The Use of Biosorbents for Removal of Actinides Elements from Phosphates El-Sibaiya West and East

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ABSTRACT: *Three freshwater microalgae; Scinaria turgid member in Radophyta; Cystoseira myrica of Phaeophyta, and Chlorodesmus casonus of Chlorophyta, were tested for tolerance and biosorption of actinides elements from the phosphates of El- Sibaiya west and east. The obtained results revealed that the metal biosorption process by Cystoseira myrica gives a great variety for the complete biosorption of uranium in the phosphate west sample 100 % and 71.6 % in the east sample, Chlorodesmus casinos give the same biosorption 63% in the east and west phosphate sample while Scinaria turgid give almost the same biosorption (56.8% - 60%) in the west and east phosphate. On the other side thorium was completely absorbed by the three types of algae, The Adsorption process could be efficient and economically cheap by Cystoseira myrica for the removal of U and Th from El-Sibaiya phosphates to be used in agriculture as compost.*

KEYWORDS: *Scinaria turgid; Cystoseira myrica; Chlorodesmus casonus*.

Introduction

Microorganisms can biosorption of uranium (U), thorium (Th) ions, and radionuclides, for example, algae, fungi, bacteria, and plants biomass, or promote their transformation to less toxic forms has enticed the interest of various environmental scientists. Therefore, various concepts for bio-removal of U and Th [1, 2]. There are many types of biosorption. They are classified into the cell's metabolism dependence or according to the location of the removed metal called Non -metabolism dependent/ metabolism independent like Cell surface sorption, precipitation, Intracellular accumulation finally extracellular accumulation [3, 4]. Biosorption is one of the foremost methods employed by algae for uranium and thorium extraction and is classified into metabolism-dependent and non-metabolism-dependent as described by [5]. The passway of biosorption can be a passive process that occurs at a faster rate than Chelation, or bioaccumulation, adsorption, surface precipitation, complexation, and ion exchange are different processes reportedly involved in biosorption [6, 7].

Algae are cheap biosorbents and efficient algae requirements of nutrients are little. Comparing algal biosorption to other micro sorbents it absorbs about 15.3% - 84.6% higher. Brown algae are known to have a high absorption capacity. Metal ions biosorption occurs on the cell surface utilizing the ion exchange method. Brown marine algae can absorb various metals like Cadmium (Cd), Nickle (Ni), Lead (Pb), and Rear Earth Elements (REEs) through chemical groups on their surface such as Sulfonate, amino, carboxyl as well as sulfhydryl [8, 9].

Thirty strains of algae were tested to biosorb lead, cadmium, zinc, and nickel by [10, 11] stated the leaching

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of heavy metals by Sargassum sp, while [12] investigated the effect of *Sphaerotilus natans* on chromium (III) by acid from industrial wastewater, especially those derived from seaweed and alginic acid, have attracted much interest in recent years as a source of inexpensive adsorbents for toxic metallic ions, we can summarize the advantages of using marine algae as a biosorbent in the following points: (1) Have on their surface varied multifunctional groups on their surface, (2) comparatively small and regular distribution of binding sites on the surface, (3) demand minimal preparatory steps, (4) the consumption of harsh chemicals is very low or sometimes not required, (5) Naturally renewable, recyclable, and easily available all year round, (6) Excellent retention capacity.

The utilization of marine algae as biosorbents has been successfully tested for several biotechnological and industrial applications, Based on the present work, *Scinaria turgid, Cystoseira myrica, and Chlorodesmus casonus* have been tested to biosorb uranium and thorium from El-Sibaiya phosphates to be used in agriculture as a fertilizer; and phosphate can also be turned into phosphoric acid, which is used in everything from like animal feed, electronics, and food.

EXPERIMENTAL SECTION

Algal collection

Three algal species, namely; *Scinaria turgid; Cystoseira myrica*, and finally *Chlorodesmus casonus* were collected from the Red Sea, Egypt, and transferred to the laboratory.

Algal processing

The samples were washed with de-ionized water to remove impurities present in the raw materials. They were air-dried, ground, and sieved at a small pore size [13].

Characterization of the algal-bio sorbent materials

To examine the functional groups of algal bio-adsorbent uranium and thorium-loaded algal bio-adsorbent were further recorded by using the infra-red spectrum (IR) of model Nexus 670 was applied to identify the functional groups in the Central National Research (CNR) and the amino acids for the algal biomasses and the pure fractions were examined under IR then the sizes of the ground algal biomasses were determined using High-Performance Liquid Chromatography (HPLC) for protein analysis.

Adsorption experiments

To investigate the ability of, *Scinaria turgid, Cystoseira myrica,* and finally *Chlorodesmus casonus* to recover (uranium and thorium) from the aqueous solutions of selected samples of phosphates from Sibaiya west and east, 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 [14]. Then chemically examined to determine uranium & thorium concentration from the biomass. The samples were examined under Infrared Spectroscopy (IR) using the model Nexus 670 FT-IR, in the Central National Research (CNR) as mentioned by [1].

