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# Use of activated carbon in removal of some radioisotopes from their waste solutions

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**Abstract**

Removal of some radioisotopes namely $^{(152+154)}$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.


*Keywords:* Activated carbon; Removal; Waste solutions; Radioisotopes

## 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].

$^{(152+154)}$Eu has been released in the environment by global fallout following atmospheric nuclear explosions; by nuclear waste discharges and by fallout from nuclear accidents [2]. On the other hand, $^{65}$Zn may be found in process waste water from nuclear instillation and institutes which utilize radioisotopes. This water is generally produced in large volumes (about 500,000 gallon/day in large plants). It usually consists of drinking water that contains traces of radioactive isotopes, small amounts of laboratory chemicals, cleaning substances and organic compounds [3].

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 [4–6]; solvent extraction [7,8]; ion exchange [9,10] and adsorption [11].

Activated carbon is one of the most popular adsorbents of the removal of metal ions from aqueous solution and has high removal capacity [12,13], although other materials have been used such as Peanutskins [14], melon seed husks [15], onion skin [16], teas leaves [17], Snail ash [18] and some other agricultural byproducts [19].

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 8 M $HNO_3$ to improve its surface characters and inhance the uptake process.

## 2. Experimental

### 2.1. Tracers

Radioactive isotopes of $^{152+154}$Eu and $^{65}$Zn were prepared by irradiation of highest purity grade metal oxides at the Egyptian Research Reactor at Inshas. Suitable weight (100–200 mg) of each target was wrapped separately in a high purity grade aluminium 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

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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 number (mg/g) | Iodine number (mg/g) | Surface area ($m^2\ g^{-1}$) |
|---|---|---|---|---|---|---|
| 4.6 | 2.94 | 0.006 | 2.826 | 82.7 | 528 | 750 |

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 [20].

### 2.2. Sorbent material

#### 2.2.1. Activated carbon

Activated carbon used in this study was a commercial one provided by the international office for trade service (Cairo).

#### 2.2.2. Oxidation process

Commercial activated carbon was immersed in 8 M $HNO_3$ for 24 h to increase the oxygen functional groups on the surface and improve the uptake process. The presence of both oxygen and nitrogen containing surface functionalities significantly increased the adsorption capacity of radioisotopes [21].

### 2.3. Sorption measurements

#### 2.3.1. Batch technique

The sorption of radioisotopes by activated carbon was carried out using a batch technique where 0.5 g of carbon was contacted with 10 ml solution of $10^{-4}$ M radioisotope metal chloride to quantify the sorption capability of activated carbon towards the removal of high concentrations of the investigated radioisotopes. The amount of 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 298 K. 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.

$$\text{Percentage uptake } U(\%) = \left(C_0 - \frac{C_e}{C_0}\right) \times 100 \quad (1)$$

where $C_0$ is the initial concentration and $C_e$ is the concentration at equilibrium.

#### 2.3.2. Continuous flow experiments

Continuous flow experiments were carried out using a column of 160 mm height, 15 mm diameter and packed with 3 g of activated carbon on a glass wool support. The column was conditioned with 100 ml of deionized water prior to a $10^{-4}$ M concentration of the investigated radioisotopes ($^{65}Zn$ and $^{152+154}Eu$) being percolated downwards by maintaining constant levels of effluent over the bed. Pump was employed to control the flow rate at 1 ml/min at $25 \pm 1\ ^\circ C$. Samples of the effluent were collected and their radioactivity levels were measured.

### 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 and 1300–800 $cm^{-1}$. 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

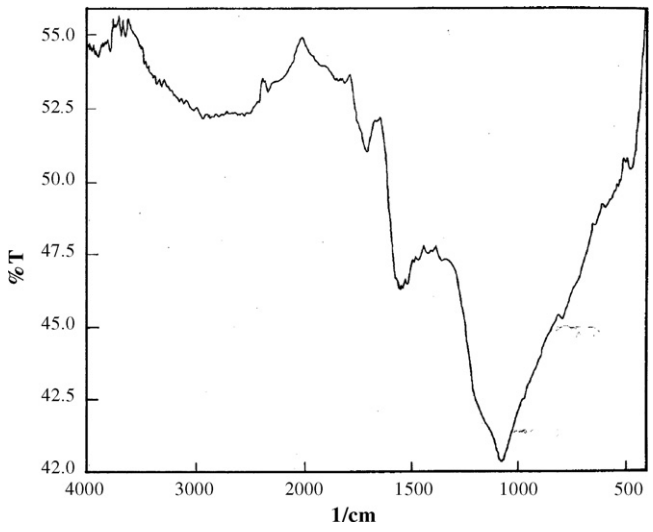


Fig. 1. FTIR-spectra of activated carbon.

