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Biosorption Capacity for Uranium and Thorium by Some Microalgae Species

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THE BIOSORPTION is an effective technique for the removal of uranium and thorium from some types of phosphate rocks of red sea area. In this study *Cystoseira osmundacea*, *Palmaria elegans and Chondrus crispus*, were used for the biosorption of uranium (U), and thorium (Th), from phosphates rocks in Egypt in Qusser and Safaga areas west red sea which characterized of shallow-water marine origin and mainly associated with sequences of white hard limestone, white chalk, yellow marls and hard cherts rocks. The obtained results showed that *Cystoseira osmundacea*, *Palmaria elegans* and *Chondrus crispus* have biosorption capacities of (81%, 89% and 90%), for U and (77%, 88% and 91%) for Th, respectively from phosphate of Safaga .and biosorption capacities of (81%, 84% and 89%), for U and (79%, 81% and 88%) for Th, respectively from phosphate of Qusser area. it is preferable to use *Chondrus crispus* on biosorption due to its high sorption capacity than the other two algae.

Keywords: Biosorption, *Chondrus crispus, Cystoseira osmundacea*, *Palmaria elegans,* Thorium, Uranium.

Introduction

The accumulation of metals by algae, bacteria, fungi and yeast was extensively studied in the last two decades. Of the studied microorganisms, algae are gaining increasing attention, due to the fact that algae (Dubin et al., 1978), particularly marine algae, are a rich source in the oceanic environment, relatively cheap to process and able to accumulate high metal content (Wilde & Benemann, 1993), owing to low cost and ease of availability (Clemens, 2006). Various species of marine alga were used as biosorbent for removal of metals from environmental samples (Yu, 1997; El-Sikaily et al., 2007; Fagundes et al., 2017; Nessim, 2011).

The algal cell wall plays an important role in metal binding (Crist et al., 1988), due to its high content in polysaccharides with acid functional groups. The main substances of this type in brown algae are alginates, which usually constitute about 20-40% of the total dry weight (Percival & McDowell, 1990).

Although adsorption on the cell surface is the dominant mechanism both surface adsorption and internal diffusion are involved in the uptake of some elements like cobalt, uranium and thorium by algae (Kuyucak & Volesky, 1989a & b). The aim of the present work is to evaluate the sorption capacity of three different algae, *Cystoseira osmundacea*, *Palmaria elegans* and *Chondrus crispus*, in respect of U and Th metals from Red sea phosphates (Safaga and Qusser areas).

Materials and Methods

Algal collection and processing

Three algal species, namely *Cystoseira osmundacea* belong to Phaeophyta; *Palmaria elegans* and *Chondrus crispus* belong to the Rhadophyta were collected from the Red Sea coast of Hurghada, Egypt and transferred to laboratory in labelled 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 pore size of 0.5 to 1mm (Matheickal et al., 1999).

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Characterization of the algal-biosorbent materials

Infra-red spectrum (IR) of model Naxux 670 in the Central National Research in Egypt (CNR), was applied in a spectrum ranges of 400–4000cm^{-1} for the sample to identify the functional groups. The morphological characteristics of the algal biomasses surface. The pore and particles fractions were examined under Environmental Scanning Electron Microscope (ESEM). Furthermore, the sizes of the grinded algal biomasses were determined using optical microscope type Olympus model PX2020 attach with digital camera at the Nuclear Materials Authority, Egypt (NMA).

Adsorption experiments

In order to investigate the ability of the *Cystoseira osmundacea*, *Palmaria elegans and Chondrus crispus* biosorbent materials to recover (U and Th) from aqueous solutions of selected samples of Red Sea phosphate (Safaga and Qusser), batch experiments were conducted by contacting the solutions with the adsorbent (1gm/L). The flasks were placed on a shaker with constant shaking for 100 rpm, and then incubated at 30ºC for 5 days. The algal biomasses were washed several times as outlined in the work of Kato et al. (2003) and Gad (2021) then examined using (ESEM) and chemically to determine U & Th concentration from the biomass. The samples were examined under Infrared spectroscopy (IR), (ESEM), and optical microscopically.

The Egyptian phosphates are shallow-water marine origin, mainly associated with sequences of limestone, chalk, marls and cherts. The Red sea phosphate (Safaga and Qusser areas) is known as Duwi Formation (EL-Nagger, 1966), which are assigned as Upper Campanian to Early Maastrichtian age (Hermina, 1973).

