# GEOLOGICAL, MINERALOGICAL AND COMPARATIVE STUDY OF BIOSORPTION FOR URANIUM AND THORIUM USING DIFFERENT TYPES OF ALGAE AT WADI DARA AREA, NORTHERN EASTERN DESERT, EGYPT.

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## ABSTRACT
Wadi (W.) Dara granitic rocks are characterized by presence of uranium occurrence in addition to the presence of another radioactive occurrence along trachytic dyke intruded along fault trend. The mineralogical investigation of radioactive samples clarify the presence of mainly zircon minerals associated with uranium, thorium and with minor amount of rare earth elements ;as well as , ferrocolumbite containing patches of the unidentified rich rare earth silicate mineral. Uranium, thorium, Niobium and Titanium elements are completely adsorbed by the three algae (*Cystoseira osmundacea*, *Palmaria elegans and Chondrus Crispus);* while zirconium element is only adsorbed by Cystoseira osmundacea and Palmaria elegans.

Sorption capacity of three different algae (*Cystoseira osmundacea*, *Palmaria elegans and Chondrus Crispus* were evaluated in the biosorption of uranium and thorium from wadi dara; in trachyte rock thorium was completely absorbed by Cystoseira *osmundacea*, *Palmaria elegans* while in granite rock *Cystoseira osmundacea* and *Chondrus Crispus* have the capability to absorb Th completely, in otherwise uranium was absorbed from the granite rock by Cystoseira *osmundacea* in a % 91 than the U in trachyte rock by *Palmaria elegans* in percent 90%.

**Keywords**: *Cystoseira osmundacea*, *Palmaria elegans*, *Chondrus Crispus*, *Geology*, uranium, thorium, Wadi Dara.

## 1. INTRODUCTION
The basement rocks of W. Dara area are composed essentially of Pan-African island arc gabbro-diorite complex, Dokhan volcanics, monzogranite, alkali feldspar granites, dykes and veins. The investigated area is bounded by latitude 27$^o$ 55' to 28$^o$ 00' N and longitudes 32$^o$ 55' and 33$^o$ 00' E and it is dissected by many faults with different trends (figure 1).

Faults trending NNW-SSE are dominant and could be considered as the oldest one at the investigated area as they show displacement by the NNE-SSW, and NE-SW trending faults. Faults trending ENE-WSW are less common. The granitic plutons of Gabal (G.) Dara is bounded by long fault striking roughly N 27° W along the western flank. It extends to more than 11km long. This fault is displaced by several faults trending NE-SW and ENE-WSW (Shalaby 1985). Abd-Elmoneim et al. (1988) studied the geology and radioactivity of G. Dara area. They mentioned that, in G. Dara area, the considerable parameters of the mineralized zones of veins and veinlets make it possible to recommend the ore occurrence for more detailed investigations.

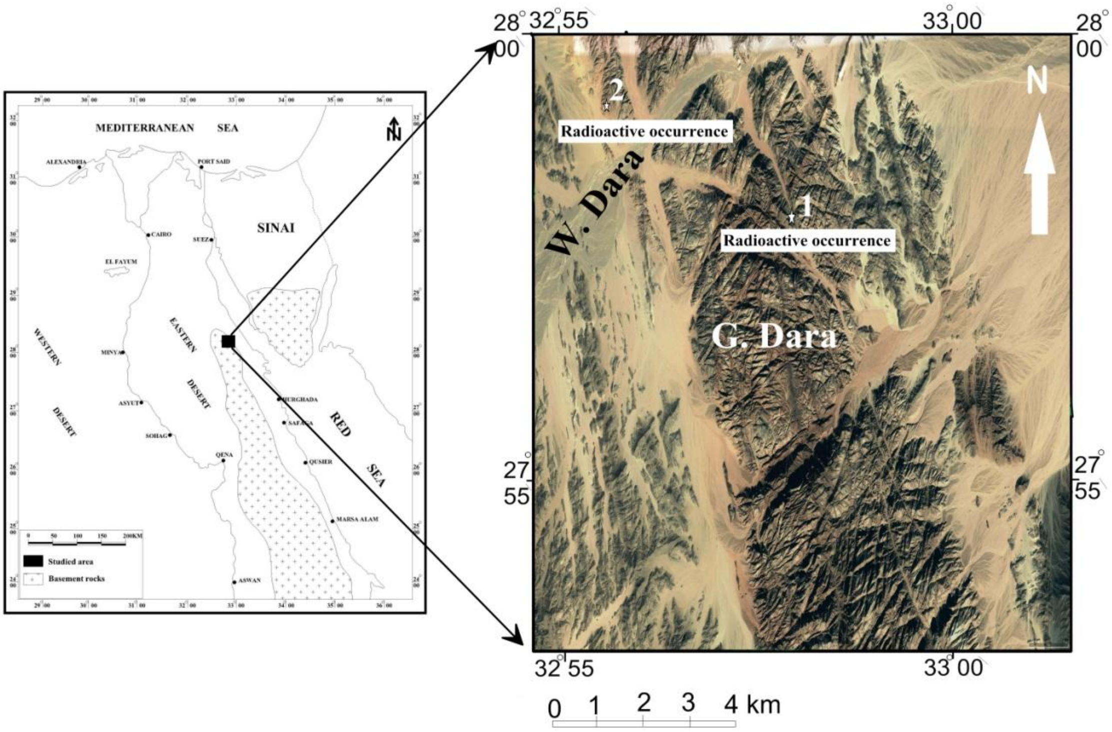


**Fig. 1: Location map and satellite image for Wadi Dara area showing the location of radioactive occurrences and samples (1: granite and 2: trachytic dyke).**

In the last decades, biosorption of metals by bacteria, yeast, algae and fungi has been studied by many researches. But algae are gaining a great attention, because algae are relatively cheap to process, a rich source in the oceanic environment, and able to accumulate high metal content (Wilde and Benemann 1993) which has high capacity for biosorption and its availability in almost unlimited amounts (Klimmek et al., 2001). The uptake of metals by algae occurs on the cell surface by adsorption and internal diffusion (Kuyucak and Volesky 1989 a & b). Biosorption occurs by conventional physicochemical methods such as electrochemical treatment, ion exchange, precipitation, reverse osmosis, evaporation, and sorption for uranium and thorium are not cost effective and hence biological approach has been considered as an alternative remediation for uranium and thorium (Congeevaram et al., 2007). Recently microbial systems like fungus, bacteria and algae have been successfully used as adsorbing agents for removal of uranium and thorium (Rubin et al., 2005).

The aim of the present work was to study the geological and mineralogical features of radioactive occurrences at W. Dara area and to evaluate the sorption capacity of the three different algae, *Cystoseira osmundacea*, Palmaria *elegans and Chondrus Crispus*, in respect of uranium and thorium metals from W. Dara.

**1.1. Geology & Radioactivity**

The main rock types crop out, in W. Dara area, is the younger granite that occurs either as large mass or small mass (figure 2). These granites intrude the other older rocks with clear intrusive contacts. The granitic rocks at W. Dara area are characterized by widely dissected by dyke swarms, joints and fractures (figure 3).

**Fig. 2: General view for the G. Dara younger granite looking SW, W. Dara area.**

**Fig. 3: Trachytic dyke swarms intrude the younger granite of G. Dara looking S to SW, W. Dara area.**

These dykes range in thickness from 0.5 to 5m and most of them are more resistant to erosion than the host rocks and hence they form prominent ridges and cutting all the above-mentioned rock units. Acidic dykes are the oldest dykes and represented by felsites, fine-grained granite and porphyritic rhyolite dykes. Intermediate dykes are represented by andesite. Basic dykes are represented by dolerites and basalts. Alkaline dykes are represented by trachytic dykes cut the Dokhan volcanics and granitic rocks.

