

## **PREPARATION OF EXTRA-BARRIER OPERATES AS SORBENT MATERIAL FOR LOW AND INTERMEDIATE-LEVEL OF RADIOACTIVE DISPOSAL SITE**

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### **ABSTRACT**

The safety of the repository, during and after institutional control period, can be improved by a liner acts as an extra-barrier. The liner will be built at known distance from the site and in lower depth than the repository. This liner has the capability to decrease the quantity of migrating radionuclides from the site. This work presents a simple and in-expansive method for reduce the mobility of cerium, strontium and cesium radionuclides. The material used as a liner is a mixture of charcoal, cellulose acetate and sand soil. A series of tests will perform to evaluate the physical and chemical properties of the liner material. The physical properties of greatest interest were the dry density, the porosity and the permeability. On the other hand, the particle size, pH, and the liner thickness. Based on the results of these tests optimum liner specifications will be select.

*Key Words: Radioactive Waste/Liner/ Barrier/Sorbent/Charcoal/Cellulose-Acetate/disposal*

### **INTRODUCTION**

The safe site for radioactive waste disposal is the site that has geological and hydrological characteristics, and its engineered barriers ensure complete isolation of the radioactive wastes from reaching the environment (biosphere). However, practically, there is no perfect site exist can offer this complete isolation of waste from the environment.

In Egypt, low and intermediate radioactive wastes will be disposed in four reinforced vaults in Inshas site. Hydrogeologically, from the geoelectrical and test holes of the area, the absolute level of the ground water ranges from 12.5 to 13m above the sea level which coincide with the level of the surface water at Inshas<sup>(1)</sup>. This fact indicates that the groundwater at Inshas is connected with the Ismailia canal (Nile water). The direction of groundwater flow is regionally towards the NW i.e. towards Ismailia Canal. Ismailia Canal is the main source of the recharge. The control and surveillance period of the site (the institutional control) is planned to be 100 years. This period of time is selected based on the type of radioactive disposed, the site characteristics, and the disposal structure.

On the other hand, the disposal structure can fail before the institutional control. The presence of sulfur and/or chlore elements in the soil can deteriorate the reinforced structure of the vault. Additionally, the reinforced concrete can be attack biologically by the bacteria exist<sup>(2)</sup>.

Also, the presence of iron waste containers can increase the possibility of container corrosion and the buildup of undesirable gases. Heat generated by radioactive decay of the waste can increase the rate of gas formation. Hydrogen gas formed by corrosion of iron will partly dissolve in the pore water of the surrounding area and diffuse out to the mobile groundwater. Gas would escape readily through a fractured concrete or porous cement backfill, but if there are no fractures, then pressure buildup may actually contribute to fracture development. And then these gases can contribute in the earlier failure of disposal structure<sup>(3)</sup>.

In this case, an additional engineered barrier, as a liner, should be considered to withstand this situation by reducing any radioactive release from the vaults. Liners may be used at mines beneath tailings impoundments, heap leach pads, water reservoirs, rock piles, or wherever the mine needs to limit seepage to the ground and hence protect groundwater quality.

Selection of liner material is dictated by a variety of factors; such as local regulations and authorization criteria, the nature of the waste, the local geology and hydrology, and the results from performance assessments of the disposal facility, and finally the funds available.

### **Aim of the study**

The objective of the study is providing an additional effective barrier beneath the burial site to protect the environment in case of an earlier failure of disposal structure. To assist this selection, specific data are required as key properties for the preparation of this barrier; strength, permeability, sorption capacity, and effect of radiation on the crystal structure of the barrier material.

The minimum requirements specified by RCRA<sup>(4)</sup> require that—to protect public health and the environment—a barrier must:

- Minimize liquid migration
- Minimize maintenance
- Have permeability equal to or less than the permeability of the natural subsoil
- Account for freeze/thaw effects
- Accommodate settling and subsidence so that the barrier's integrity is maintained.