Determination of Th and U in algal samples

To determine the equation between biosorbent material (*Cystoseira osmundacea*, *Palmaria elegans and Chondrus crispus* biosorbent materials to recover U and Th from the aqueous solutions of selected samples of phosphates from Safaga and Qusser areas, by calcuting the Initial and final concentrations of Th and U in solution which are measured with ICP-MS. The uptake amount (A) of Th and U due to each sample was estimated by subtracting the final concentrations (Cf) from initial concentrations (Ci) in the liquid phase expressed as the following equation:

$A = (Ci - Cf)\ V/M\ m$[mole g^{-1}] (El-Sikaily et al., 2007; Aziz et al., 2015).

where V is the volume of the solution, M is the atomic weight of each element and m is the dry weight of each sample.

Results and Discussion

This investigation was focused on the tolerance of *Cystoseira osmundacea*, *Palmaria elegans and Chondrus crispus* biosorbent materials to recover U and Th from the aqueous solutions of selected samples of Safaga and Qusser phosphates areas

Chemical analysis

Biosorption of uranium and thorium from Safaga and Qusser phosphate areas by three types of biosorbent materials *Cystoseira osmundacea*, *Palmaria elegans and Chondrus crispus*, the date reveled that:

A- Qusser area

Chemical analysis for uranium and thorium for the initial sample of phosphate Qusser area were 48ppm U and 59ppm Th , treating with *Cystoseira osmundacea* indicate that the percent of uranium reach 9.12ppm, thorium about 12.39ppm, % of biosorption for uranium 81%, thorium 79%, by acting with *Chondrus crispus* the percent of uranium reach 5.28ppm and for thorium 7.08ppm (% of biosorption of U 89%, 88% for Th) finally acting phosphate Qusser area with *Palmaria elegans* the date reveled that uranium reach to 7.68ppm while thorium become 11.21ppm (percent of biosorption is 84% for uranium, 81% for thorium) therefore we can conclude that *Chondrus crispus* is the best for biosorption for uranium and thorium from Qusser phosphate area as seen in Table 1 and Fig. 1A &B .

TABLE 1. Biosorption of uranium and thorium from Qusser phosphate area

	Initial sample	***Cystoseira osmundacea***	**% of biosorption**	***Palmaria elegans***	**% of biosorption**	***Chondrus crispus***	**% of biosorption**
U	48(ppm)	9.12ppm	81%	7.68ppm	84%	5.28ppm	89%
Th	59(ppm)	12.39ppm	79%	11.21ppm	81%	7.08ppm	88%

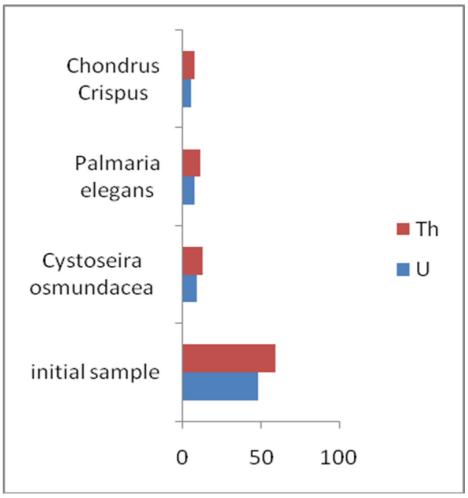


Fig. 1A. Biosorption of uranium and thorium from Qusser phosphate area

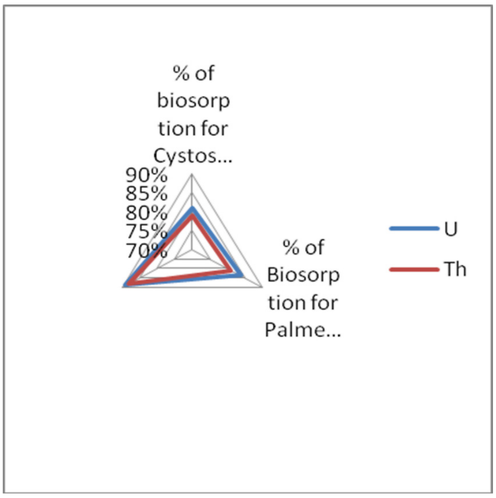


Fig. 1B. The percent of biosorption for uranium and thorium from Qusser phosphate area