The radiometric investigations were achieved through field measurements in terms of total gamma radioactivity (ppm); a systematic radiometric survey has been carried out on the various rock exposures. The granitic rock of G. Dara, at the investigated area, has the highest radioactivity level among the rocks cropping out in the area. This result is coinciding with (Rogers and Adams, 1969, Deer et al., 1992, Scheepers 2000); who mentioned that the radioactivity of igneous rocks is related to the acidity of these rocks as the acidity increase the radioactivity increase.

The uranium content of this younger granite ranges from 25 ppm to 150ppm; in addition to, there is a radioactive occurrence recorded along fault zone (radioactive occurrence 1, figure 1). The gamma radioactivity measured along this fault zone reach as up to 2200 ppm with eU content of 100 ppm, Th content 150 ppm and K content 30%, where strong alterations occur at this fault zone such as iron oxides and manganese oxides. Detailed geology, structure and radioactivity studies carried out on this radioactive occurrence (figures 4 and 5).

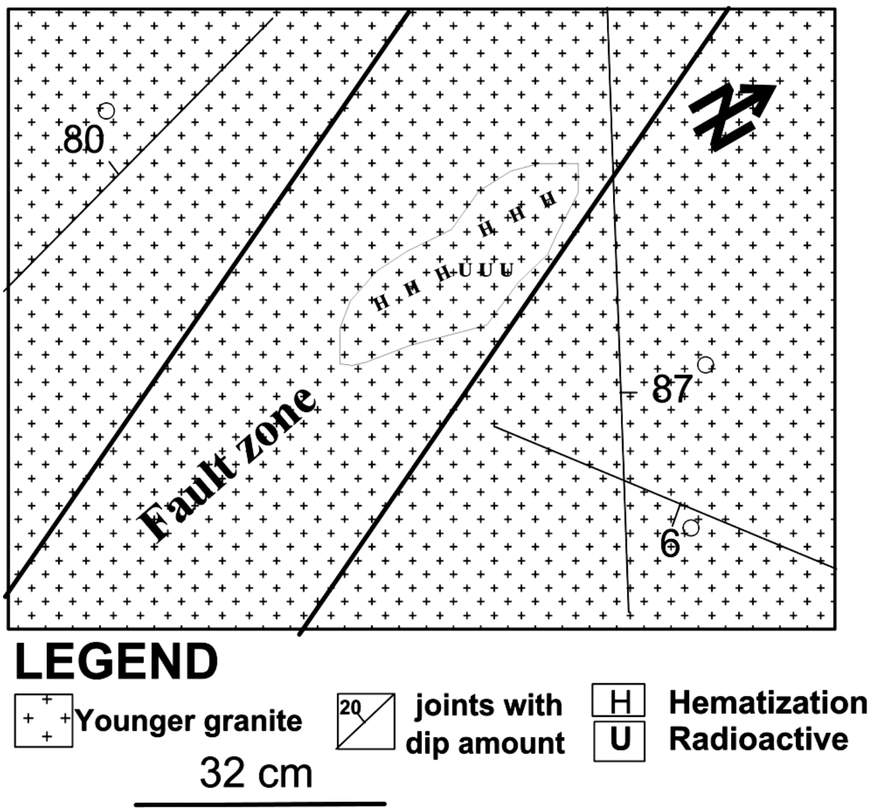


**Fig. 4: Geological sketch map of radioactive occurrence (No. 1), W. Dara area.**

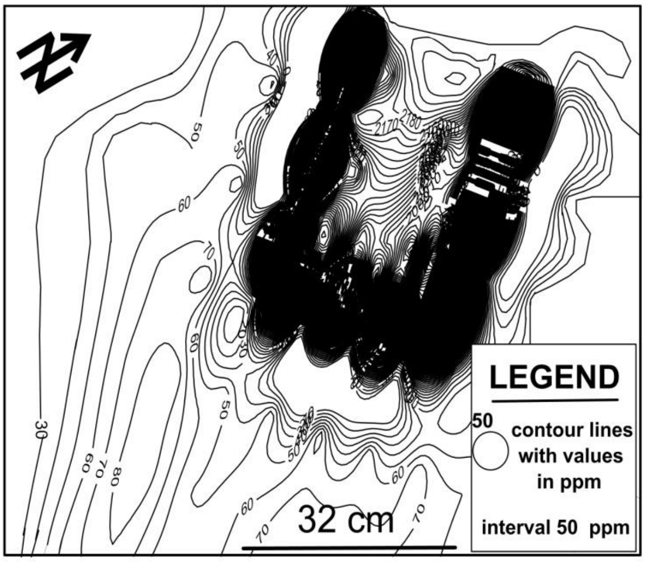


**Fig. 5: Isorad map of radioactive occurrence (No. 1), W. Dara area.**

The authors mentioned above that W. Dara granite is highly dissected by dyke swarms of different composition among these dykes the trachytic dykes contains a radioactive occurrence ((radioactive occurrence 2, figure 1) at its contact with younger granite. This radioactive occurrence is represented by a spot of about 100 x 50 cm in dimensions at the contact between trachytic dyke and younger granite of W. Dara area. The gamma radioactivity measured at this anomaly reach as up to 1000 ppm with eU content 100 ppm, Th content 80 ppm and K content 40%. Figures 6 and 7 show detailed geology, structure and radioactivity studies at that occurrence. Representative samples for these radioactive occurrences were collected for more analytical analysis.