## **EXPERIMENTAL**

### **Materials and reagents**

All the chemicals employed were of analytical grade and used without further purification. Cesium chloride (CsCl), Strontium Chloride( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ) and Cerium Nitrate [ $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] were obtained from WINLAB Laboratory chemicals U.K. Cellulose acetate and Charcoal activated were obtained from Fluka Chemika GmbH comp. and ADWIC Nasr pharmaceutical chemical comp, Egypt respectively, while sand soil was obtained from Inshas site. The chemical materials were dissolved in ground water. The ground water used was obtained from a well at Inshas site near from the disposal facility. The pH values were adjusted by using dilute solution of HCl and NaOH.

### **Preparation of the liner material**

The liner selected, as an additional effective barrier, should act as a sorbent material for elements that may be exist in the possible leachate from the disposal site. Also, it should have the capability of gases absorption.

The use of charcoal as an adsorbent, like most of its other applications, has a very long history to adsorb vapors and gases. Additionally the adsorptive properties of charcoal have been proved. There were still relatively few applications for charcoal as an adsorbent. Therefore, the use of charcoal is of enormous importance in the purification of water and air<sup>(6)</sup>.

Cellulose is the most abundant natural polymer. The cellulose structure shows a chain-like extended linear macromolecule of anhydro-D-glucopyranose units linked at the 1 and 4 positions by glycosidic bonds. The empirical formula of cellulose is  $(C_6H_{10}O_5)_n$ . The use of cellulose together with its derivatives has wide spread. Cellulose derivatives (cellulosics) come in all forms and structures. The hydroxyl groups of cellulose can be partially or fully reacted with various reagent to afford derivatives with useful properties. Cellulose esters and cellulose ethers are the most important materials. Among the esters are cellulose acetate.

Cellulose acetate is used to improve the sorption property of the charcoal. And then to increase the capability and capacity of the liner used<sup>(5)</sup>.

On the other hand, the mixture of charcoal and cellulose acetate shows poor permeability for water. That can affect the stability of area surrounding the disposal site and increase the rate of dissolved elements. Therefore, sand soil is added to the mixture to increase the permeability. Sand soil used is from the same area.

Various parameters, which can affect the behavior of the liner as sorbent material, are studied such as:

- a) Effect of sand particle size
- b) Effect of sand weight
- c) Effect of pH
- d) Effect of temperature
- e) Effect of contact time
- 1- Effect of element (Cesium, strontium, and cerium) concentration

### **Measurements**

The concentrations of the metal ions were measured with atomic absorption spectrophotometer. The results were recorded for the different concentrations after proper calibration of the equipment. The pH values of the buffer solutions were determined with a pH meter (Beckman, Beckman Instrument). The ground water was analysis by using

### **Sand particle size analysis**

A particle size analysis was performed on the sand which was subsequently used for tests to measure the physical properties of sand-cellulose acetate-charcoal mixture. These mixtures were studied as candidate extra-barrier (linear adsorbent material) for low and intermediate low level radioactive waste disposal repository.

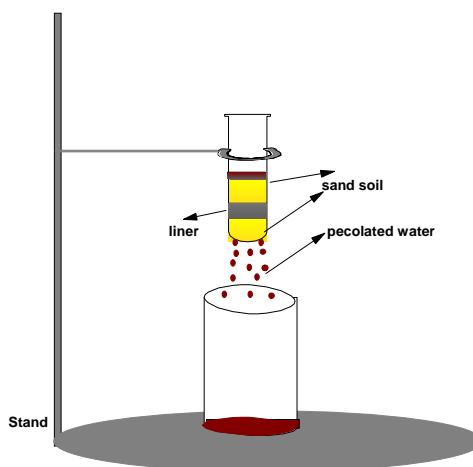
The particle size analysis was performed as described in the ASTM method<sup>(2)</sup>. The main steps of this method are: The soil sample was dried over night at 110 °C in drying oven (Gravity Convection Oven Model 18 EG) and sieved with a sieve (VEB MLW LABORATECHNIK Model) to obtain six samples with different particle size (0.63 mm, 0.4 mm, 0.315 mm, 0.25 mm, 0.2 mm and 0.09 mm) denoted as C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub>. Different weight from each sample (1, 2, 3, 4, and 5 g) mixed with 0.25 g cellulose acetate (CA) and 1 g charcoal.

