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Effect of chelating agents on removal of ^{137}Cs from contaminated soil

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Abstract

In the present research, the chemical washing method has been selected using three chelating agents: citric acid, acetic acid and Ethylene Diamine Tetraacetic Acid (EDTA) to remove ^{137}Cs from two different contaminated soil samples were classified as fine and coarse grained. The factors that affecting removal efficiency such as type of soil, mixing ratio and molarity have been investigated. The results revealed that no correlation relation was found between removal efficiency and the studied factors. The results also showed that conventional chemical washing method was not effective in removing ^{137}Cs and that there are further studies still need to achieve this objective.

Key words

Cesium, soil washing, chelating agents.

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تأثير بعض العوامل المخلبية على ازالة السيزيوم من التربة الملوثة

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الخلاصة

في هذا البحث تم استخدام ثلاثة انواع من الاحماض العضوية، حامض الستريك و حامض الخليك اضافه الى حامض ثنائي امين ايثيلين رباعي حامض الخليك (EDTA) لازالة السيزيوم المشع من عينتين من التربة الملوثة. العينة الاولى ذات الصنف الحبيبي الناعم، اما العينة الاخرى صنفت ذات الصنف الحبيبي الرملي الخشن. تمت دراسة بعض العوامل المؤثرة على كفاءة الازالة مثل تركيز الحامض و نسبة خلط الصلب الى السائل. بينت النتائج ان ليس هناك علاقة ترابطية بين تركيز الحامض المستخدم مع كفاءة الازالة حيث تم الحصول على بعض القيم غير المنتظمة لكفاءة الازالة. نسبة الخلط هي الاخرى لم تكن مؤثرة على عملية ازالة السيزيوم و ان النتائج التي تم الحصول عليها غير منتظمة و لا يمكن ربطها بعلاقة تناسبية. بالرغم من ذلك فأن النتائج اظهرت ان هناك بعض القيم المميزة لكفاءة الازالة عند تراكيز الاحماض 0.005، 0.05 و 0.01 مولاري حيث لم تتعدى كفاءة الازالة 20%.

Introduction

Pure ^{137}Cs metal is silvery white in color and very soft, and it is not expected to be found in the environment. Radioactive forms of ^{137}Cs are produced by the fission of uranium in fuel elements during the normal operation of nuclear power plants, or when nuclear weapons are exploded [1].

^{137}Cs has received much attention over the last four decades because of the nuclear accidents that occurred during this period. Serious radiation accidents include the Chernobyl disaster (Ukraine 1986) [2], Goiania accident (1987) [3] and Fukushima Daiichi nuclear disaster [4].

Iraq has large quantities of different types and forms of radioactive waste as a result of the former nuclear program, which is usually stored in drums inside the Al- Tuwaitha nuclear complex [5].
The aim of this study is to evaluate the performance of three chelating agents in removing ^{137}Cs from two different contaminated soils taking into consideration that secondary waste not

to be produced in significant quantities. This work is a part of an integrated approach concerning in removing radioactive isotopes from contaminated soil and can be a solution for recovering the contaminated environment which can be done by washing the contaminated soil with chemical solution to separate the contaminants.

Materials and methods

Two soil samples of 2 kg each have been selected to conduct bench scale chemical soil washing experiments to remove the contaminants. The first contaminated soil sample was taken from a 200 liter steel drum stored in a bunker inside Al-Tuwaitha nuclear site, while the second soil sample has been taken from uncontaminated (clean) area inside Al-Tuwaitha site. The second sample was deliberately contaminated with ^{137}Cs by mixing it with liquid waste containing ^{137}Cs. The purpose is to investigate the type of soil as a factor affecting the removal efficiency.

Gravel and plant debris were removed from the selected samples. Grinding and sieving processes were performed. To ensure getting a representative sample, shaker was used for about six hours. Sieving is the process of physically sorting a sample to obtain uniform particle sizes and homogenization is the mixing or blending of a soil sample in an attempt to provide uniform distribution of contaminants [6]. The pH of soil has been measured in a 1:1 of soil weight to distilled water volume using a pH-meter. Texture of soil sample was determined by pipette method according to United States Department of Agriculture, USDA, hand book No.60 (1954) described in Kilmer and Alexander [7]. Wet oxidation method was used to determine Organic materials using chromic acid according to method of Walkley-Black (1934), which was described by Hesse (1972) [8].