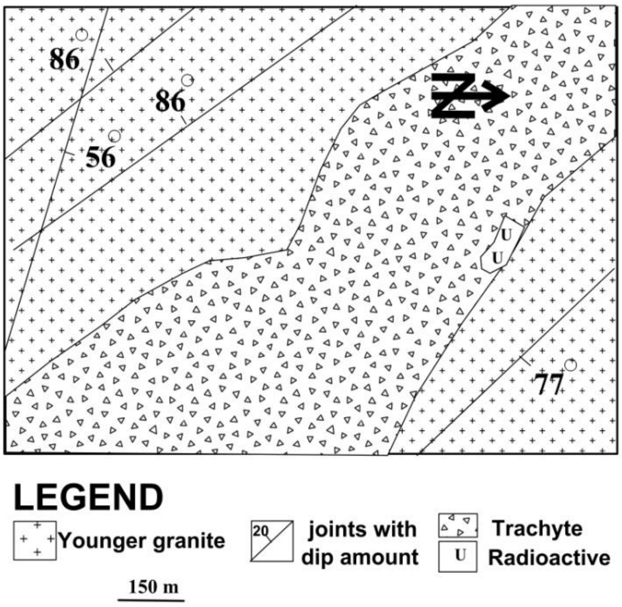


**Fig. 6: Geological sketch map of radioactive occurrence (No. 2), W. Dara area.**

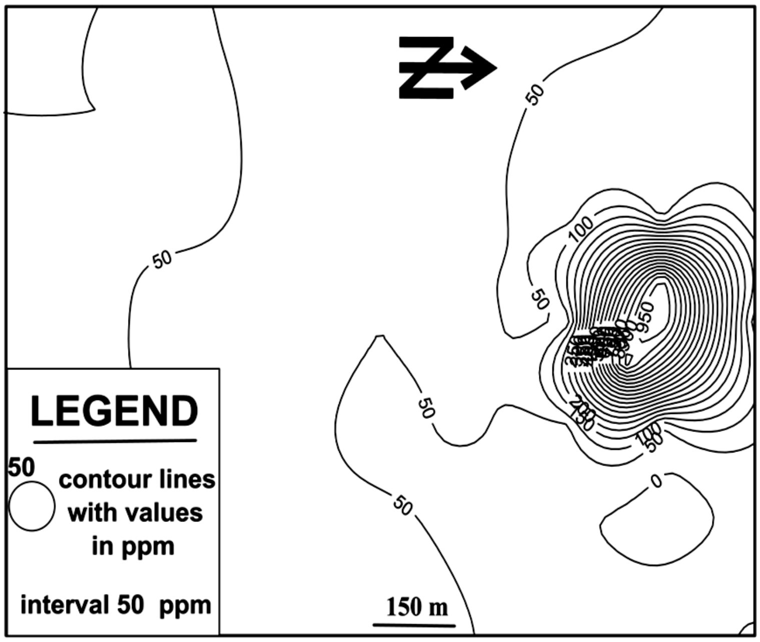


**Fig. 7: Isorad map of radioactive occurrence (No. 2), W. Dara area.**

## 2. MATERIALS AND METHODS

Field and laboratory works, which includes infrared spectrum (IR), mineralogical studies by using Environmental Scanning Electron Microscope (ESEM) and chemical analyses. The gamma ray scintillometer; model RS-320is used for the field radioactivity measurements. This instrument gives the radioactivity of the rock in terms of part per million (ppm).

Representative radioactive specimens were collected including two different radioactive rock types that are trachytic dyke and radioactive Dara granite. Field photographs were taken showing the general features for the investigated area.

### 2.1. Algal Collection and Processing

Three algal species, namely (*Cystoseira osmundacea* belong to Phaeophyta), *(Palmaria elegans and Chondrus Crispus* belong to Rhadophyta) were collected from Red Sea on the coast of Hurghada, Egypt, transferred to laboratory in labeled polyethylene bags. The samples were washed several times with de-ionized water to remove dirt, and/or other impurities present in the raw materials. They were air dried for 10 days, then grinded and sieved at the pore size of 0.5 to 1 mm [Matheickal et al 1999].

### 2.2. Characterization of the Algal-biosorbent Materials

infra-red spectrum (IR) of model Naxux 670 was applied in a spectrum ranges of 400–4000 cm-1 for the sample to identify the functional groups in the central national research (CNR) and the morphological characteristics of the algal biomasses surface and the pore and particles fractions were examined under environmental scanning electron microscope (ESEM), field imission gun (FIG) in the central national research (NMA) Furthermore, the sizes of the grinded algal biomasses were determined using microscope type olympes PX2020 attach with digital camera.

### 2.3. Adsorption Experiments

In order to investigate the ability of the *Cystoseira osmundacea* , *Palmaria elegans and Chondrus Crispus* biosorbent materials to recover (uranium and thorium) from the aqueous solutions of selected samples of wadi dara, batch experiments were conducted by contacting (uranium and thorium) solutions with the adsorbent (1 g/l). The flasks were placed on a shaker with constant shaking for 100 rpm, and then incubated at 30 ºC for 5 days. The algal biomasses were washed several times as outlined in the work of Kato et al. (2003). Then examined using (ESEM) and chemically to determine uranium & thorium concentration from the biomass. The samples were examined under Infrared Spectroscopy (IR) using the model Naxux 670 FTIR, in the Central National Research (CNR), Environmental scanning electron microscope (ESEM), field imission gun (FIG) in the nuclear material authority (NMA) and olympes PX2020 attach with digital camera.

## 3. RESULTS

### 3.1. Mineralogy

The mineralogical study for the rock samples indicated the presence of uranium (U)and thorium (Th) bearing zircon mineral with minor amount of cesium(Ce) and yttrium(Y)(figure 8) at granitic sample; in addition to, ferrocolumbite containing patches of the unidentified rich rare earth (REE) silicate mineral and zircon contain uranium (figures 9 and 10) at trachytic sample. The uranium and thorium and zirconium (Zr) elements are completely adsorbed from the uranium and thorium bearing zircon mineral at granitic sample by Cystoseira osmundacea and *Palmaria elegans* (figures 11 and 12); while *Chondrus Crispus* is completely adsorb uranium and thorium but it can't adsorb zirconium element (figure 13).