### **Sorption procedures**

Aqueous standard solutions of cesium, strontium and cerium were prepared by dissolving an accurately weight amount of the relevant salts in deionized water so as to yield a metal ion concentration 1000 ppm. Appropriate aliquots were taken from these standards for subsequent dilution for various concentrations. The adsorbent materials were placed in a plastic container between two layers of soil samples as shown in the figure. The base of these containers is perforate to allow the percolation of water. A 20 ml of the aqueous solution were added to the container and it passed downward through the prepared adsorbent linear. Samples of the decanted were collected and analysis by using atomic absorption spectrometry. The uptake percent, R, was calculated according to:

$$R = (C_0 - C_e) / C_0 * 100$$

Where R is the percentage uptake,  $C_0$  is the initial concentration (ppm) and  $C_e$  is the decanted concentration (ppm).



## RESULTS AND DISCUSSION

The weight of sand retained on each sieve, according to the particle size analysis of the sand, is recorded in Table 1. From this table, it is clear that the weight retained decreases from 267.4 g to 3.2 g with the decreasing of the mesh size. This reveals that the sand soil in inshas site is characterized by coarse particles.

**Table -1.** Particle size analysis of sand soil

Mesh size	Weight retained on the sieve (g)	Weight passing from the sieve (g)	% of weight passing
0.63	267.3588	732.6412	73.26412
0.4	327.0021	405.6391	40.56391
0.315	172.6763	232.9628	23.29628
0.25	83.562	149.4008	14.94008
0.2	51.2556	98.1452	9.81452
0.09	67.805	30.3402	3.03402
0.071	3.2303	27.1099	2.71099
Remaining	5.5213	21.5886	2.15886

### Effect of cellulose acetate additive on the adsorption process

In order to enhance the sorbent materials different amount of cellulose acetate added to 1g charcoal and 1 g sand. The effect of cellulose acetate, as an additive, on the adsorption of cesium was studied within range 0.05-0.35 g cellulose acetate and the results are represented in Fig.(1). From this figure it's clear that, with increasing the weight of CA the uptake of cesium increased up to 0.15 g and then it tended to level off. This may be due to the presence of active group on the structure of CA, and also the presence of acetate group that enhance the adsorption process. A selected weight of 0.25 g was chosen as a suitable weight for all metal ions studied.

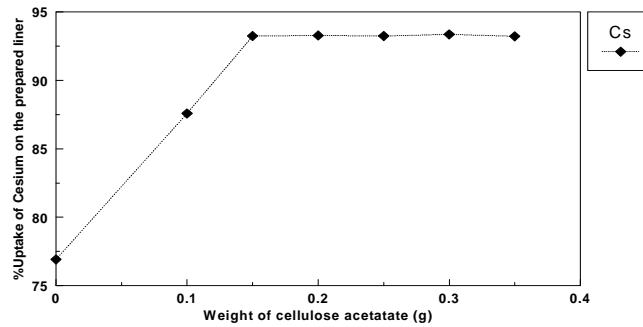


Fig1. Effect of the weight of the cellulose acetate

### Effect of weight of sand on the adsorption process

Different weights of sand soil in the preparation of the liner were studied to select the optimum conditions of the liner. Fig. (2) shows the effects of sand weight on the uptake of cesium, strontium, and cerium under different mesh size. As shown, the adsorption increases with decreasing mesh size. By using 1g of sand soil, the amount of Cs adsorbed at equilibrium was approximately 95.58, 97.35, 98.18, and 98.92% at mesh size 0.4, 0.315, 0.25, 0.09 respectively. The effect of mesh size has the same behavior with the other two metals as shown in table (2).