1. Radiological measurements

The soil samples have been radiologically characterized in terms of cesium contents to determine the initial concentrations for each sample. This process repeated after each washing process to calculate the removal efficiency percentage of contaminants. This was done using high- purity germanium (HPGe) detector with 60% relative efficiency and 1.8 keV energy resolutions at 1332 keV. The detector coupled to computerized data acquisition system for spectra analysis, gamma vision version 6.08. The detector and the program supplied by ORTEC AMETEC Company.

The energy calibration curve was performed using marinelli beaker multi gamma standard source (Table 1). The spectrum of the standard source has been accumulated for 3600s and depicted in Fig.1. The energy calibration parameters are listed in Table 2.

Table 1: Characteristics of Marinelli multi gamma standard source.

Radionuclide	**Energy keV**	**Intensity %**	**Half life**
Am-241	59.5	35.9	432.2 y
Cd-109	88	3.61	462.6 d
Co-57	122	85.6	271.8 d
Co-57	136.47	10.68	271.8 d
Ce-139	165.8	79.88	137.6 d
Hg-203	279.19	81.55	46.62 d
Sr-85	514	96	64.84 d
Cs-137	661.66	85.100	30.07 y
Y-88	898.04	93.7	106.7 d
Co-60	1173.24	99.97	5.271 y
Co-60	1332.5	99.98	5.271 y