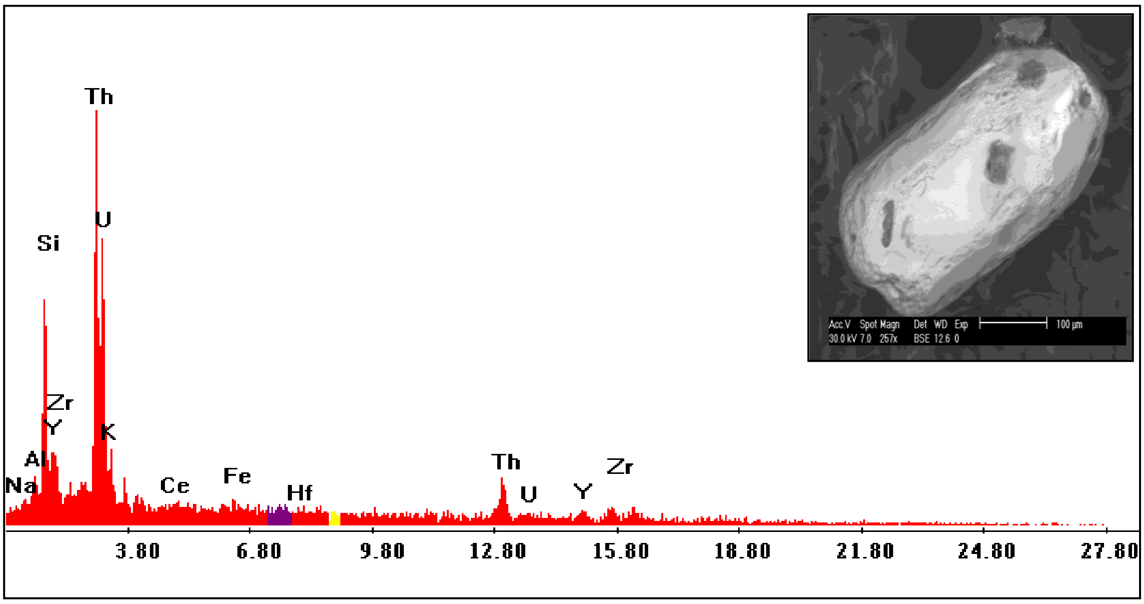


**Fig. 8: Back-scattered electron image and EDAX chart of zircon mineral including uranium and thorium, W. Dara area.**

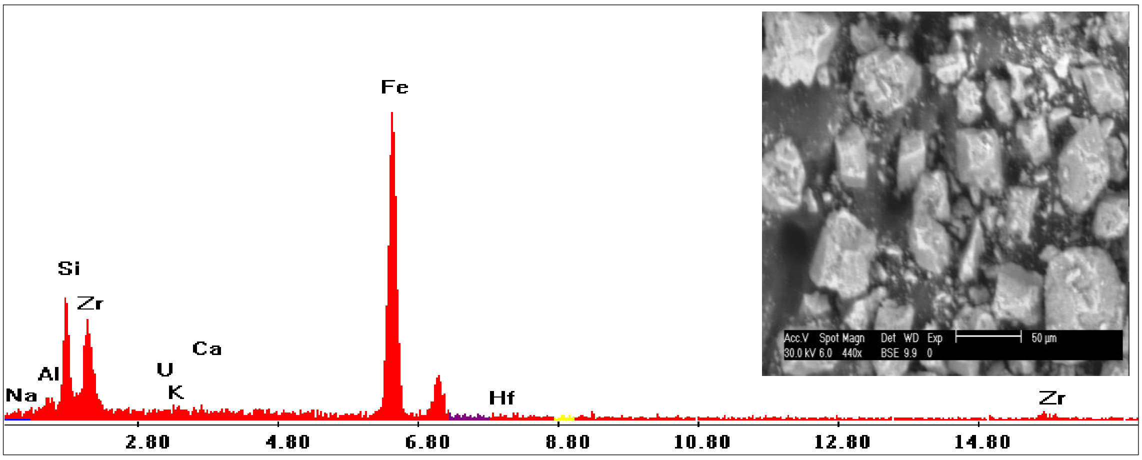


**Fig. 9: Back-scattered electron image and EDAX chart of zircon mineral including uranium, W. Dara area.**

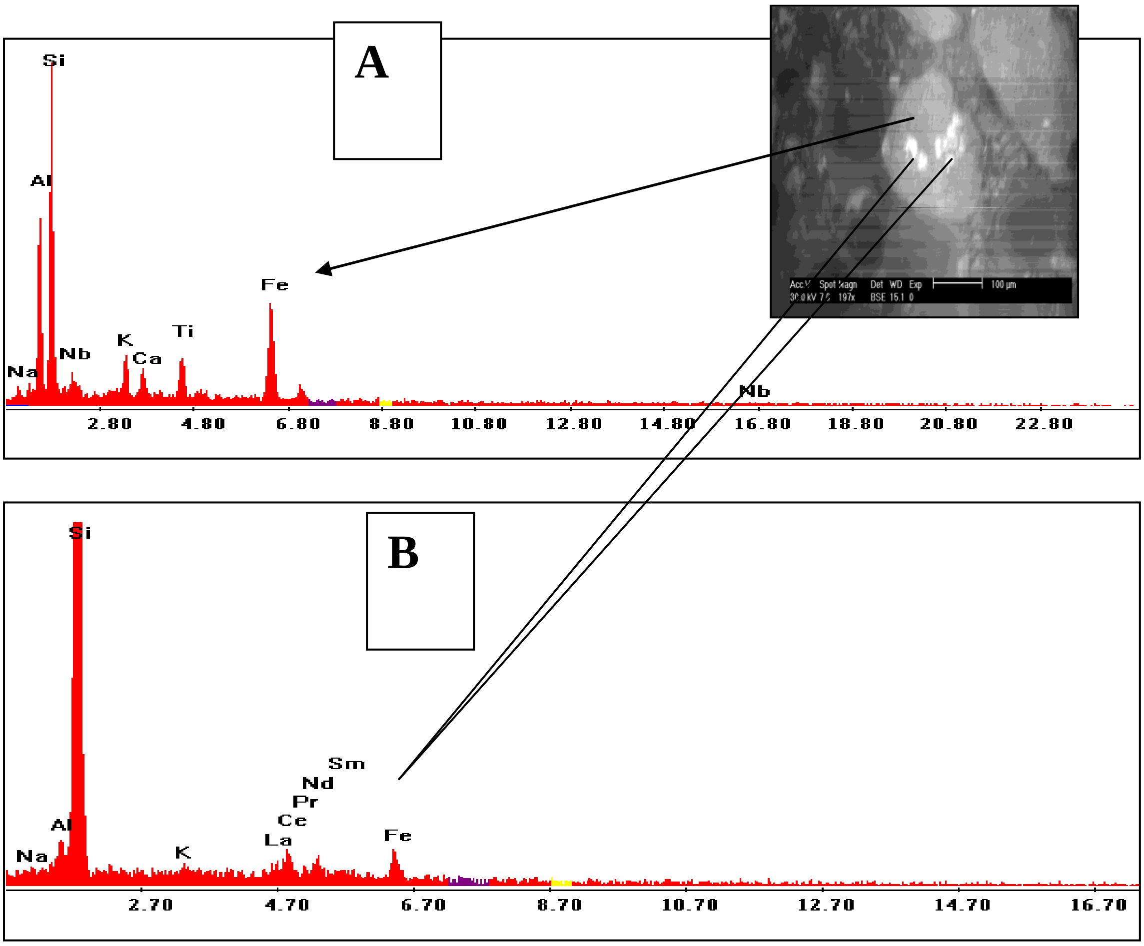


**Fig. 10: Back-scattered electron image and EDAX chart of ferrocolumbite (A) containing patches of unidentified rich rear earth silicate mineral (B), W. Dara area.**

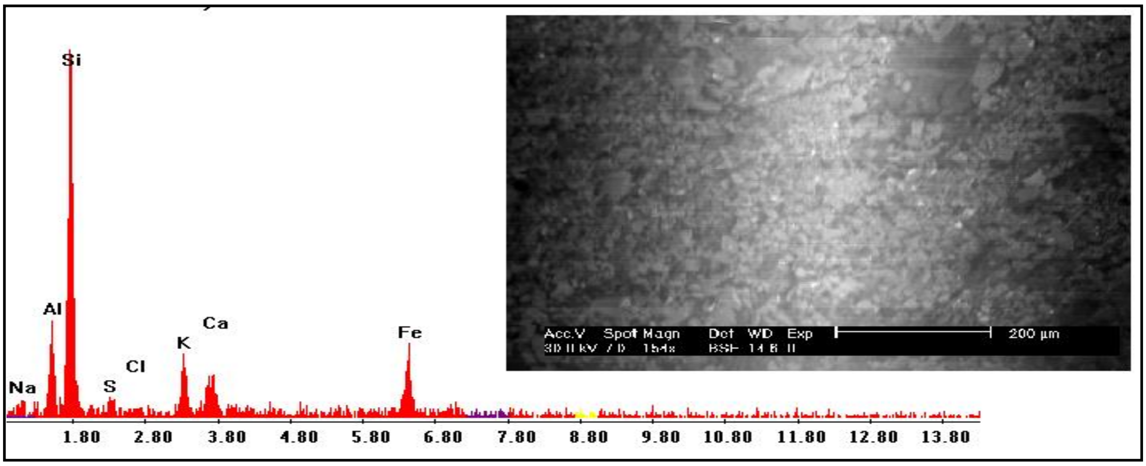


**Fig. 11: Back-scattered electron image and EDAX chart of zircon mineral without uranium and thorium or zirconium (Zr) element after *Cystoseira osmundacea* algae, W. Dara area.**