B- Safaga area

Safaga phosphate is characterized by its content of uranium and thorium (35ppm U and 44ppm Th), treating with *Cystoseira osmundacea* the content of uranium and thorium decreased to reach about (6.65ppm U and 10.12ppm Th) by calcuting the percent of biosorption (81% U & 77% Th). Treating with *Chondrus crispus* was a very promising data because percent of U decreased to reach about 3.5ppm U and 3.96ppm Th. the percent of biosorption was (90% U and 91% Th). *Palmaria elegans* treated with U and Th of Safaga phosphate data indicate that the percent of U reaches 3.85ppm while Th after treatment was 5.28ppm, the percent of biosorption become (89% U and 88% Th). From the previous data we can conclude that *Chondrus crispus*> *Palmaria elegans*> *Cystoseira osmundacea* for the biosorption of uranium and thorium so *Chondrus crispus* is the best for biosorption of uranium and thorium from Safaga phosphate as seen in Table 2 and Fig. 2A & B.

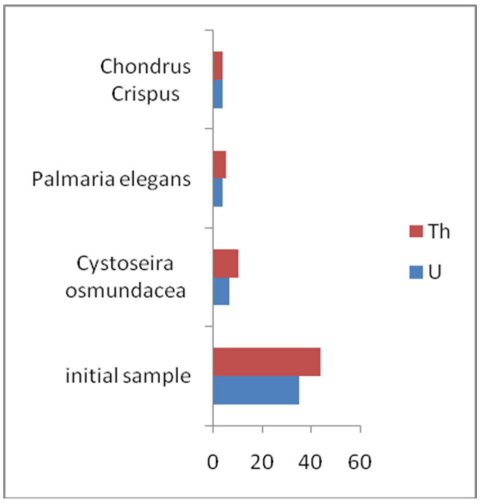
Infra red (IR)

Metal biosorption depends especially on the components of the cell wall, IR spectrogram of original biomass of the three algae were compared with the samples of phosphate of Qusser & Safaga areas so we can detect the changes associated with the influence of metal sorption.

FT-IR spectra ranges from (0-4000cm^{-1}) studying the vibrational stretches of functional groups of dried biosorbent materials *Cystoseira osmundacea*, *Palmaria elegans* and *Chondrus crispus*. Treated with the adsorbate phosphate of Qusser area, the main three peaks emerged at 3400cm^{-1}, 2900cm^{-1} and 1030cm^{-1} have been assigned O-H stretching band, C-H bending band, C-O-C, respectively were appeared in the initial sample with the biosorbent materials *Cystoseira osmundacea*, *Palmaria elegans* and *Chondrus crispus* treated with phosphate of Qusser. While the C=C stretching band appeared only with initial and *Cystoseira osmundacea* which appeared at, 1650cm^{-1}, *Cystoseira osmundacea* and *Chondrus crispus* have record appearance of C=C=N bending band at 2000cm^{-1}, CH bending at 750cm^{-1} and C-I at 550cm^{-1}, finally appearance of CH_3 bending double bands with the disappearance of C-Br from the initial sample with *Chondrus crispus*. These results exposed that *Chondrus crispus* have functional groups which can act as metal binding sites and found at polysaccharides, proteins and lipid on the cell wall surface of algal biomass as seen in Fig. 3.

TABLE 2. Biosorption of uranium and thorium from phosphate of Safaga area

	Mother sample	*Cystoseira osmundacea*	% of biosorption	*Palmaria elegans*	% of biosorption	*Chondrus crispus*	% of biosorption
U	35ppm	6.65ppm	81%	3.85ppm	89%	3.5ppm	90%
Th	44ppm	10.12ppm	77%	5.28ppm	88%	3.96ppm	91%



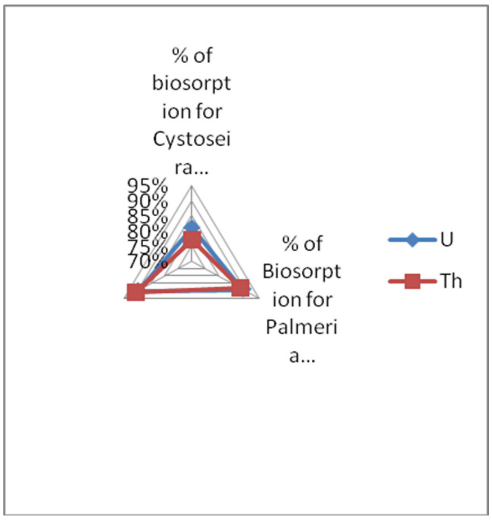


Fig. 2A. Biosorption of uranium and thorium from Safaga phosphate area

Fig. 2B. The percent of biosorption for uranium and thorium from Safaga phosphate area

