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Removal of Uranium from Contaminated Soil Using Different Chelating Agents in Baghdad

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Abstract : In the present work, three chelating agents; EthyleneDiamineTetraaceticAcid (EDTA)as synthetic chelate, acetic and citric acids asLow Molecular Weight Organic Acids (LMWOA), were used to evaluate their performance in removing uranium from soil. Laboratory physical and chemical tests were performed for soil sample characterization.TheFluorometry technique was used for measuring uranium content. Effect of changing molarity and mixing ratios were studied as factors affecting removal efficiency. The results revealed that the removal efficiency increases withincreasing molarity and mixing ratio. Furthermore, the study showed that EDTA was highly effective in removing uranium. The removal efficiency of up to 92% was achieved from citric acid.

Keywords : Uranium, soil, chelating agents, soil washing.

Introduction

Soil contamination with radioactive materials, uranium in particular, has become a big problem worldwide due to development of nuclear industry around the world[1]. Radioactive contamination means elevated radionuclide's concentration above acceptance level which may give rise to need applying treatment process in order to reduce risk from humans and environment[2] in addition to restore the contaminated sites[3]. In Iraq we can summarized sources of radioactive wastes as follows: wastes related to the production of yellow cake from the past Iraqi nuclear programwhich is now stored in Al-Tuwaitha nuclear center. Most of the waste contains uranium, cesium and cobalt, in addition wastes due to decommissioning activities of the destroyed facilities during 2nd gulf war in 1991[4]and several locations contaminated with depleted uranium munitions found in different places due to military operations since last two decades.

There are several technical options for removal of uranium from contaminated soil which are selected according to the type and nature of contaminants[5]. However, the application of any remedial technology should take into account the potential of exposure to workers and the need to keep the exposure As low As Reasonable Achievable (ALLARA),.In addition, the choice of the appropriate remediation option, several factors should be considered, and effects on health, safety and theenvironment should be considered together with technical, cost and social factors[6]. The chemical soil washing method was adopted in the present work due to its high efficiency and low cost[7]. The aim of the present work is to assess the performance of three chelating agent in removing uranium from soil taking into account that no significant change in the physical and chemical properties of the soil and not to produce secondary waste that difficult to manage or dispose of.

1. Materials and Methods

1.1. Selection and Preparation of Sample

One kilogram of contaminated soil was selected from Al-Tuwaithanuclear research centre, about 18 kilometers southeast of Baghdad.The sample was cleaned from gravel and plant debris. Grinding and sieving processes were performed and a sieve of 200 micron was used. To ensure getting arepresentative sample, shaker was used for about six hours.The pH of soil was measured in a 1:1 of soil weightto distilled water volumeusing 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[8]. 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)[9].

A qualitative analysis of radionuclides 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,gammavisionversion 6.08.The detector and the program supplied by ORTECcompany.The gamma analysis is necessary as initial and non destructivedetection of uranium in the soil sample. Measuring of uranium content was also done using flourometry technique in soil samples which based on fluorescence of uranium salts under specific conditions.

1.2. Soil Washing Methodology

Samples of 10 g of each were taken to perform bench scale chemical soil washing experiments using three chelating agents:EDTA, acetic acid and citric acid. Different concentrations were used for washing the samples starting from 0.001, 0.005, 0, 01, 0.05, 0.1, 0.2, 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 mixing ratio 1:1 and 1:2. Air drying, grinding and homogeneously by hands was performed to prepare samples for fluorometry analysis.Fig.s (1-4) illustratesthe steps of washing process mentioned above.

Fig.1 Sample of 10 g was selected

Fig.2 Adding acids for washing soils

Fig.3 Filtration process

Fig.4 Grinding process

A specific procedure was made for preparation the sample for analysis with fluorometry technique.The fluorometry technique is a sensitive and effective method to obtain uranium concentration. In this method uranium sample prepared as an acidic solution using mixture of nitric and perchloric acids. Uranium nitrate is Precipitates as a result of reaction, which is dried and melted with sodium fluoride to enhance fluorescence as illustrates in Fig1. In general, level of fluorescence proportional to the concentration [10]. This procedure involves the following steps; chemical digestion of the sample in 30 ml of nitricandperchloricacidsmixture was performed and left for about two hours for air drying. Uranium nitrate deposited were washed with 5% of the hot nitric acid. The sample was diluted to approve the reading of fluorimeter, which it is from 1 to 10 ppm. The dilution is necessary when amount of uranium in the sample is large. The diluted sample was dried in 110 C^o and finally exposed to high temperature with sodium fluoride to enhance fluorescence which proportional to the amount of uranium in the sample.The sample now is ready for analysis.Figs.(5-7) illustrate the main preparation stages of samples to fluorescence state.