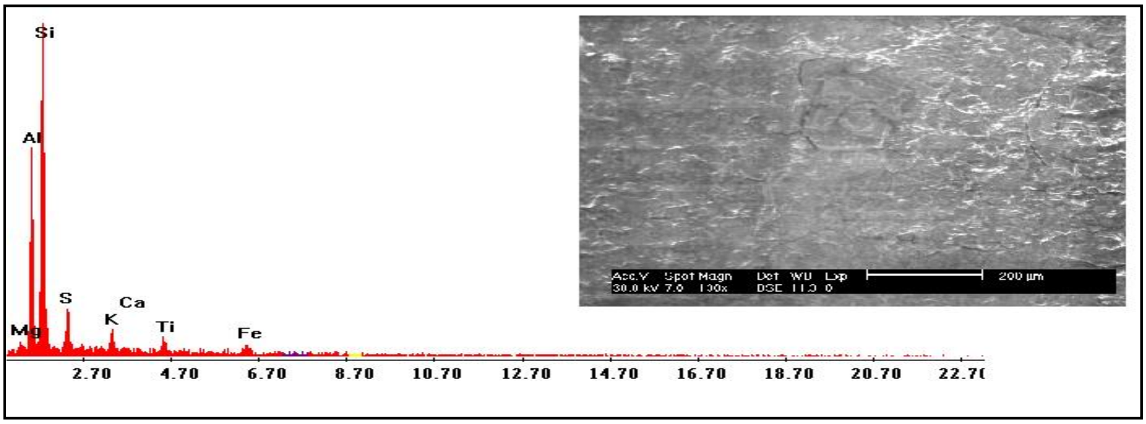


**Fig. 12: Back-scattered electron image and EDAX chart of zircon mineral without uranium and thorium or zirconium (Zr) element after *Palmaria elegans* algae, W. Dara area.**

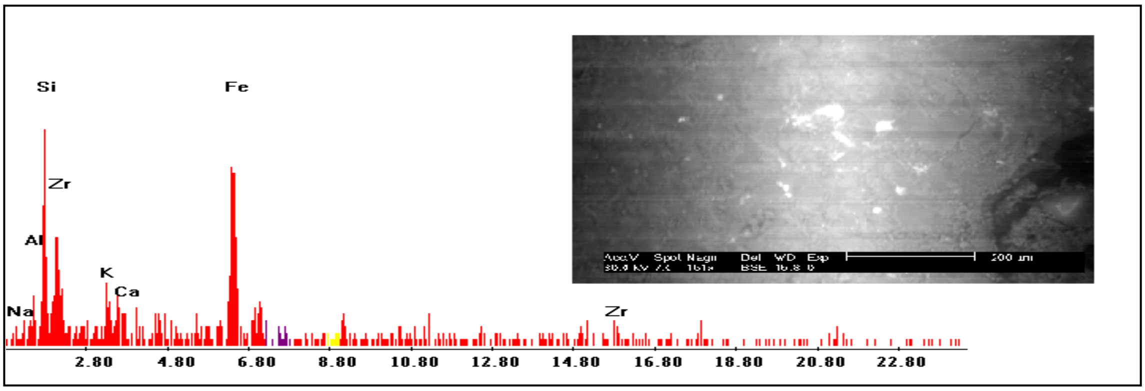


**Fig. 13: Back-scattered electron image and EDAX chart of zircon mineral without uranium and thorium but with zirconium (Zr) element after *Chondrus Crispus* algae, W. Dara area.**

With trachytic sample; the uranium are completely adsorb and also the authors note that from ferrocolumbite the Niobium (Nb) and Titanium (Ti) are also completely adsorb by the three algae (figures 14, 15 and 16).

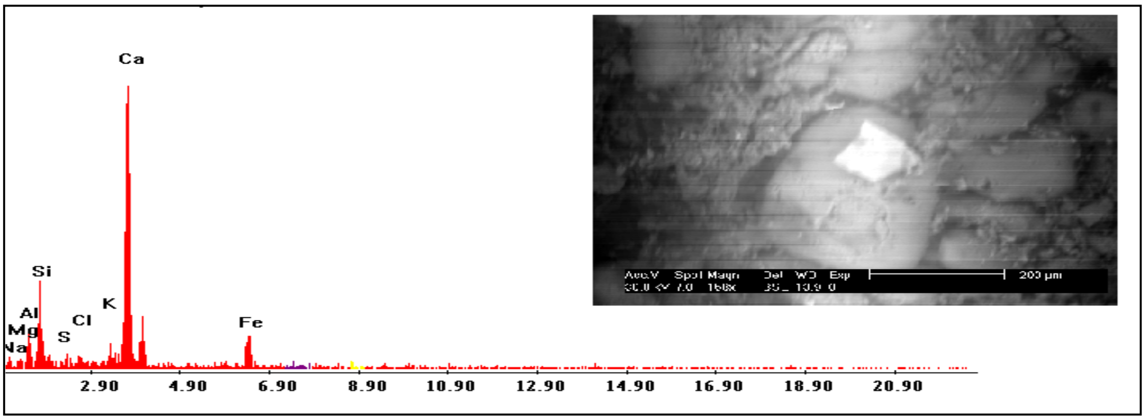


**Fig. 14: Back-scattered electron image and EDAX chart of mineral without uranium and Niobium (Nb) or Titanium (Ti) element after *Chondrus Crispus* algae, W. Dara area.**

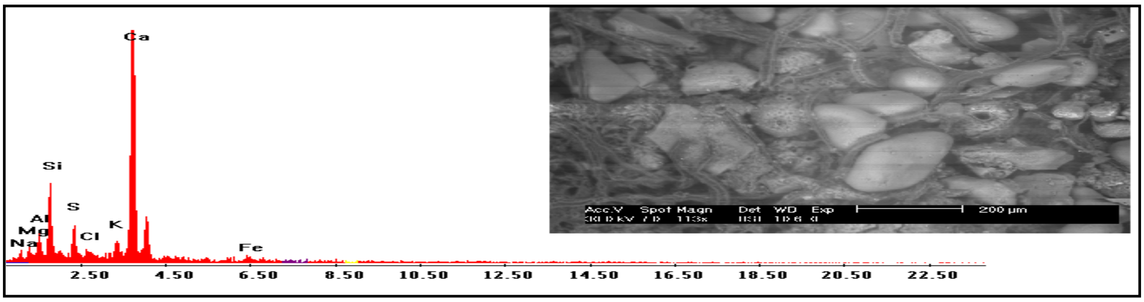


**Fig. 15: Back-scattered electron image and EDAX chart of mineral without uranium and Niobium (Nb) or Titanium (Ti) element after *Palmaria elegans* algae, W. Dara area.**

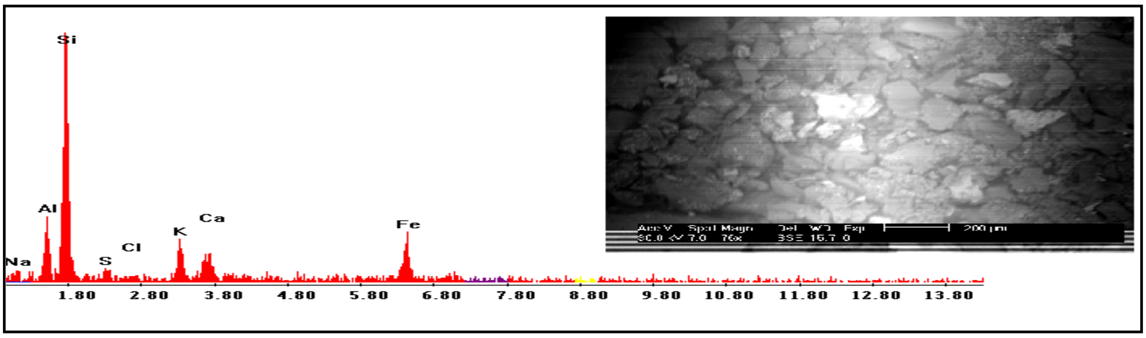


**Fig. 16: Back-scattered electron image and EDAX chart of mineral without uranium and Niobium (Nb) or Titanium (Ti) element after Cystoseira osmundacea algae, W. Dara area.**

**3.2. Spectroscopy Analysis:**

Metal biosorption depends especially on the components of the cell wall, IR spectrogram of original biomass of the three algae were compared with the trachyte and granite rocks of W. Dara area , So we can detect the changes associated with the influence of metal sorption.