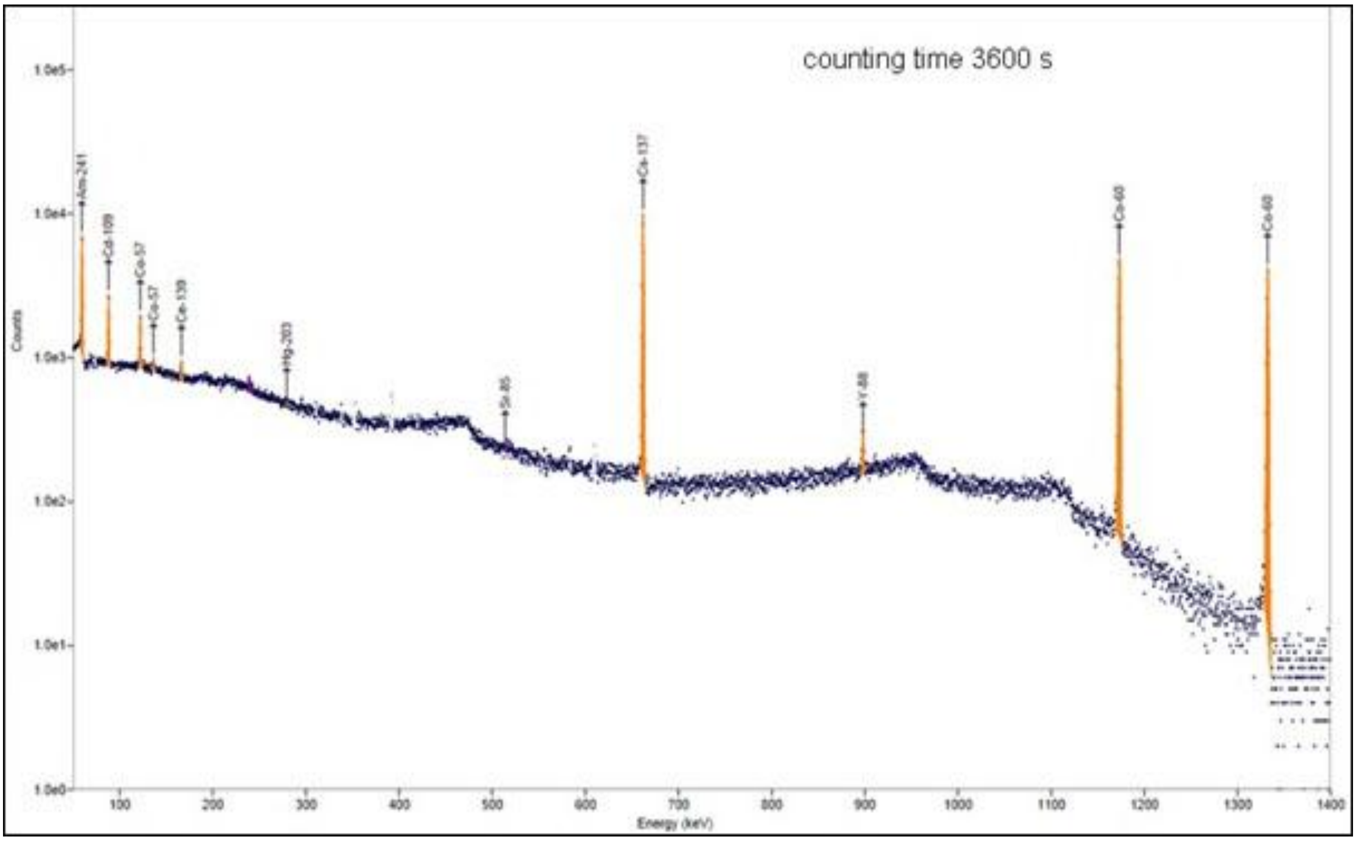


Fig.1: The spectrum of the standard source.

Table 2: The parameters of energy and efficiency calibration.

Nuclide	Peak channel	Centroid Energy (keV)	Net area (counts/hr)	FWHM (keV)	Eff %
Am-241	162.20	59.48	23208	1.379	3.1008E-003
Cd-109	240.19	88.00	7174	1.366	1.2538E-002
Co-57	333.34	122.06	4273	1.371	1.9465E-002
Co-57	372.48	136.38	781	1.443	1.1E-002
Ce-139	453.75	166.10	977	1.473	0.81E-002
Hg-203	762.84	279.15	141	0.654	0.74E-002
Sr-85	1404.94	514.01	40	1.549	6.2E-003
Cs-137	1808.89	661.77	46628	1.676	5.1896E-003
Y-88	2454.89	898.10	782	1.628	4.4893E-003
Co-60	3206.73	1173.18	27490	2.005	3.0981E-003
Co-60	3642.14	1332.49	24038	1.997	2.7102E-003

In order to verify efficiency of the detection system, the energy and efficiency curves have been measured and plotted in Figs. 2 and 3.

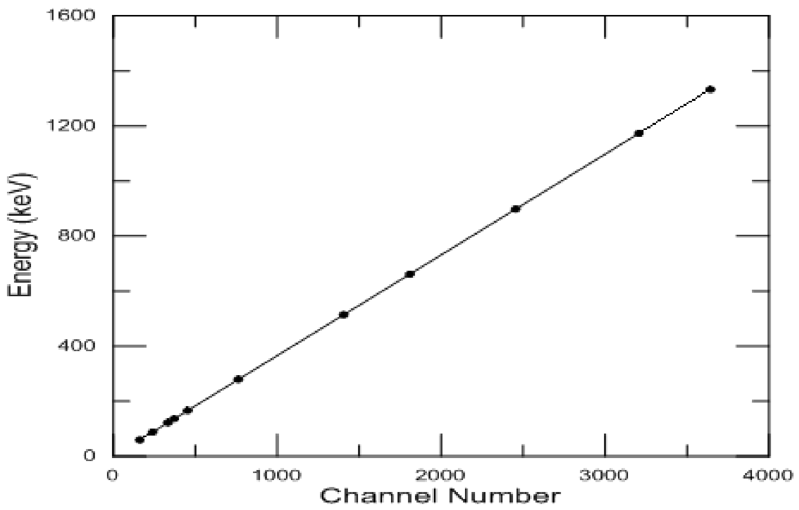


Fig. 2: Energy calibration curve.