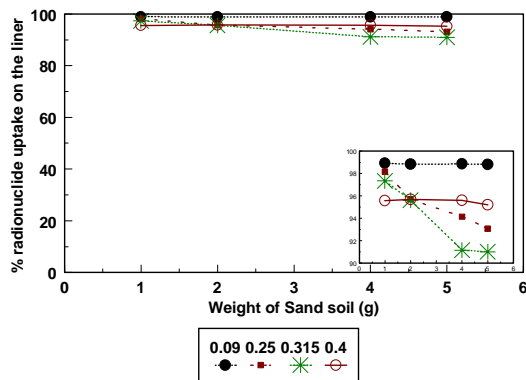


Fig 2. a. Cesium uptake on the liner for different sand mesh size

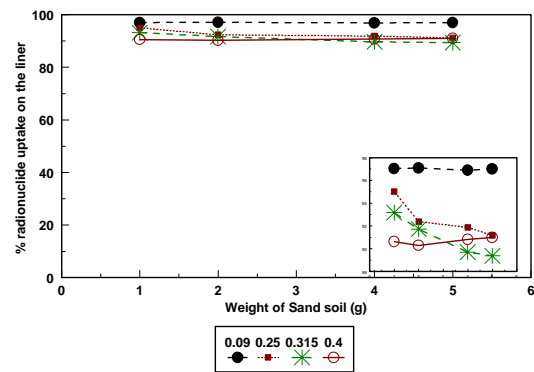


Fig 2. b. Strontium uptake on the liner for different sand mesh size

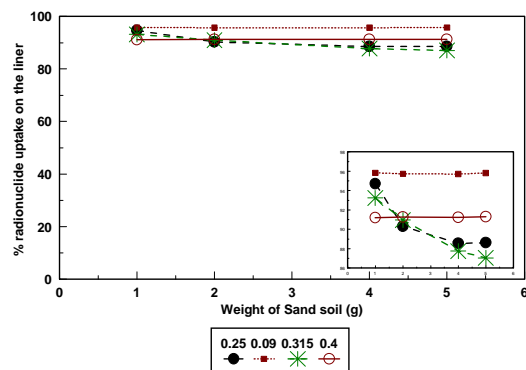


Fig 2. c. Cerium uptake on the liner for different sand mesh size

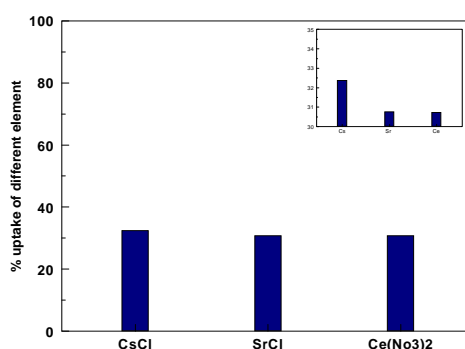
Fig. 2. Percentage uptake of radionuclide for different sand mesh size

**Table 3.** Maximum Percentage uptake for different sand mesh size

Element	Maximum Percentage uptake for different sand mesh size			
	0.09	0.25	0.315	0.4
Cesium	98.92	98.18	97.35	95.58
Strontium	97.04	95.02	93.18	90.618
Cerium	95.84	94.72	93.24	91.22

### Sorption selectivity of element on the liner

In real situation, no individual element is released. But, all radio-elements are available to dissolve in the intruded water in the disposal unit and can migrate until reach the liner. In the present work, three important elements only have been studied. Therefore, the study of sorbent liner selectivity is an important issue. The selectivity of these elements is shown in Fig. 3.



**Fig. 3.** Selectivity of element on the liner

The liner shows slightly high affinity for the cesium than the strontium and cerium. The percentage affinity for Cs, Sr, Ce are 32.4, 30.7 and 30.7% respectively .

### Effect of pH

The adsorption experiments of cesium, strontium and cerium were conducted by batch process. 15 ml of 50 ppm cesium chloride, strontium chloride and cerium nitrate solution were treated with 2.25 g of sorbent materials (1g charcoal, 1 g sand, 0.25 cellulose acetate) at different pH, at 23 °C, for hours.