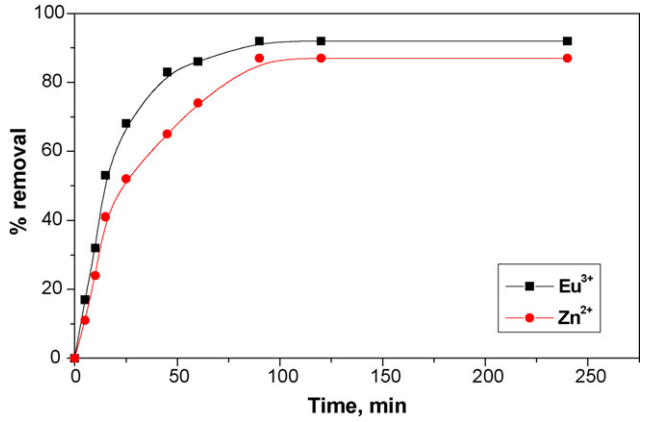


Fig. 2. Effect of contact time on the removal of $Eu^{3+}$ and $Zn^{2+}$ by activated carbon.

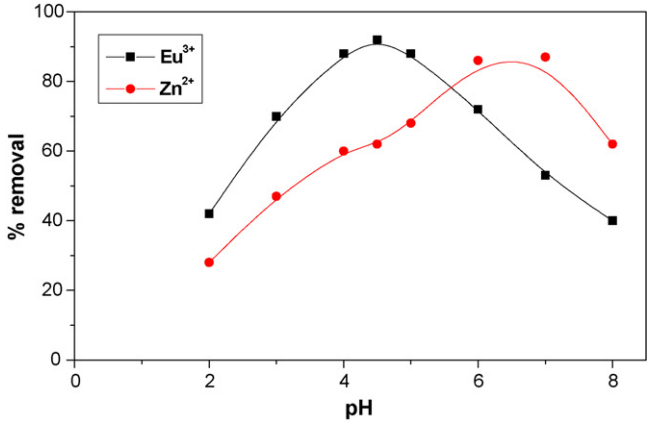


Fig. 3. Effect of pH value on the removal of $Eu^{3+}$ and $Zn^{2+}$ by activated carbon.

lower wave numbers ($\geq$830 $cm^{-1}$) 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 1820–1300 $cm^{-1}$. For the $HNO_3$-oxidized carbon the characteristic vibration of unionized and uncoordinated carboxyl is shown as a strong peak of $COO^-$ stretching at 1720 $cm^{-1}$ and a shoulder of OH deformation vibration at 1455 $cm^{-1}$ [22].

### 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. Similar results have previously been reported [23].

#### 3.2.2. Effect of solution pH

The removal of metal ions from aqueous solution by adsorption is highly dependent on pH of the solution, which affects the surface charge of the adsorbent and the degree of ionization and speciation of adsorbate. 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 [24].

#### 3.2.3. Carbon dose

Effect of adsorbent weight on the sorption process of the investigated radioisotopes is 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 stay nearly constant with no significant increase in % removal. This was proved by Daifullah and Moloukhia [25].

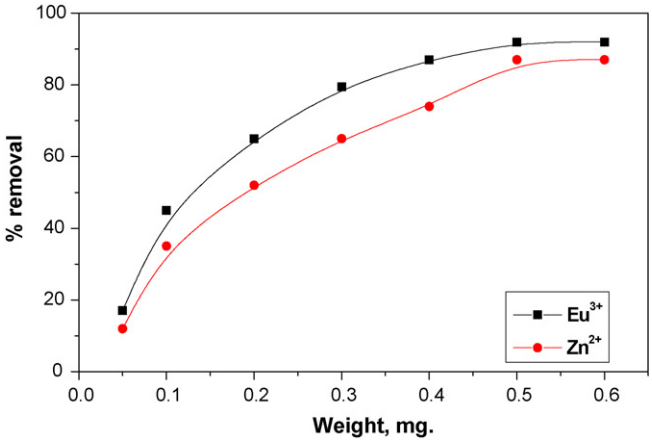


Fig. 4. Effect of mass on the removal of $Eu^{3+}$ and $Zn^{2+}$ by activated carbon.