***A: trachyte rock of W. Dara area:***

The surface characterization of trachyte rock with the help of IR spectrum showed the presence of C-O-C, $SO_2$ and N-O, which was compared with the three algae, some changes of the functional groups, appear which indicate the influence of uranium and thorium sorption by *Cystoseira osmundacea, Palmaria elegans and Chondrus Crispus* biosorbent materials. The shift in the IR vibration indicate the binding of uranium and thorium ion on the surface of Cystoseira osmundacea the spectrum showed the presence of $CH_2$, $CH_3$ (methyl and methylene) with coupling amide with the vanishement of $SO_2$ functional group, dealing with Chondrus Crispus the IR spectrum showed the presence of $CH_2$, $CH_3$ (methyl and methylene) with C-O alcoholic at 1000-1200$CM^{-1}$, C=O carbonyls while $SO_2$ is evanescence from the spectrum finally Palmaria elegans give a characteristic wavelength of sulplur ($SO_3$) $CH_2$, $CH_3$ (methyl and methylene) and OH group SO is receded from view as it appear in figure (17).

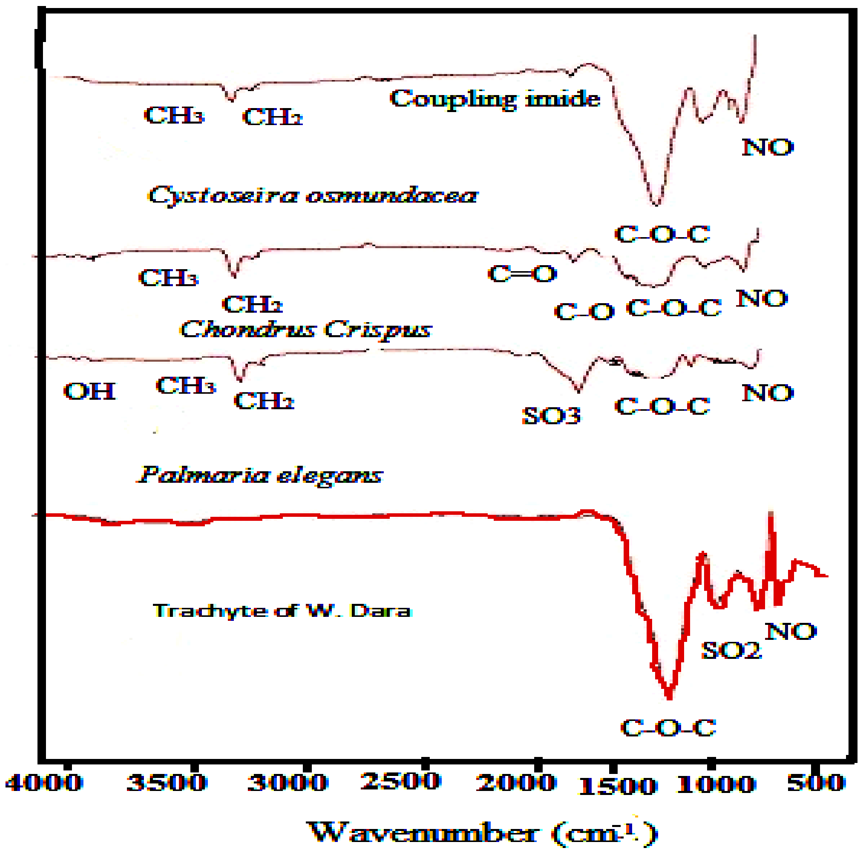


**Fig. 17: Vibrational stretches of functional groups of adsorbate for trachyte rock of W. Dara area in the infrared spectroscopy analysis with the three biosorbent materials.**

***B: Granite rock of W. Dara area:***

The surface characterization of the granite rock with the help of IR spectrum showed the presence of C-O-C, $SO_2$ and N-O, which was compared with the three algae, some changes of the functional groups, appear as seen in figure (18).

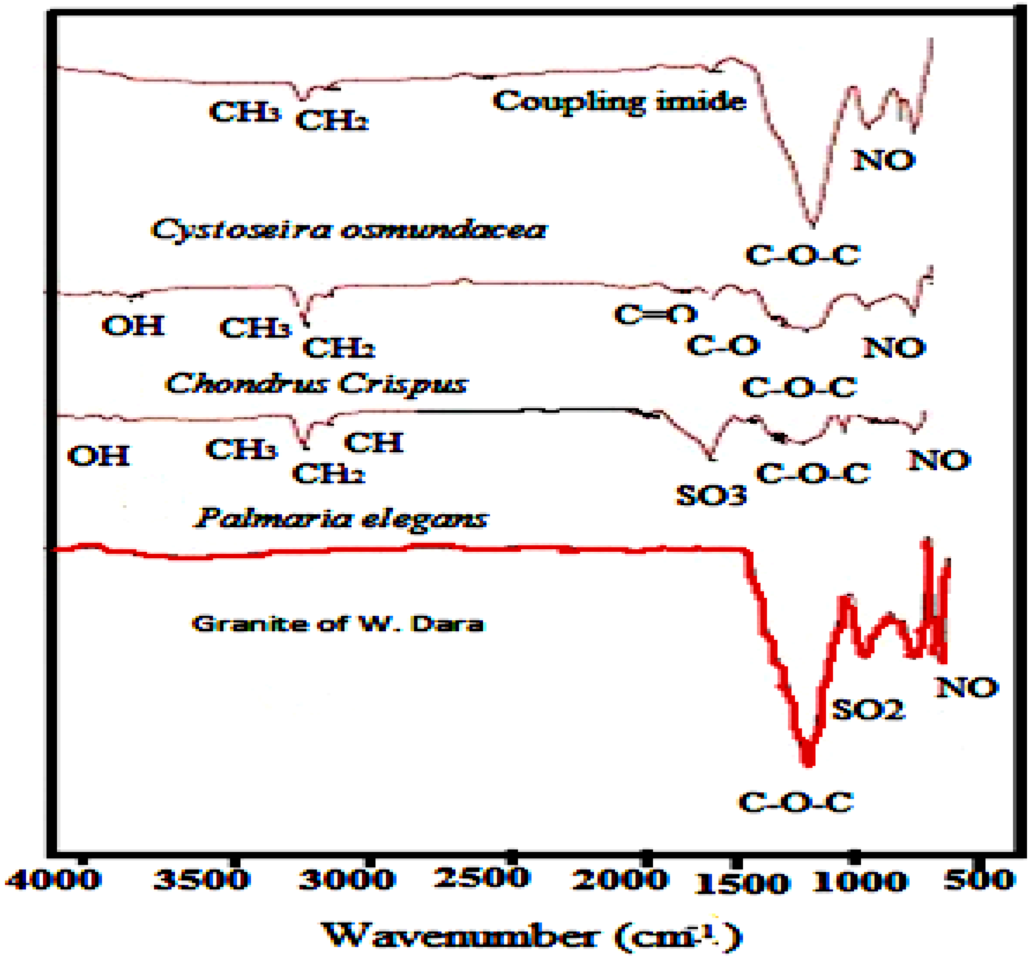


**Fig. 18: Vibrational stretches of functional groups of adsorbate for granite rock of W. Dara area in the infrared spectroscopy analysis with the three biosorbent materials.**

IR spectrogram of original biomass of *Cystoseira osmundacea* was compared with the granite sample indicate changes associated with the influence of uranium and thorium sorption appearance of $CH_2$, $CH_3$ (methyl and methylene) with coupling amide, *Chondrus Crispus* IR spectrum showed the presence of OH, $CH_2$, $CH_3$ (methyl and methylene), C=O carbonyls with C-O alcoholic, finally *Palmaria elegans* spectrum show $CH_2$, $CH_3$ (methyl and methylene) with CH alkane and OH from the spectrums of the three algal biomass indicate the demise of $SO_2$ functional group. There are evidences that confirm that functional groups containing $O^-$, $N^-$, $S^-$, or $P^-$, participate directly in binding certain metals (Wang and Dei 1999). The carboxyl, hydroxyl, sulphate and amino groups in algal cell wall polysaccharides act as binding sites for metals (Lesmana et al. 2009).