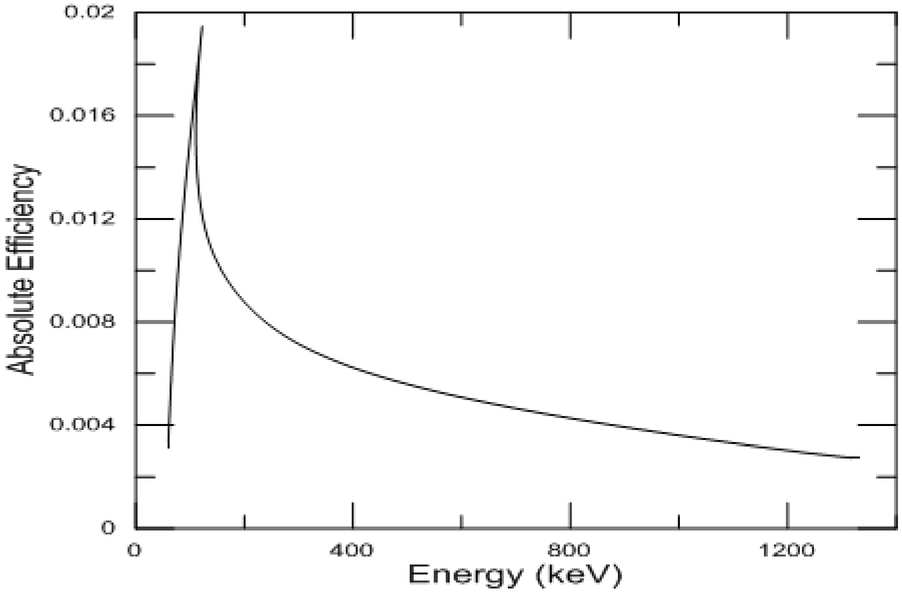


Fig. 3: Efficiency calibration curve.

Since the detection efficiency of a nuclide for specific energy can be calculated using.

$$\epsilon = \frac{\text{net area under the peak}}{\mathrm{I}\gamma \times \mathrm{T} \times \mathrm{Ac}} \quad (1)$$

where ε is the absolute efficiency of the energy peak; Iγ is the energy peak branching ratio; T is the counting time and Ac is the activity of the cesium.

2. Soil washing methodology

Samples of 10 g of each have been taken to perform bench scale chemical soil washing experiments using three chelating agents: citric acid, acetic acid and EDTA. Different concentrations of acids were used for washing the samples (0.001, 0.005, 0.01, 0.05, 0.1, 0.2 up to 1 M) for 2 hour contact time. Filtration process was done with ash less paper filter, Whatman no.42. This process was performed for 1:1 and 1:2 mixing ratio. Air drying, grinding and homogeneously by hands was performed to prepare samples for gamma analysis.

Cesium concentrations were determined after each washing process to evaluate the removal efficiency percentage which can be calculated from the formula:

$$\text{Percent of cesium removed (\%)} = \frac{\mathrm{Co} - \mathrm{Ct}}{\mathrm{Co}} \times 100 \quad (2)$$

where C_o is the concentration of cesiumt in the sample before washing process and C_t is the concentration of cesium in the sample after washing process.

Results and discussion

The analysis of the soil composition is very important to select the appropriate cleaning process, since cleaning method depend mainly on type of soil and nature of contaminants [10]. In addition, the most of contaminants are distributed in the fine particles of the soil [11]. Also, the presence of organic material increases the chance of retaining of contaminants in the soil [12]. Based on that, for our case, chemical washing is the most appropriate technique can be applied to remove the contaminants.

Chemical and physical composition properties of the two soil samples are listed in Tables 3 and 4. From those tables we can clearly notice that the soil characteristics of both samples are rather different. The soil-1 sample is classified as fine grained since it contains high levels of fine textured particles (clay, silt) and high organic materials, whereas, the soil-2 sample is classified as coarse grained since it contains high level of sand.

Table 3: Properties of contaminated soil-1 sample.

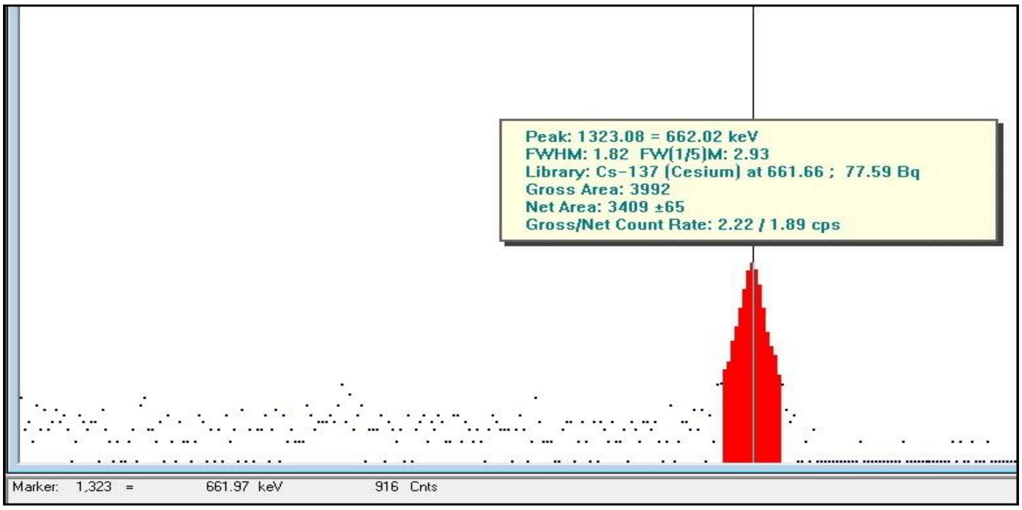
Soil properties		**value**
pH		7.69
Texture	clay	35.1%
	sand	24
	silt	39.7
	OM	1.11

