined from the Langmuir plots and tabulated in Table 3. The higher fractional value of 1/n [0< (1/n) <1] signifies that strong adsorptive forces are operative on the surface of activated carbon.

3.4. Fixed-bed Experiment:

A fixed-bed sorption experiment was carried out, and the ratio of the concentration of effluent to that of influent (C/C_o) vs. volume as shown in Fig.7. The breakthrough occurred in the beginning of the experiment, and the column reached saturation at 2500 ml. The fixed-bed result indicates the high capacity of the activated carbon for the removal of europium and zinc ions. In this experiment, a column with height of 160 mm, diameter of 25 mm and contains 3g of activated carbon was used with flow rate of 1ml/1min. Fixed bed experiments carried out under optimum conditions (10^{-4}M solution, pH 4.5 for Eu^{3+} and 6 for Zn^{2+}). The results show, the effluent solutions is initially europium and zinc ions free until a certain (breakthrough point) is attained when ions appears in the effluent in concentration which increase with the increase of the effluent until a maximum is reached at which the carbon samples are fully loaded. The maximum ions capacity under the conditions of the experiment can be easily estimated from Fig.7 and was found to be 7.49 and 6.5 $mg.g^{-1}$ for Eu^{3+} and Zn^{2+}, respectively according to the equation:

$$Breakthrough\ capacity = V50\%.\ Co\ /\ m \qquad "eq\ 4"$$

where V50% is the volume at 50%, Co initial concentration of ions and m is the amount of the bed material.

4. CONCLUSION

It was found that adsorption of zinc and europium from liquid solutions by activated carbon has been shown to depend on the pH, carbon dose and contact time. The adsorption of these radionuclides can be represented by both Freundlish and Langmuir adsorption isotherms. It can be concluded that this activated carbon can be utilized for removal of radioisotopes from waste solutions.

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Table 1 Physico-chemical characterization of activated carbon

pH	Carboxylic group m equiv/g	Phenolic group m equiv/g	Total acidity	Phenol No. mg/g	Iodine No. mg/g	Surface area m^2g^{-1}
4.6	2.94	0.006	2.83	82.7	528	750

Table 2 Freündlich isotherm parameters of Zn^{2+} and Eu^{3+} uptake by activated carbon

Samples	A	1/n	r^2
Eu^{3+}	0.61	0.55	0.991
Zn^{2+}	0.32	0.60	0.994

Table 3 Langmuir isotherm parameters of Zn^{2+} and Eu^{3+} uptake by activated carbon

Samples	bQ_o	b	Q_o mg/g	r
Eu^{3+}	0.217	0.011	18.41	0.966
Zn^{2+}	0.160	0.014	11.33	0.958

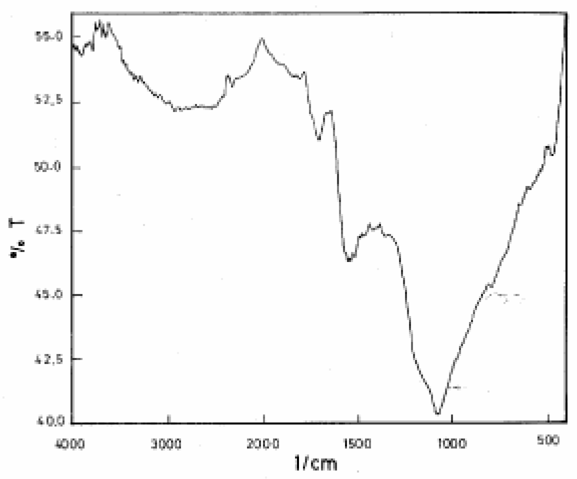

Fig.1 FTIR spectra of activated carbon

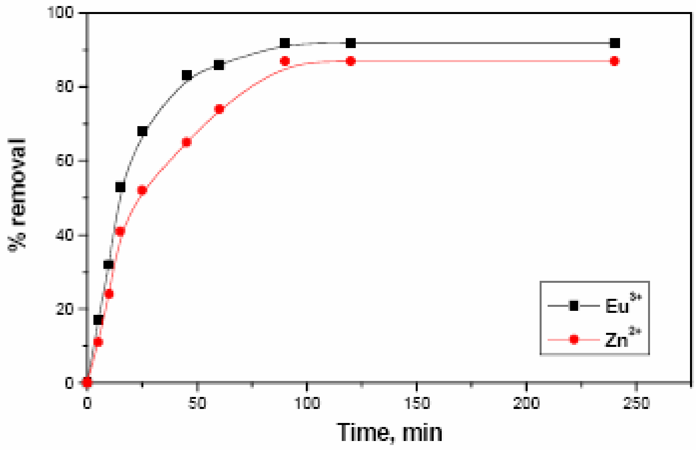

Fig. 2 Effect of contact time on the removal of Eu^{3+} and Zn^{2+} by activated carbon

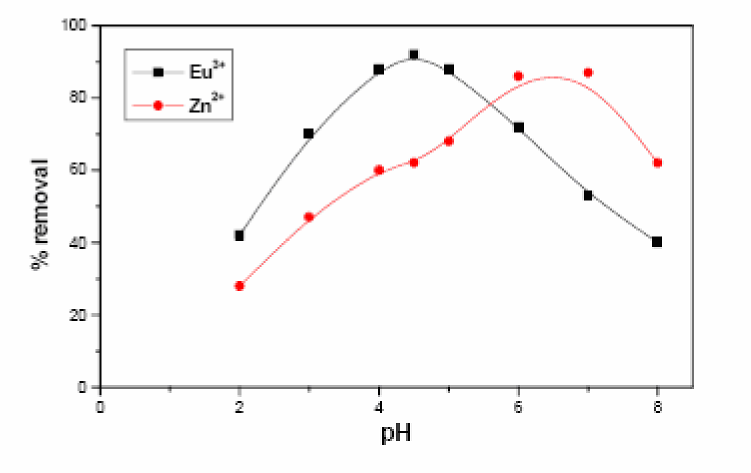

Fig. 3 Effect of pH value on the removal of Eu^{3+} and Zn^{2+} by activated carbon