### 3.3. Chemical Analysis

Trachyte rock of W. Dara area characterized by its content of uranium about 30 ppm and thorium 29 ppm dealing with *Cystoseira osmundacea* , *Palmaria elegans and Chondrus Crispus* as a biosorbent materials appeared in table (1) and figure (19). *Cystoseira osmundacea* as a biosorbent materials for uranium and thorium in the trachyte rock of W. Dara area indicate the % of biosorption (62.93% U and 100 % Th) the mother sample was (30 ppm U and 29 ppm Th) after biosorption with *Cystoseira osmundacea* it became 11.12 ppm U and N.D for thorium , dealing with *Palmaria elegans* biosorption for uranium reach to 90% & thorium 100 % biosorption after treatment become (3 ppm U & N.D for Th). Finally *Chondrus Crispus* dealing with trachyte rock of W. Dara area the uranium biosorption was not effective it was 30 ppm after biosorption reach to 22 ppm while thorium was 29 ppm it become after treatment 10.25 ppm the percent for biosorption summarized as the following (26.66 % U and 64.65 % Th).

Granite rock of W. Dara area dealing with the *Cystoseira osmundacea*, *Palmaria elegans and Chondrus Crispus* as a biosorbent materials to recover (uranium and thorium) were seen in table (2) and figure (20).

*Cystoseira osmundacea* biosorption for uranium detected as 2 ppm, compared with the mother sample of Granite rock of W. Dara area was 23 ppm while thorium after biosorption become not detected compeered with the mother sample was 58.36 ppm. The percent of biosorption for uranium and thorium ( 91.3 % U & 100 % Th) table (3) and figure (21), dealing with *Palmaria elegans* as a biosorbent material for uranium and thorium detected after analysis as 9.91 ppm for uranium & 24.91 ppm for thorium we can conclude that the percent of biosorption is ( 56.91% U & 57.31 % Th ) table (4) and figure (22); finally *Chondrus Crispus* biosorbe about 78.26 % uranium and 100% thorium from granite rock of W. Dara area.

**Table (1): Chemical analysis of uranium and thorium from trachyte rock of W. Dara area compared with the three biosorbent materials Cystoseira osmundacea, Palmaria elegans and Chondrus Crispus.**

| | Uranium (ppm) | Thorium (ppm) |
|---|---|---|
| Trachyte rock of W. Dara area | 30 | 29 |
| *Cystoseira osmundacea* | 11.12 | N.D |
| *Palmaria elegans* | 3 | N.D |
| *Chondrus Crispus* | 22 | 10.25 |

**Table (2): Chemical analysis of uranium and thorium from granite rock of W. Dara area compared with the three biosorbent materials *Cystoseira osmundacea, Palmaria elegans and Chondrus Crispus*.**

| | Uranium (ppm) | Thorium (ppm) |
|---|---|---|
| Granite rock of W. Dara area | 23 | 58.36 |
| *Cystoseira osmundacea* | 2 | N.D |
| *Palmaria elegans* | 9.91 | 24.91 |
| *Chondrus Crispus* | 5 | N.D |

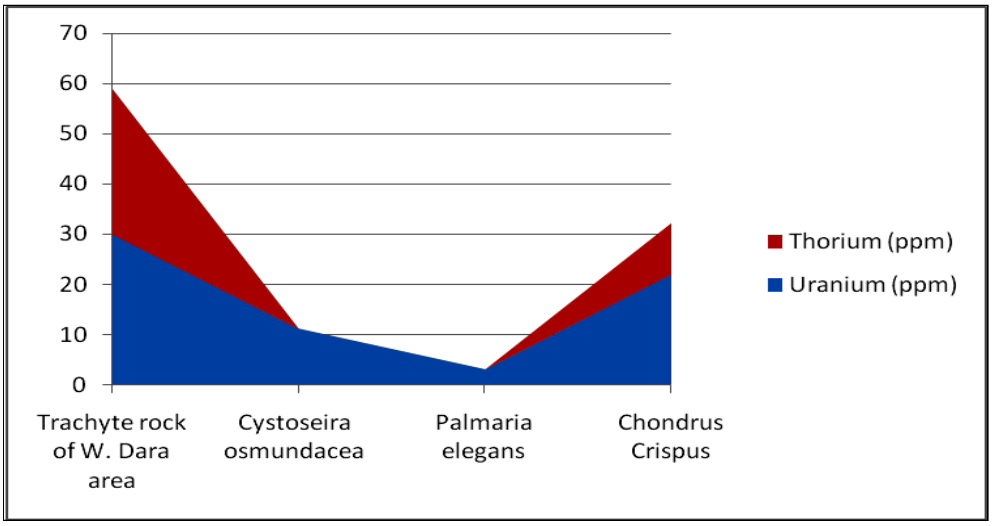


**Fig. 19: Chemical analysis of uranium and thorium from trachytic rock of W. Dara area compared with the three biosorbent materials *Cystoseira osmundacea, Palmaria elegans and Chondrus Crispus*.**

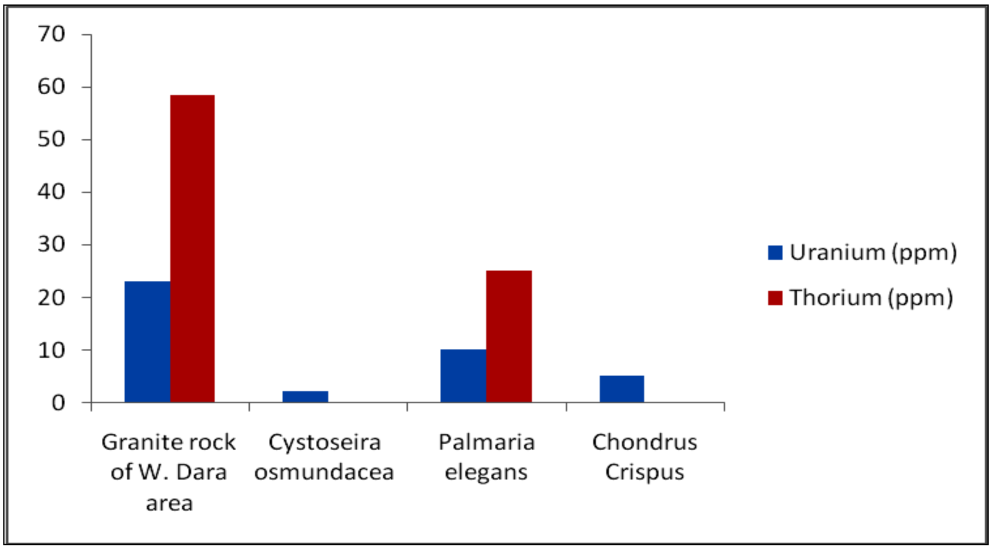


**Fig. 20: Chemical analysis of uranium and thorium from granite rock of W. Dara area compared with the three biosorbent materials *Cystoseira osmundacea, Palmaria elegans and Chondrus Crispus*.**