Different pH values of these solutions were adjusted with 1M NaOH and 1M HCl . The supernates were filtered through a filter paper (Whatman No. 41) and the concentrations of strontium were determined by . The uptake percentages (*Ads%*) were calculated by:

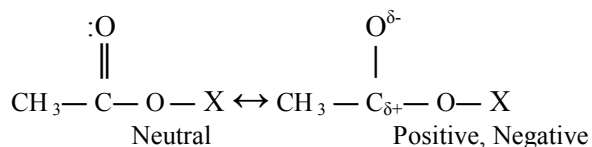
$$\text{Uptake \%} = (C_i - C_e / C_e) \cdot 100$$

Where  $C_i$  and  $C_e$  are the initial and final concentration of cesium, strontium and cerium in solution. Figure shows the effect of pH on the adsorption efficiency of cesium, strontium and cerium on the prepared sorbent materials (charcoal, sand, cellulose acetate).

Table 4. pH values for different materials and mixtures used

Element	pH	TDS	Conductivity(μS)
Groundwater (GW)	8.7	1720	2309
GW+Sand	8.6	1460	2060
GW+Sand+Charcoal ( C)	9	1611	2252
GW+Sand+C+ Acetate (A)	8.7	1450	2050
Cesium chloride (Cs Cl)	9.1	1990	2730
Strontium chloride (Sr Cl)	8.6	1793	2485
Cerium Chloride (CeCl)	6.5	2273	3080
Mixture (Cs Cl + SrCl + CeCl)	6.3	1777	2704
GW+Sand+C+ Cellulose Acetate (A) + Mixture	8.3	1806	2498

The plot shows a marked influence with a gradual rise in the metal uptake with the increase in pH from 2.5 to 4, then it becomes nearly constant between the pH range of 4–8, followed by a sharp decrease with a further rise in the pH. The increase in the adsorption of Cs, Sr, and Ce ions on the prepared sorbent material with increasing pH of the aqueous solution is explicable on the basis of prepared sorbent materials surface can exist as positive, negative or neutral according the following reactions<sup>(7)</sup>:



Where  
X is (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>

At a lower pH, the surfaces will have positive character and less affinity for Cs<sup>+</sup>, Sr<sup>+2</sup>, Ce<sup>+2</sup>, on the other hand at higher pH, the oxide will behave as negatively charged surface, as a result of which the uptake is a maximum in basic solutions. This is confirmed by the present results which shows a slightly decrease with the pH as a general trend as shown in Fig.5.