Fig.5 Fusion dishes contains prepared samples

Fig.6 expose samples to high temp

Fig.7. prepared Samples in the flourimeter

The concentration of uranium in the sample can be calculated from the following equation[11]:

$$U(ppm) = E \times K\, \frac{A-B}{D-A} \qquad (1)$$

where Uisthe concentration of uranium in micrograms per liter; A is the fluorimeter reading of sample; B isfluorimeter reading of blank; Dis thefluorimeter readingof sample plusstandard added solutioncontent micrograms ofuranium; E is the micrograms of uranium in the standard solution and K is the dilution factor.

The percent of uranium removed was calculated from the equation:

$$\text{percent of uranium removed }(\%) = \frac{\text{Uo}-\text{Ut}}{\text{Uo}} \times 100 \qquad (2)$$

whereU_o is the concentration of uranium in the sample before washing andU_t is the concentration of uranium in the sample after washing.

2. Result and Discussion

Fig.8 illustrates the gamma spectrometry analysis for the sample which shows common peaks related to U -238 and Ac series such as Th-234, Bi-214 and U-235, in addition the peaks related to individual radionuclide such as K-40.The gamma analysis is very important as initial detection to find out the content of other radinuclides, besidesuranium, in the soil sample.

Chemical and physical composition properties are listed in Table 1. The sample is contains high levels of fine textured particles (clay, silt) and high organic materials. 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[12]. In addition, the most of contaminants are distributed in the fine particles of the soil [13].Also, the presence of organic material increases the chance of retaining of contaminants in the soil[14].Based on that, for our case, chemical washing is most appropriate technique applied to remove the contaminants.