**Table (3): Percentage of biosorption for uranium and thorium from trachyte rock of W. Dara area by with the three biosorbent materials *Cystoseira osmundacea, Palmaria elegans and Chondrus Crispus*.**

| % of biosorption for trachyte rock of W. Dara area | Uranium | Thorium |
|---|---|---|
| *Cystoseira osmundacea* | 62.93 | 100 |
| *Palmaria elegans* | 90 | 64.65 |
| *Chondrus Crispus* | 26.66 | 100 |

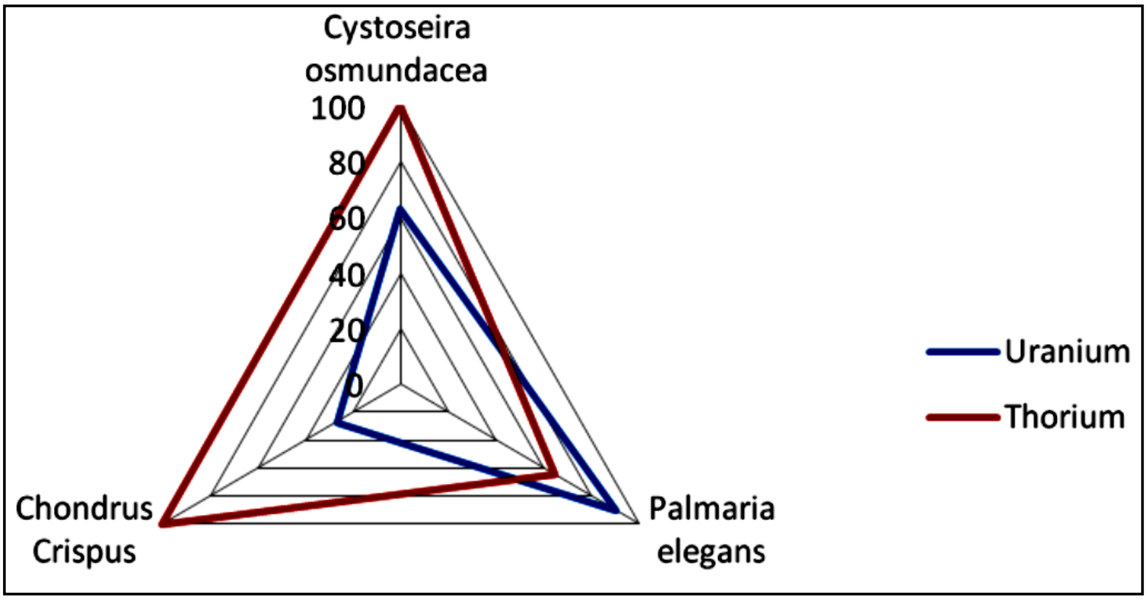


**Fig. 21: Percentage of biosorption for uranium and thorium from trachyte rock of W. Dara area by with the three biosorbent materials *Cystoseira osmundacea, Palmaria elegans and Chondrus Crispus*.**

**Table (4): Percentage of biosorption for uranium and thorium from granite rock of W. Dara area by with the three biosorbent materials *Cystoseira osmundacea, Palmaria elegans and Chondrus Crispus*.**

| % of biosorption for granite rock of W. Dara area | Uranium | Thorium |
|---|---|---|
| *Cystoseira osmundacea* | 91.3 | 100 |
| *Palmaria elegans* | 56.91 | 57.31 |
| *Chondrus Crispus* | 78.26 | 100 |

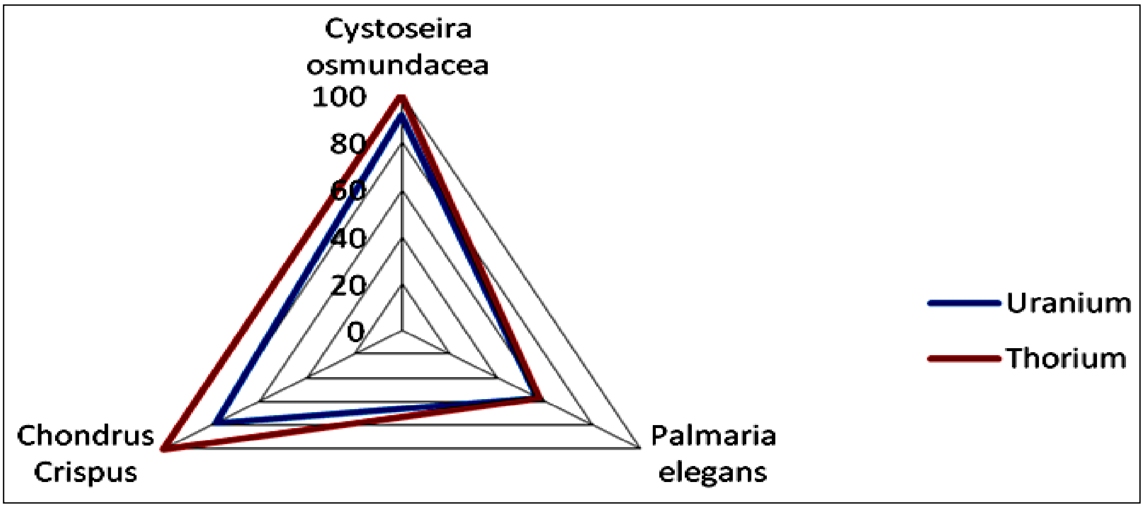


**Fig. 22: Percentage of biosorption for uranium and thorium from granite rock of W. Dara area by with the three biosorbent materials *Cystoseira osmundacea, Palmaria elegans and Chondrus Crispus*.**

## 4. CONCLUSION

W. Dara area characterized by the presence of granitic rocks highly affected by structural deformation; the granitic rock of G. Dara has the highest radioactivity level among the rocks cropping out in the area; there is a radioactive occurrence recorded along fault zone, The gamma radioactivity measured along this fault zone reach as up to 2200 ppm with eU content of 100 ppm, Th content 150 ppm and K content 30%, as well as, it is highly dissected by dyke swarms of different composition among these dykes the trachytic dykes contains a radioactive occurrence. The gamma radioactivity measured at this anomaly reach as up to 1000 ppm with eU content 100 ppm, Th content 80 ppm and K content 40%.

The effectiveness of the two algae *(Cystoseira osmundacea*, Palmaria *elegans*) as biosorbent material were confirmed to biosorbe thorium completely from trachyte rock of W. Dara area while *Cystoseira osmundacea and Chondrus Crispus* were attempted to biosorbe thorium from granite rock of W. Dara area to reach its maximum sorption 100% biosorption. On the other hand *Palmaria elegans* achieve a high percent of biosorption about 90% for uranium with trachyte rock of W. Dara area compared with the other while *Cystoseira osmundacea* reach its maximum sorption for uranium from granite rock of W. Dara area about 91.3 % than the other two algae, so we can conclude that *Cystoseira osmundacea*, *Palmaria elegans and Chondrus Crispus* can be a very good biosorbent for uranium and thorium from trachyte and granite rock of W. Dara area.

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