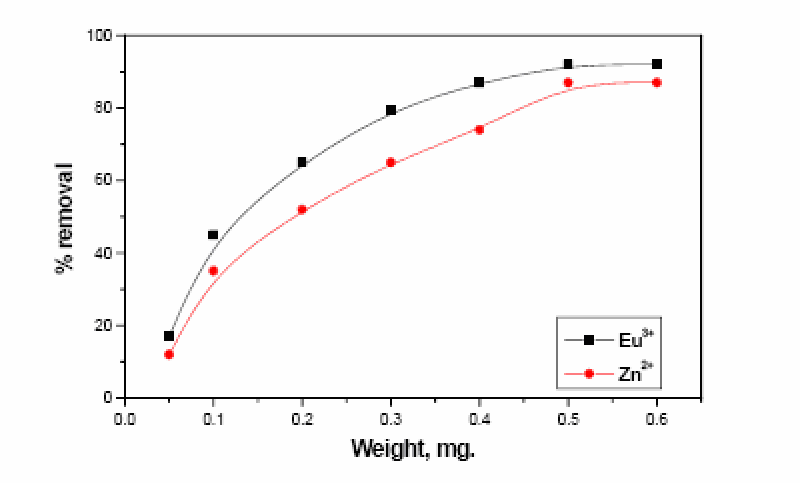

Fig. 4 Effect of mass on the removal of Eu^{3+} and Zn^{2+} by activated carbon

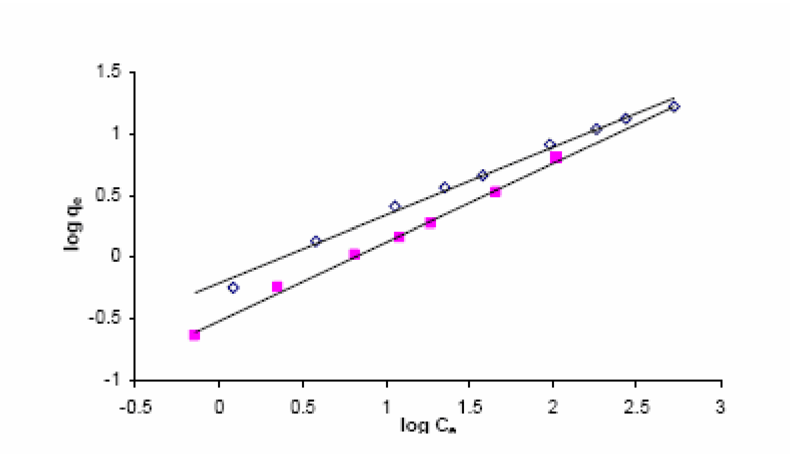

Fig. 5 Freunlich plot of Eu^{3+} and Zn^{2+} by activated carbon

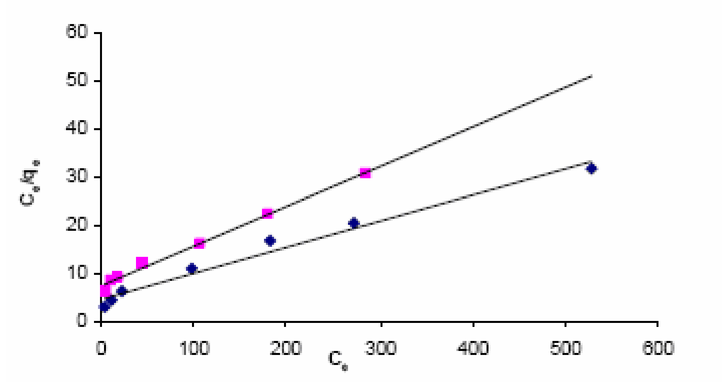

Fig. 6 Langmuir plot of Eu^{3+} and Zn^{2+} sorption by activated carbon

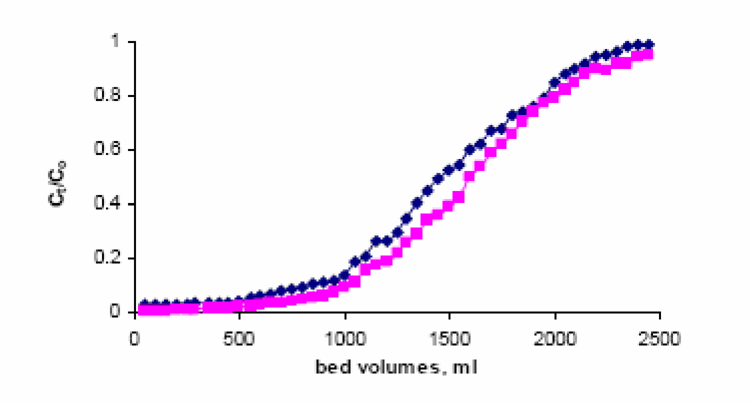

Fig. 7 Breakthrough curve of Eu^{3+} and Zn^{2+} uptake by activated carbon