Table 4: Properties of contaminated soil-2 sample.

Soil properties		**value**
pH		7.32
Texture	clay	38.5%
	sand	34.4%
	silt	23%
	OM	3.9%

1. Radiological characterization of the soil samples

Fig. 4 shows the spectrum of the fine grained soil sample, soil-1 which revealed that the net area under the photo peak is 3409 counts per one hour (1.89 cps). The important thing that should we say is that we described the concentration of the cesium in terms of "net area" instead of activity because of the lack of a small volume standard source. Fig. 5 shows the spectrum of coarse grained soil sample, soil-2 which revealed that the net area under the photo peak is 13761 counts per one hour (11.47 cps).



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Peak: 1323.08 = 662.02 keV
FWHM: 1.82  FW(1/5)M: 2.93
Library: Cs-137 (Cesium) at 661.66 ;  77.59 Bq
Gross Area: 3992
Net Area: 3409 ±65
Gross/Net Count Rate: 2.22 / 1.89 cps
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Marker:   1,323   =        661.97  keV          916  Cnts
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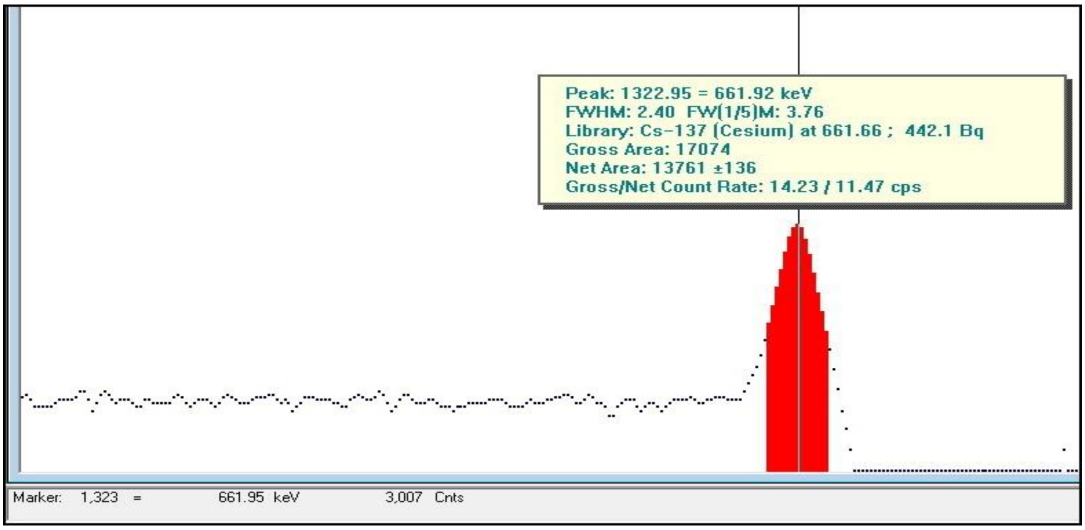
Fig. 4: Net count of the soil-1, sample.



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Peak: 1322.95 = 661.92 keV
FWHM: 2.40  FW(1/5)M: 3.76
Library: Cs-137 (Cesium) at 661.66 ;  442.1 Bq
Gross Area: 17074
Net Area: 13761 ±136
Gross/Net Count Rate: 14.23 / 11.47 cps
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Marker:   1,323   =        661.95  keV          3,007  Cnts
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Fig. 5: Net count of the soil-2 sample.

2. Effect of chelating agents on removal of cesium from soil-1 sample

2.1 Effect of molarity on removal efficiency

Fig. 6 shows that there was no correlation between removal efficiency and molarity applied that is mean, the results obtained were not subject to a regular effect of the acid concentration applied.