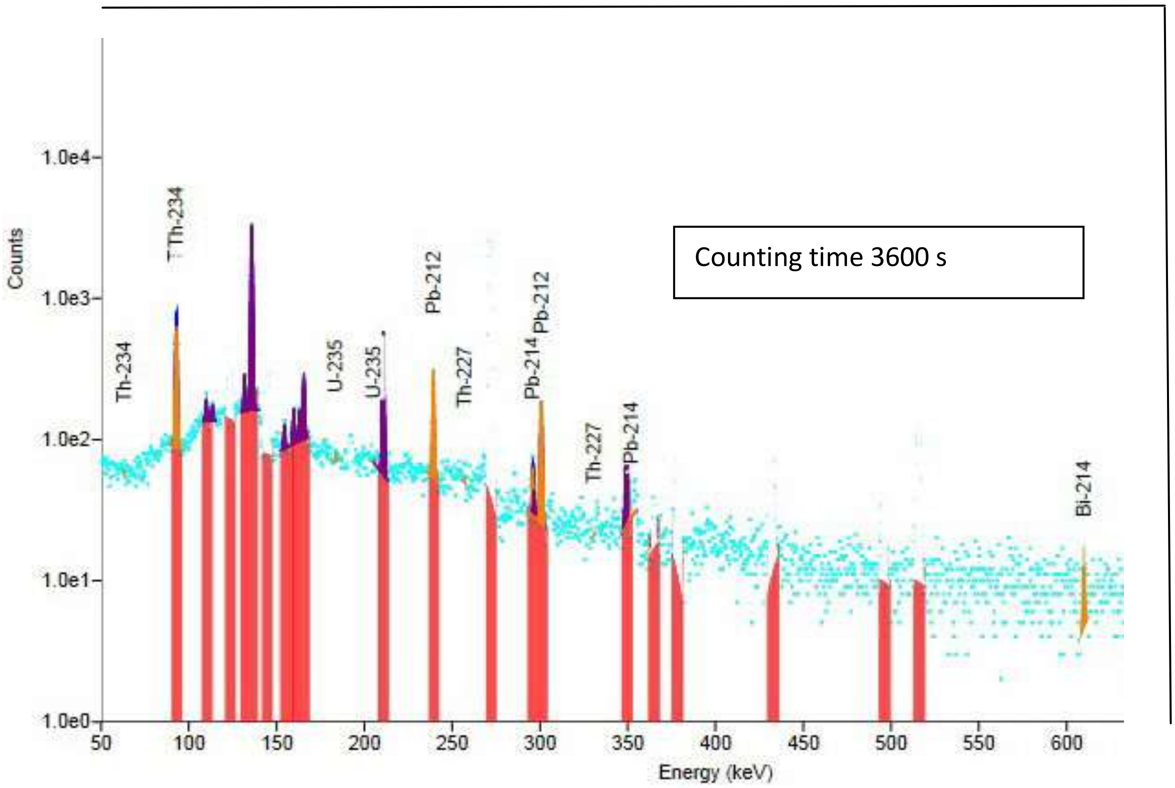


Table1. Chemical and physical properties of the soil sample.

Soil properties		value
pH		7.69
Texture	clay	355 g kg^{-1}
	sand	243 g kg^{-1}
	silt	402 g kg^{-1}
Organic materials		11.25 g kg^{-1}
U cconcentration		344 ppm

3.1 Effect of Molarity on Removal Efficiency

It is well knownthat the advantage of using LMWOAs, in particular citric acid, is to their efficiency in removing heavy metals in the low molarity range, commonly between 0.001 to 0.1M. In the present work, we preferred investigate the performance of the molarity of the agents used to the extents that significant changes occurs in the physical properties of the soil sample. That's why the range of molarity used was up to 1M for acetic and citric acids.

From Figs.9 (a) and 10 (a), it is clearly to notice thatthe removal efficiency values increases with the increasing of molarity for all the chelating agents used. Of the three agents, EDTA was the most efficientin removing uranium from soil than acetic and citric acids. For the range of molarity applied from 0.001 to 0.4 M (for 1:1 mixing ratio) and from 0.001 to 0.7 M (for 1:2 mixing ratio) acetic acid was more efficient than citric acid, and they had equal efficiency at " meeting point" 0.4M and 0.7Mrespectively. After these meeting points and up to 1 M, citric acid became more efficient than acetic acid.

It is *noteworthy*that *citric acid* demonstrated a remarkable behavior at 0.05M, for 1:1 mixing ratio, (Fig.9 b) and at 0.1M, for mixing ratio1:2(Fig.10 b). Thisbehaviorshowed that there were a reduction in the removal efficiency values at 0.05 and 0.1M. This means that the removal efficiency increases after and before these "inversion points". If we had to make a decisions about which of these two points is the best for washing process, then we should choose the points with less costly and less liquid secondary waste.For 1:1 mixing ratio, the experimental results revealed that the maximum removal efficiency values were 74 % and 53 % for citric and acetic acids respectively at 1M, while for EDTA were 58 % at 0.5M. For 1:2 mixing ratio, the maximum removal efficiency values were 92% and 76% for citric and acetic acids respectively at 1M, while for EDTA was 69 % at 0.5M.