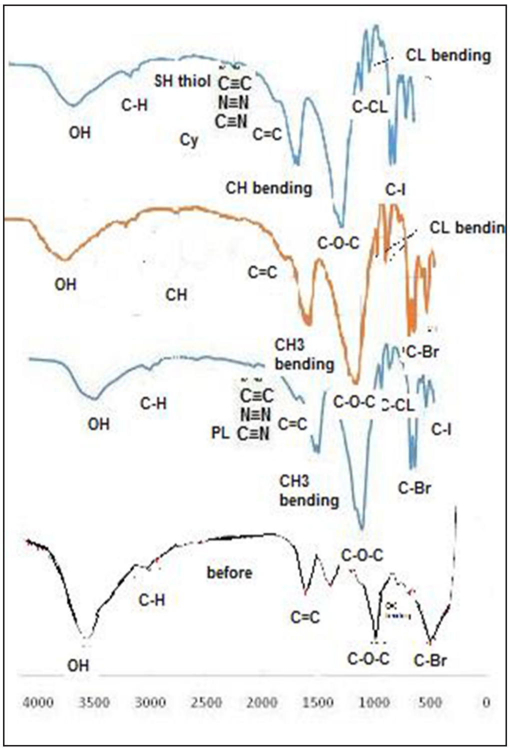


Fig. 3. Vibrational stretches of functional groups of the adsorbate of Qusser phosphate area in the infrared spectroscopy analysis with the biosorbent materials *Cystoseira osmundacea, Palmaria elegans* and *Chondrus crispus*

Studying the vibrational stretches of functional groups of dried biosorbent materials *Cystoseira osmundacea*, *Palmaria elegans* and *Chondrus crispus***,** treated with the adsorbate phosphate of Safaga area as seen in Fig. 4, the main three peaks emerged at 3450cm^{-1}, 2850cm^{-1}and 1050cm^{-1} have been assigned O-H stretching band, C-H bending band, C-O-C, respectively were appeared in the initial sample with the biosorbent materials *Cystoseira osmundacea*, *Palmaria elegans* and *Chondrus crispus* treated with phosphate of Safaga, the group S-H thiol at 2500cm^{-1} exist in *Cystoseira osmundacea* and *Palmaria elegans*, but S=O at 1428cm^{-1} disappeared from the three type of algae and appeared only in the initial sample, while C-Br group at 500 to 600cm^{-1} appeared in initial sample and *Cystoseira osmundacea* and *Palmaria elegans* , on the other hand C=C=N bending band at 1890cm^{-1} and C=O weak band at 1640cm^{-1} seen in *Cystoseira osmundacea* and *Palmaria elegans*, C-H bending appeared first at *Palmaria elegans* at 1410cm^{-1}and Scand appearance was in position 820cm^{-1} with *Chondrus crispus***,** C-I bending band appeared at 550cm^{-1}. Therefore, by comparing the wave numbers before and after uranium and thorium biosorption, it suggested that the functional groups appeared contribute to the uranium and thorium biosorption.

Field emission gun (FIG) data analysis

The Environmental Scanning Electron Microscopy (ESEM) gave that *Chondrus crispus*, *Palmaria elegans* and *cystoseira osmundacea*, make changes in the chemical composition of the mineral content; some elements disappeared or decreased while other elements increased.