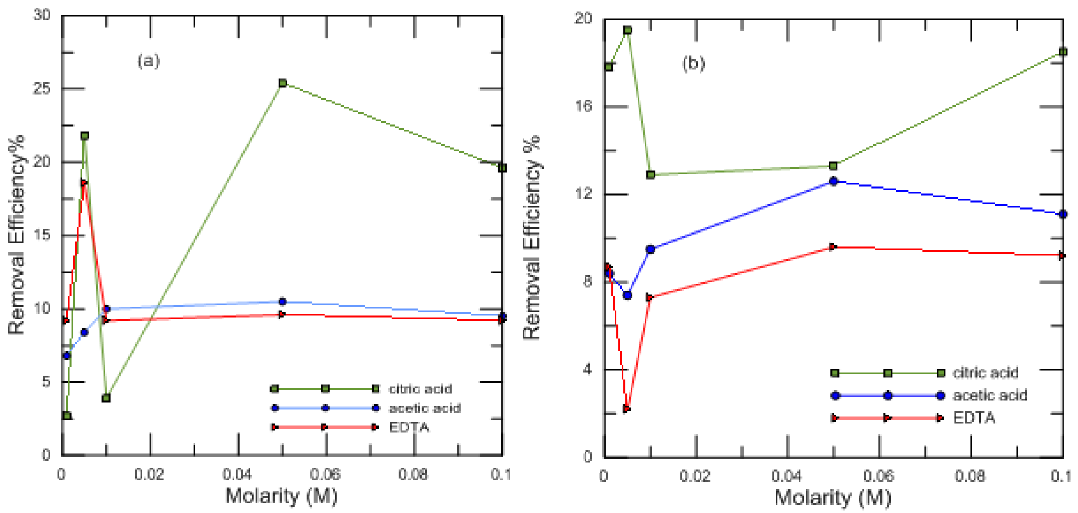

Fig. 6: Removal efficiency vs molarity of the three chelating agents of soil-1 for (a) 1:1 mixing ratio; (b) 1:2 mixing ratio.

We can clearly notice that the values of removal efficiency rises and falls without clear factors control the washing process.

2.2 Effect of mixing ratio on removal efficiency

The results in Figs. 6 revealed that, contrary to expectations, there was no effect of mixing ratio on removal efficiency.

2.3 Weight loss percentage

As shown in Fig. 7 we can clearly notice that there is a good correlation between percent of weight loose and the concentration of the acids used this is possibly because the soil-1 sample describes As fine grained soil type, and high organic contents which can be more soluble in an acidic solution. The results also revealed that mixing ratio strongly effecting weight loss of soil. Of the three agents, EDTA was highly effective for both cases 1: 1 and 1:2 mixing ratio.

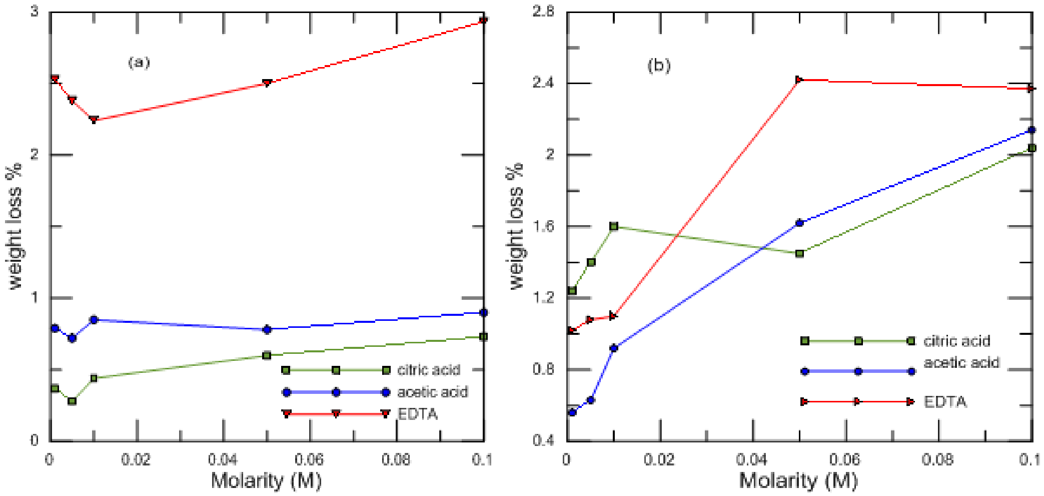

Fig. 7: Percent of weight loss of the three agents for (a) 1:1 mixing ratio; (b) 1:2 mixing ratio.