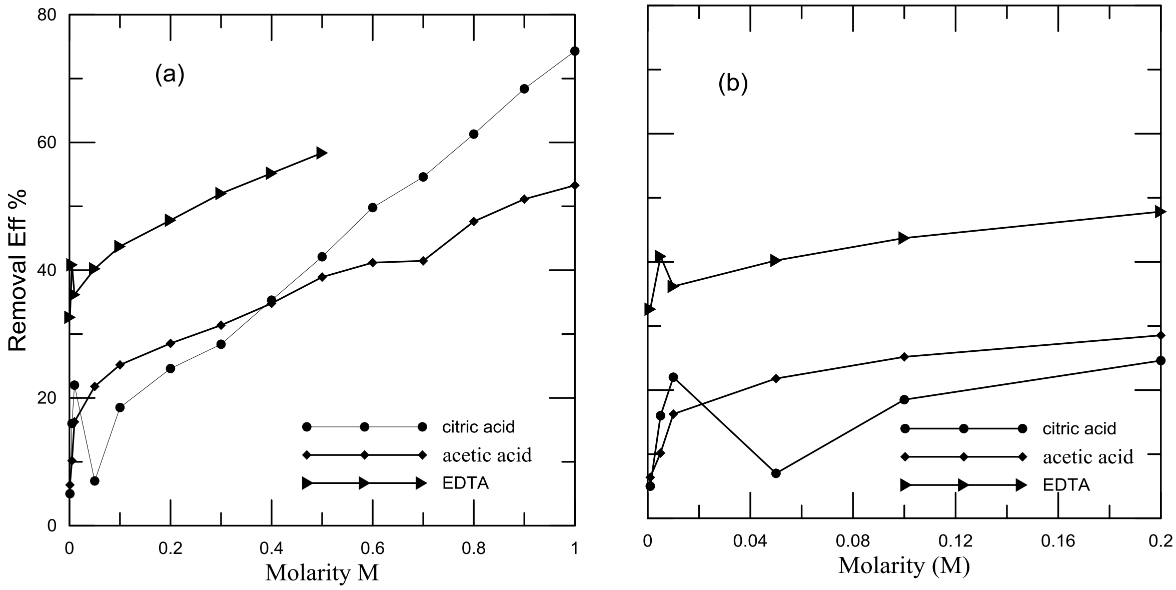


Fig.9.removal efficiency vs molarity for 1:1 mixing ratio; (a) effect of molarity on removal efficiency., (b) zoom of low molarity to illustrate inversion point of citric acid

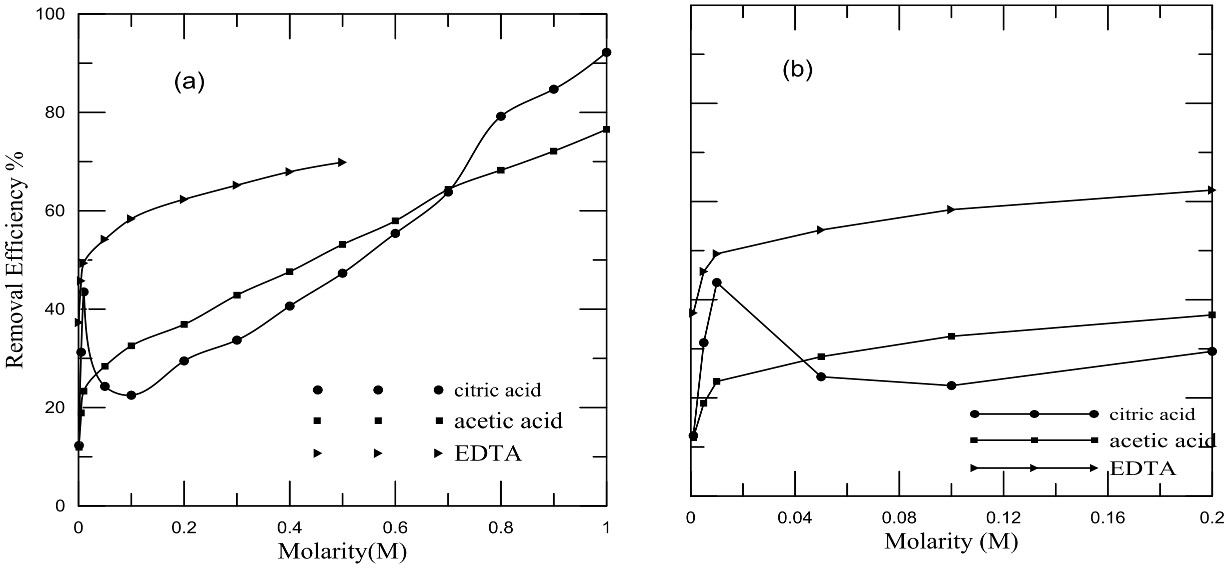


Fig10. Removal efficiency vs. molarity for 1:2 mixingratio; (a) effect of molarity on removal efficiency., (b) zoom of low molarity to illustrate inversion point of citric acid

3.2. Effect of Mixing Ratio onRemoval efficiency

Back to experimental results represented by Figs.(9 - a) and (10 - a) we can easily conclude that for each mixing ratio experiments conducted, the removal efficiency values of 1:2 is higher than those of 1:1. But we should notice that increasing in mixing ratio means increasing liquid secondary waste which is very important to keep it as low as possible. In fact increasing mixing ratio is not the only factor that affects the amount of liquid secondary waste, the type of soil is also another factor that should taking into account. On the other hand, a sufficient of liquids is needed to complete the washing process, since the important action of the washing process is to separate the contaminants from soil and transferred to washing solution[15].