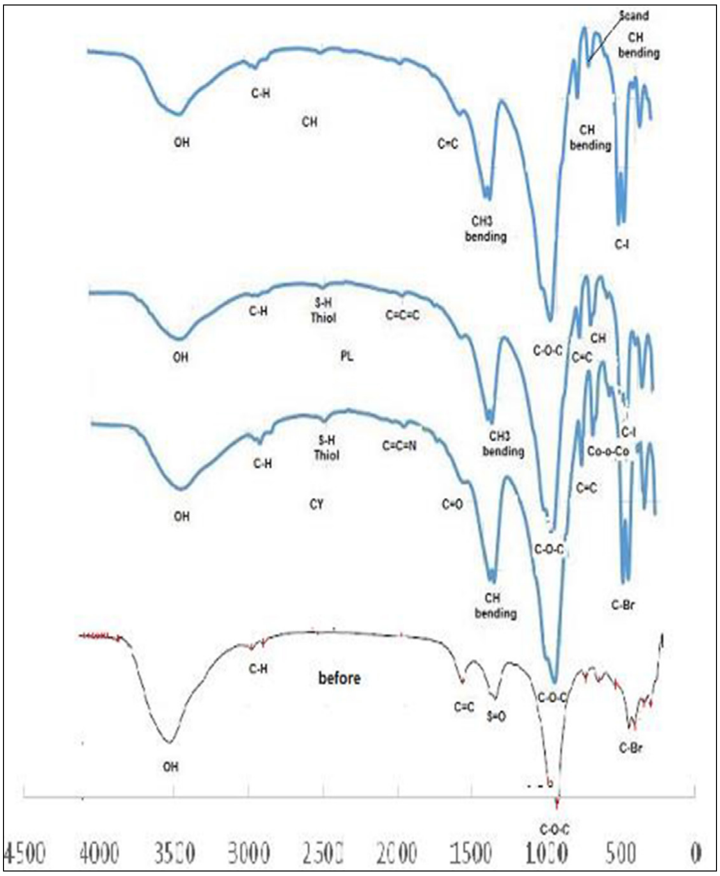


Fig. 4. Vibrational stretches of functional groups of the adsorbate of Safaga phosphate area in the infrared spectroscopy analysis with the biosorbent materials *Cystoseira osmundacea, Palmaria elegans* and *Chondrus crispus*

The samples were examined by Environmental Scanning Electron Microscope (ESEM), by using back scatter detector (BSE). This instrument includes a Philips XL 30 energy-dispersive X-ray (EDAX) unit. The applied analytical conditions were an accelerating voltage of 30kV these analyses were carried out at Nuclear Materials Authority (NMA), Egypt.

The initial sample of Qusser area after the study with ESEM (Fig. 5A) show that it is high in U content (Bright spots), disseminated on the ESEM image. After treatment by different algae (*Chondrus crispus*, *Palmaria elegans, cystoseira osmundacea*), the U in the samples disappeared from EDX charts and ESEM image (Fig. 5B, C and D)

The initial sample of the Safaga area also after the study with ESEM (Fig. 5E) show that it is very high in U content (Bright spots), disseminated at large area on the ESEM image. After treatment by (*Chondrus crispus*, *Palmaria elegans, Cystoseira osmundacea*), the U in the samples disappears from EDX charts and ESEM image (Fig. 5F, G, and H).

Conclusion

Uranium and thorium removing capability were investigated by some algal-specific; (*Cystoseira osmundacea*, *Palmaria elegans* and *Chondrus crispus*), certain algae (*Chondrus crispus*) performed better overall than the other. Its relative performance varied according on treating with Safaga phosphate area biosorption percent reach about 90% of uranium and 91 % for thorium, while in Qusser phosphate the percent of biosorption reach about 89% for uranium and 88% for thorium. Depending on the results, *Chondrus crispus* can be used as an effective biomass for the removal of uranium and thorium in terms of high biosorption capacity, ease of availability and low cost.