3. Effect of chelating agents on removal of cesium from Soil-2 sample

3.1 Effect of morality on removal efficiency

The results of the experiments Fig.8 shows that there is no correlation between removal efficiency and molarity applied. Significant values of removal efficiency were found at 0.05 M for all chelators used.

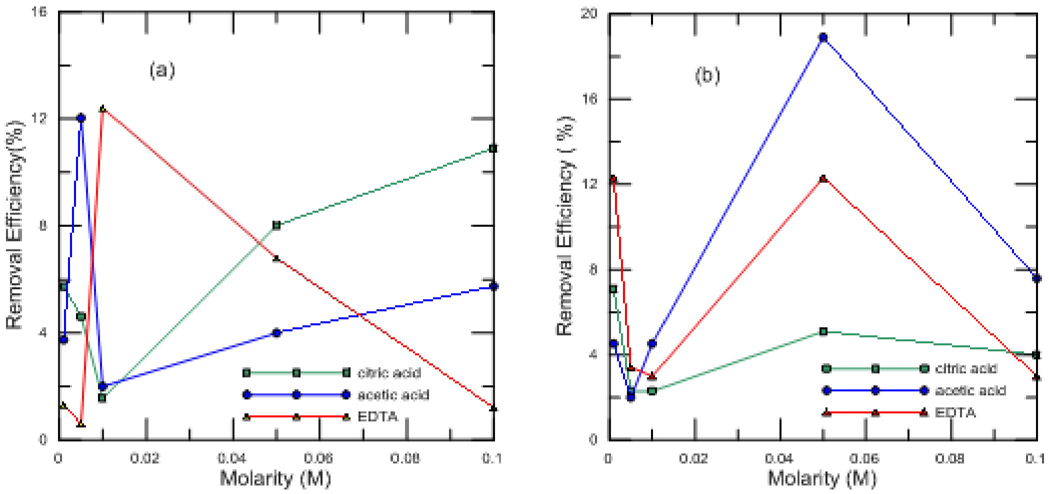

Fig. 8: Effect of molarity on removal efficiency of soil-2 (a) for 1:1 mixing ratio; (b) for 1:2 mixing ratio.

3.2 Effect of mixing ratio on removal efficiency

Refer to Figs. 8, generally speaking, with a few exceptions, our results show that mixing ratio did not affect removal efficiency. As example, in the case of citric acid Fig.8 (b), for 1:2 mixing ratio, maximum values were 7% and

4% at 0.001 and 0.1M respectively, whereas, for 1:1 mixing ratio Fig.8 (a), maximum ratio values were 8% and 10% at 0.05 and 0.1 respectively.

Interestingly, for higher values of mixing ratio (1:2), removal efficiency was found in lower values.

As well as in acetic acid and EDTA, there were no regular correlation between mixing ratio and removal efficiency and we can clearly conclude that mixing ratio did not improve removal efficiency.

Fig. 9 shows compare the performance of the three agents that used at more specific molarities applied, 0.005. 0.01 and 0.05 M for both fine and coarse grained soil samples. For fine grained soil samples Fig.9(a), citric acid is highly effective in removing cesium, while Fig.9 (b) shows that at lower molarity (0.005M), the three agents are almost equal in efficient, while acetic acid is more efficient at bigger molarity (0.05M). The most remarkable result to emerge from the rustle of both case is that citric acid and acetic acid have similar behavior.