Figs.(11) and (12)revealed the percent of solution loss as a result of increasing molarity. In general the results showed that the loosing in washing solution increases with the in increasing of molarity. In addition, the loosing in solution of 1:1 mixing ratio (fig.12) was larger than of 1:2 mixing ratio.In the present study, the 1:2 mixing ratio was very suitableaccording to high removal efficiency obtained.

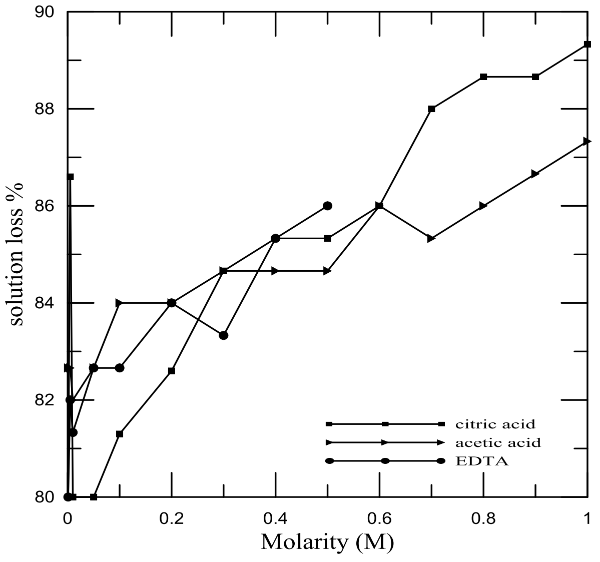


Fig.11 Percent of solution loss for 1:1 mixing ratio

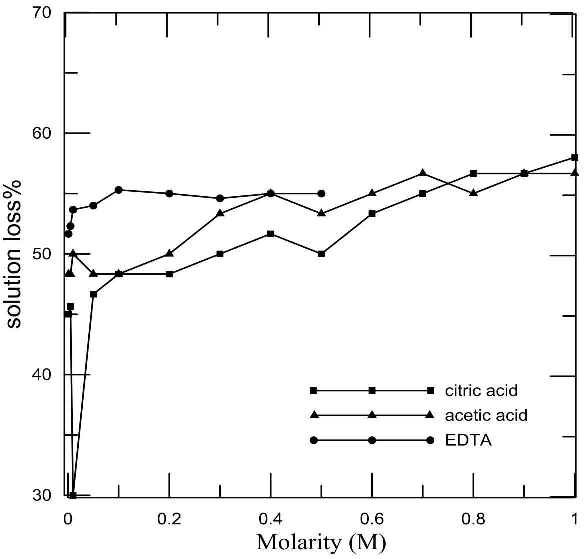


Fig.12 Percent of solution loss for 1:2 mixing ratio

3.3. Effect of Chelators on the Nature of the Soil Sample

Of the three solvents used, EDTA was the most efficient in removing uranium from soil for all molarity values applied,but at the same time it hadnegativeeffect on the physical characteristics of the soil.This effect was started from 0.1M and Increased dramaticallyat 0.5M, since,the nature of the sample waschanged in terms ofcolor and hardness, since it became very difficult to grind by hand. Fig.(13)shows the changes of the nature of the soil samples due tothe molarity applied.