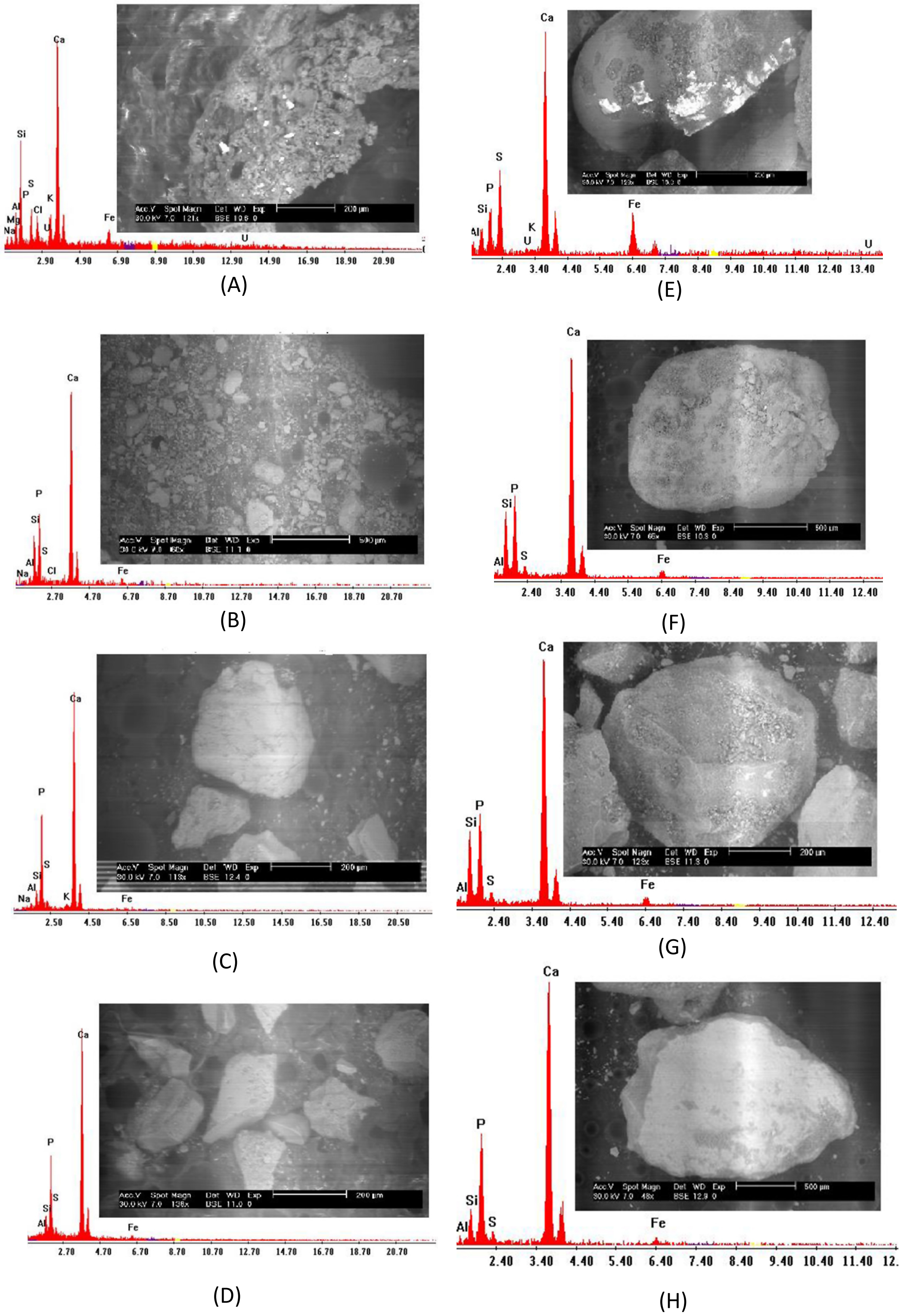


Fig. 5. ESEM image of uranium in Qusser and Safaga, A): ESEM image of uranium in Qusser before treatment; B): ESEM image in Qusser after treatment by *Cystoseira osmundacea*; C): ESEM Image in Qusser after treatment by *Palmaria elegans*; D): ESEM image in Qusser after treatment by *Chondrus crispus*; E): ESEM image of uranium in Safaga before treatment; F): ESEM image in Safaga after treatment by *Cystoseira osmundacea*; G): ESEM image in Safaga after treatment by *Palmaria elegans*; H): ESEM image in Safaga after treatment by *Chondrus crispus*

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قدرة بعض أنواع الطحالب الدقيقة على امتصاص اليورانيوم والثوريوم

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يعتبر الامتصاص الحيوي تقنية فعالة لإزالة اليورانيوم والثوريوم من بعض أنواع صخور الفوسفات بمنطقة البحر الأحمر. في هذه الدراسة تم استخدام *Cystoseira osmundacea*، *Palmaria elegans* و *Chondrus crispus* في الامتصاص الحيوي لليورانيوم والثوريوم من صخور الفوسفات في مصر في منطقتي القصير وسفاجا غرب البحر الأحمر حيث انها تتميز جولوجيا بأصل بحري في المياه الضحلة وترتبط أساسًا بتسلسل اللون الأبيض للحجر الجيري الصلب والطباشير الأبيض والمارل الأصفر وصخور الكرز الصلبة. و قد أظهرت النتائج التي تم الحصول عليها: أن *Cystoseira osmundacea*، *Palmaria elegans* و *Chondrus crispus* لديهم امتصاص حيوي سعة (81%، 89% و 90%)، لليورانيوم و (77%، 88% و 91%) للثوريوم، على التوالي من فوسفات سفاجا وقدرات امتصاص حيوي تبلغ (81%، 84% و 89%) لأحجار اليورانيوم و (79%، 81% و 88%) للثوريوم على التوالي من فوسفات منطقة القصير. لذا يفضل استخدام *Chondrus* على الامتصاص الحيوي بسبب قدرته العالية على الامتصاص من الطحالبين الأخريين.