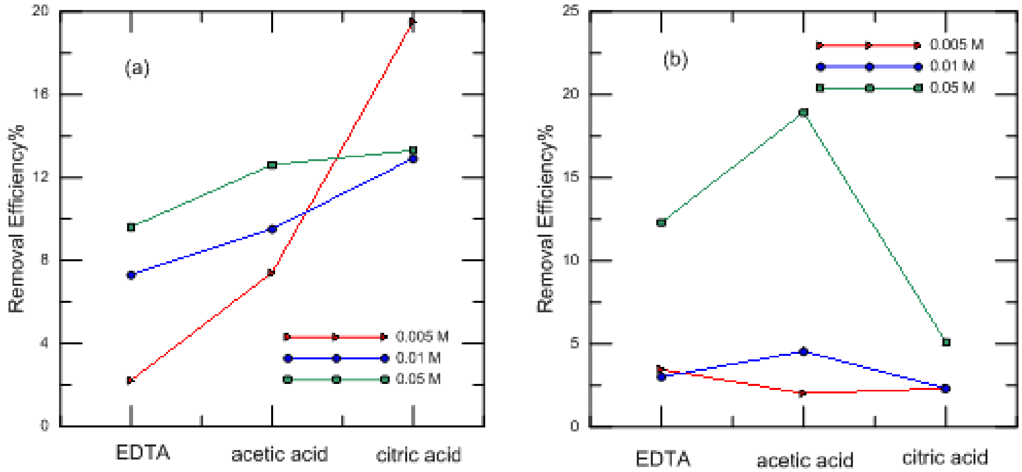

Fig.9: Compare the performance of agents at 0.005, 0.01 and 0.05 M with 1:2 mixing ratio; (a) for fine grained soil sample; (b) for coarse grained soil sample.

In short, all results obtained from experiments of chemical washing of cesium contaminated soil showed that it is difficult to remove cesium from contaminated soil using the common chemical washing method. Accordingly, our experiments confirm with previous results. Since, Shand et al. (1994) [13] stated that organic material and minerals components are important for the fixation of cesium in soils. Hird et al. (1996) [14]were suggested that the fixation of cesium is caused by interlayer breakdown of the illitic clay. Eisenbud (1997) [15] was stated that cesium is so tightly bound by the clay minerals of the soil.

3.3 Weight loss percentage

As shown in Fig.10, the values of the percent of soil weight loss due to chemical washing process is increasing with increasing of molarity and mixing ratio.

The data obtained are broadly consistent with the major trends, since the solubility of the soil content increases with increasing of water and concentration of solvents.

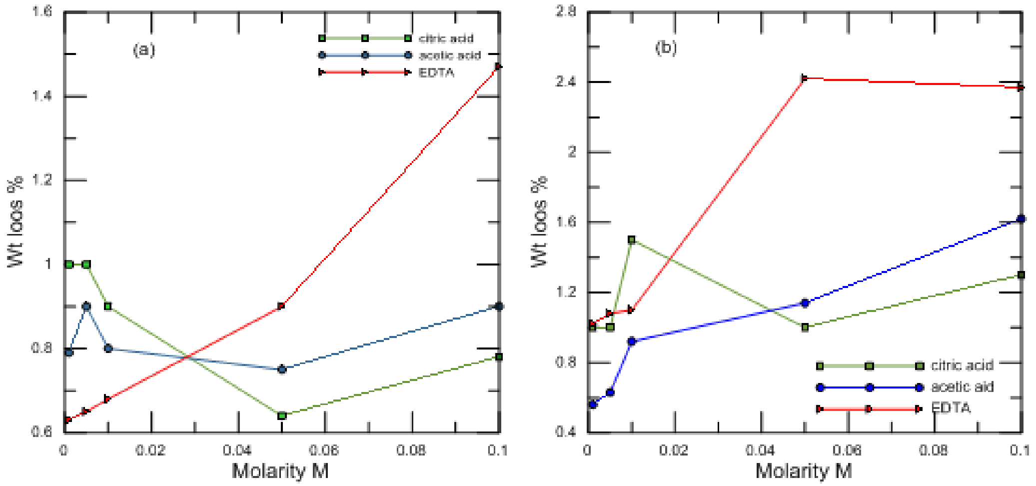

Fig.10: Percent of weight loss for (a) 1:1 mixing ratio; (b) 1:2 mixing ratio.

Conclusions

The main objective of this work is restoring the environment by removing of uranium and cesium from contaminated soil using chelating agents such as citric acid, acetic acid and EDTA, taking into accounts the economic aspect and saving time. Recovery of Contaminated Soil is an appropriate choice instead of conditioning and storing, so as to save security cost and prevent needed to establish new bunkers.

In Iraq, it has not yet been documented establishing projects for restoring the radioactive contaminated soil, this is may be of thinking that store the contaminated soil in metal drums is more easier than removal the contaminants. We believe that this study provides a springboard and encouragement for a new way to recycle the radioactive contaminated soil and further experimental studies are needed to achieve the objective.

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