### 3.3. Isotherm studies

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

$$\log\ q_e = \log\ A + \frac{1}{n}\log\ C_e \qquad (2)$$

where, $q_e$ is the amount of $Eu^{3+}$ and $Zn^{2+}$ ions sorbed per unit weight of activated carbon (mg/g) and $C_e$ 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

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 |

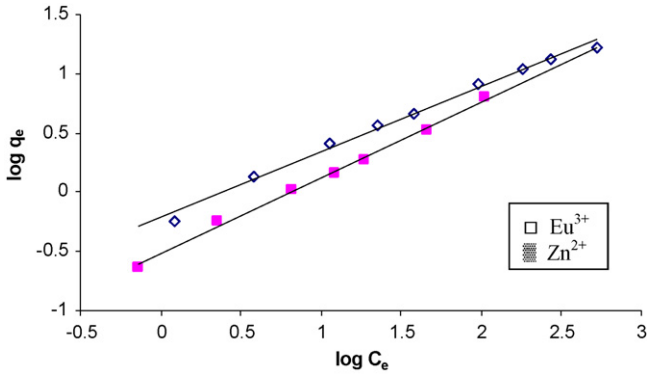


Fig. 5. Freündlich plot of $Eu^{3+}$ and $Zn^{2+}$ sorption by activated carbon.

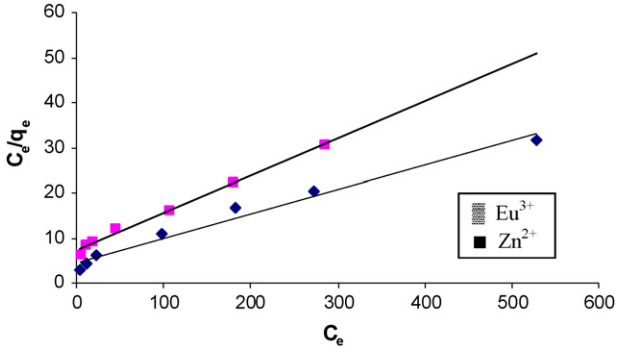


Fig. 6. Langmuir plot of $Eu^{3+}$ and $Zn^{2+}$ sorption by activated carbon.

place through the formation of a single monolayer of the sorbed species. The Freündlich equation was found to fit the data in the whole range of $Eu^{3+}$ and $Zn^{2+}$ concentrations tested.

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

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (3)$$

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 $Q_0$ 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, $Q_0$ 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. This is in agreement with Monser and Adhoum [23].

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

| Samples | $bQ_0$ | $b$ | $Q_0$ (mg/g) | $r$ |
|---|---|---|---|---|
| $Eu^{3+}$ | 0.217 | 0.011 | 18.41 | 0.966 |
| $Zn^{2+}$ | 0.160 | 0.014 | 11.33 | 0.958 |

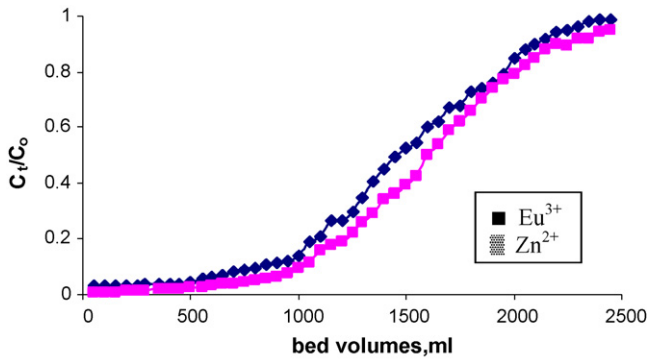


Fig. 7. Breakthrough curve of $Eu^{3+}$ and $Zn^{2+}$ uptake by activated carbon.

### 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 ($C/C_0$) vs. volume is shown in Fig. 7. The breakthrough occurred in the beginning of the experiment, and the column reached saturation at 2500 ml. Continuous flow experiments were carried out using a column of 160 mm height, 15 mm diameter and packed with 3 g of activated carbon on a glass wool support. Pump was employed to control the flow rate of 1 ml/min at $25 \pm 1$ °C. Optimum conditions were adjusted at $10^{-4}$ M concentration of the investigated cations, pH 4.5 and 6 for $Eu^{3+}$ and $Zn^{2+}$, respectively. The maximum ions capacity under the conditions of the experiment can be easily estimated from Fig. 7 and was calculated and found to be 7.49 and 6.5 mg $g^{-1}$ for $Eu^{3+}$ and $Zn^{2+}$, respectively according to the equation:

$$\text{breakthrough capacity} = V_{50\%}\frac{C_0}{m} \quad (4)$$

where $V_{50\%}$ is the volume at 50%, $C_0$ initial concentration of ions and $m$ is the amount of the bed material. Similar results have previously been reported [26].

## 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 Freündlich 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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