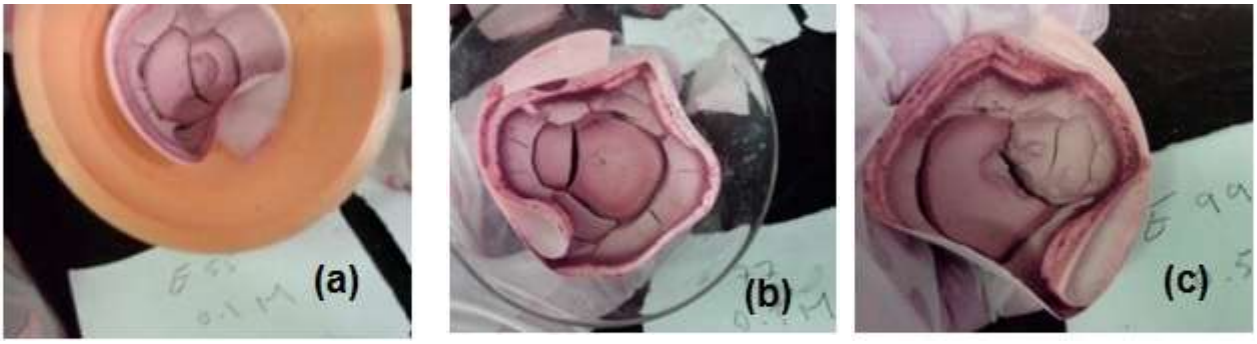
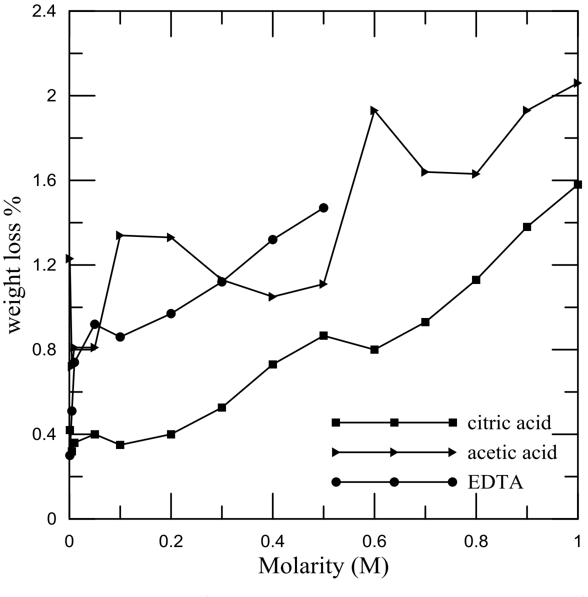


Fig.13The changes in physical properties of the soil as a result of increasing the concentration ofEDTA; (a) 0.1 M (b) 0.3 M (c) 0.3 M. On the other hand, a slightly effect was occurred at 0.8M in the citric and acetic acids experiments.

3.4 Weight Loss percentage

Figures (14) and (15) showthe percentof losing weight of the samples as a result of molarity.It is clear that the losing in weight increases with increasing of the molarity and mixing ratio because of increasing solubility of soil contents, in particular organic materials.In general the results showed that the maximum percent loss in weight was in the case of EDTA experiments and the minimum was in the citric acid experiments.



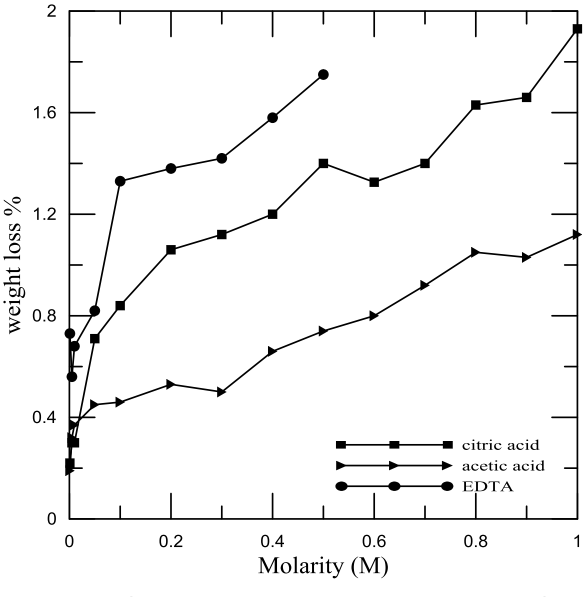


Fig.14Percent of losing weightFig.15Percent of losing weightfor 1:1 mixing ratio experiments.for 1:2 mixing ratio experiments.

3. Conclusion

Experimental results assessment of removing uranium from soil sample revealed that removal efficiency affected strongly by mixing ratio of liquid/mass, type of chelators and molarity. Of the three chelating agents used, EDTA was the most effective in removing uranium from soil but strongly effect the physical properties of the soil than citric and acetic acids. A removal efficiency of up to 92% at 1M was achieved using citric acid with no significant change in the physical properties of the soil sample, characterized by high levels of fine textured particles (Clay, Silt) and high organic materials.

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