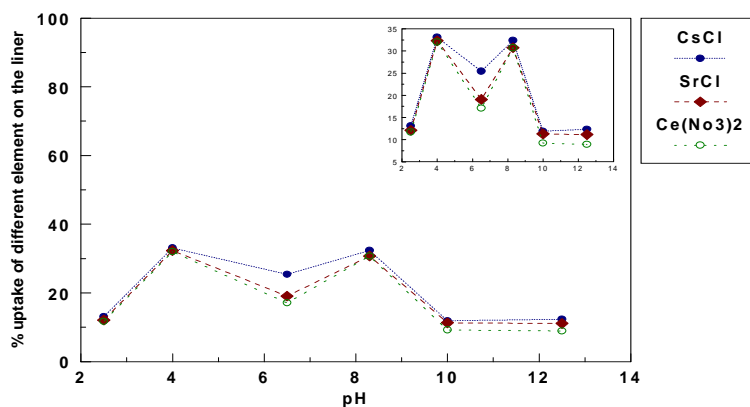


Fig. 4. Effect of pH on the percentage uptake of element on the liner

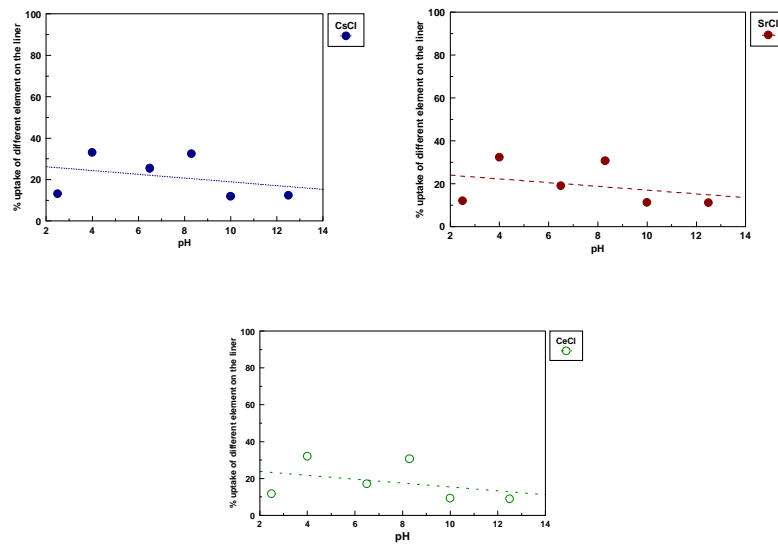


Fig 5. The trend of radionuclide behavior with the change of pH

### Effect of temperature on the adsorption

The effect of temperature on the adsorption of cesium, strontium, and cerium onto 2.25 g of sorbent materials (1g charcoal, 1 g sand, 0.25 cellulose acetate) was studied within range 15-70 °C. The results are shown in Fig. (6). From this figure its clear that, with increasing adsorption temperature, the adsorption amount of cesium, strontium, and cerium are increased, this means that the adsorption of these elements is endothermic. This could be attributed to the increase in the kinetic energy of the ions with the temperature<sup>(9)</sup>, also it might be due to the the number of active surface centers available for adsorption increases with increasing temperature<sup>(10,11)</sup>.

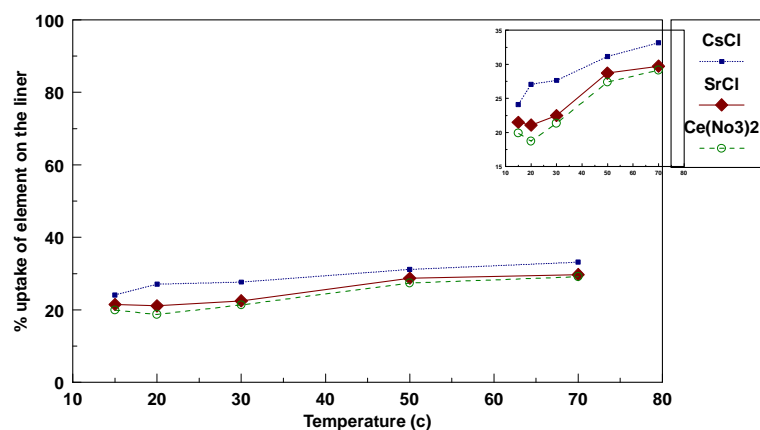


Fig. 6. Effect of temperature on the percentage uptake of element on the liner

### Effect of contact time

The efficiency of the prepared sorbent linear in the uptake of cesium, strontium, and cerium can be determined from the time required to adsorb the maximum capacity of the metal ions. 2.25 g of sorbent materials (1 g charcoal, 1 g sand and 0.25 cellulose acetate) was equilibrated in 15 ml of 50 ppm cesium, strontium, and cerium mixture and shaken for different times at 25 °C. Fig. (7) shows the effect of contact time on the uptake percent of the prepared adsorbent linear. From this figure it is clear that the percentage uptake for Cs, Sr, and Ce after 15 min. was 33.3, 33.0, and 32.5 respectively, while after 120 min. the uptake percent was 32.3, 33.2, and 33.16 for Cs, Sr, and Ce respectively. This means that the trend of the maximum uptake was constant after 15 min. A period of 15 min. was chosen as a suitable contact time for all experimental studied.

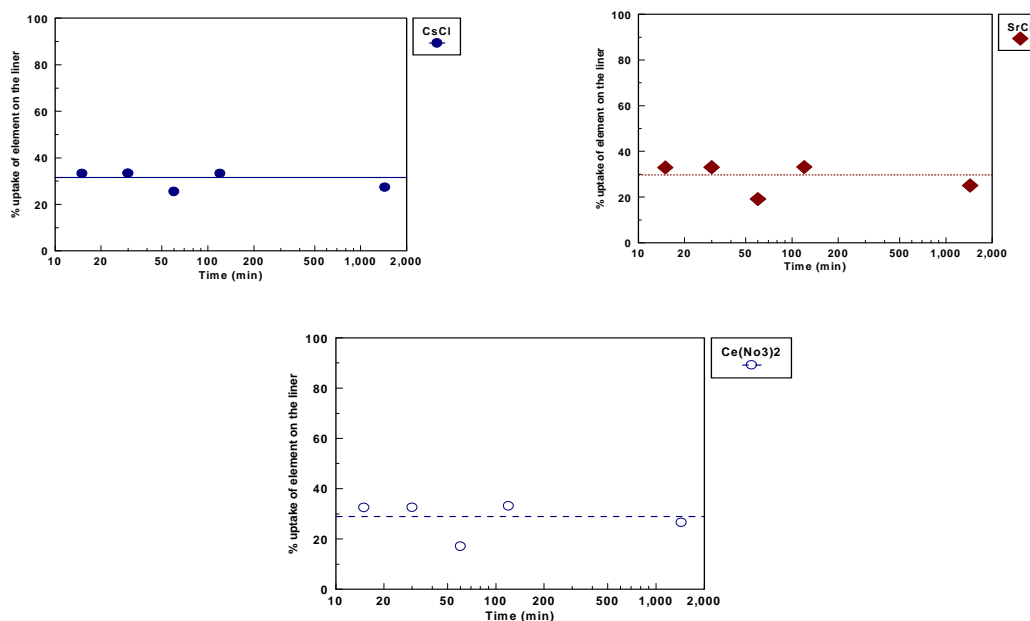


Fig. 7. Effect of contact time on the percentage uptake of element on the liner

### Effect of concentration

The uptake percent of cesium, strontium, and cerium as a function of their concentration was studied at 25 °C ± 2 °C, pH... and 15 min. contact time by varying the concentration from 10 to 50 ppm. The results are represented in Fig.(8). The adsorption process increased with increasing the metal ion concentration. At 20 ppm the uptake percent of Cs, Sr, and Ce was 33, 31.05, and 30.25 respectively, while at 50 ppm the uptake percent was 32.4, 30.8, and 30.7 for Cs, Sr, and Ce respectively.

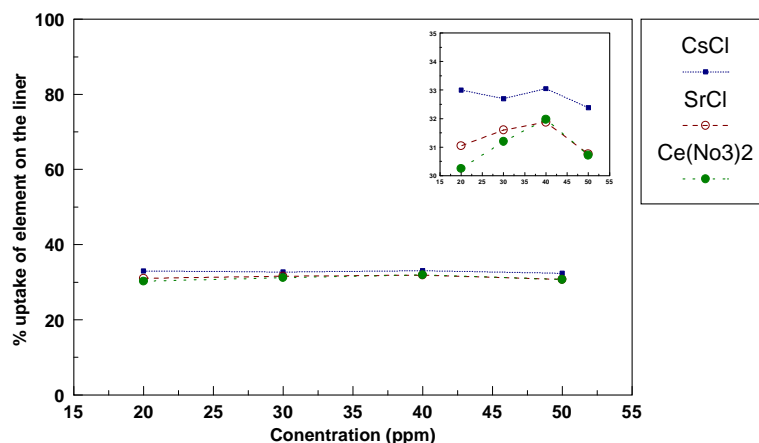


Fig. 8. Effect of concentration on the percentage uptake of element on the liner

## CONCLUSION

Activated carbons have been used for many years for safety removal of toxic metals ions. Addition of cellulose acetate with sand enhanced the safety removal capacity of cesium, strontium, and cerium (97% Cs, 93% Sr, and 93% Ce). In the studied conditions the order of the adsorption capacity of the prepared adsorbent material (1 g charcoal, 1 g sand and 0.25 g cellulose acetate) was Cs > Sr > Ce. The observed metal ion uptake is thought not only a simple ion-exchange process but also ion complex formation and surface adsorption mechanisms play role in the whole adsorption process of ester group OH group of cellulose acetate mixed with charcoal.

This previous works are considered preliminary studies for the liner prepared. A very detailed and various experiments should be performed to overcome the disadvantages of the liner and to improve the capability of the liner.

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