High-Performance Liquid Chromatography

Samples are subjected to HPLC (High-performance liquid chromatography) to determine the amino acids of the samples in the National Center for Research in Cairo, Egypt, the model of the instrument is Eppendr of Germany, LC3000 Amino acid analyzer. Condition is: flow rate is 0.2mL / min, the pressure of buffer from 0 to 50 bar, the pressure of reagent to 0- 150 bar, and reaction temperature 123°C.

Sample location

El Sibaiya area is lactated between latitude 24°00 to 26°00 N and longitude 32°00 to 34°00 E. in the Nile Valley Region. The contact between the Sibaiya (Phosphate) Formation and the underlying Quseir Variegated Shale is difficult to define [15, 16] placed this boundary near the top of the shale units (Fig.1) just below the appearance. However, the lower portions of these shales are grey at outcrop and black when freshly broken as seen in Fig. 1.

Determination of Th, and U in algal samples:

To determine the equation between bio-sorbent material *Scinaria turgid*; *Cystoseira myrica* and finally *Chlorodesmus casonus* bio-sorbent materials to recover uranium and thorium from the aqueous solutions of selected samples of phosphate of Sibaiya west and east, by calculating the initial and final concentrations of Th and U in solution which is measured with ICP-MS. The uptake amount (A) of Th and U due to each sample was estimated by subtracting the final concentrations (C_f) from initial

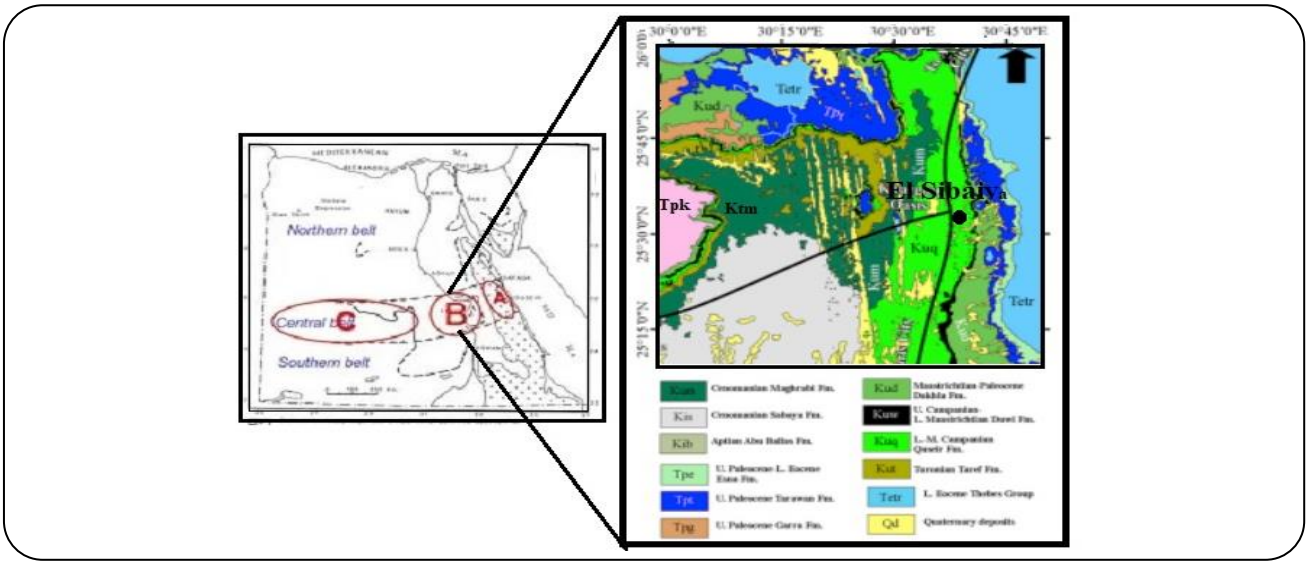

Fig. 1: Geological map of the El Sibaiya area.

concentrations (C_i) in the liquid phase expressed as the following Equation [17, 18]:

$$A = \frac{(Ci - Cf)\ V}{M\ m} \quad [mole/g]$$

The volume of the solution (*V*), the atomic weight of each element (*M*), and the dry weight of each sample are (*m*).

RESULT AND DISCUSSION

Interaction of algae with a high concentration of metals induces morphological and physicochemical changes in them. To surmount these toxic effects, algae have evolved active defense mechanisms. Biosorption, bioaccumulation, sequestration, chelation, and efflux transport are the basic microbial strategies to fight heavy metal stress. Though immense studies have been carried out to identify the defense measures used by genera of algae, still a lot is needed to understand the complete mechanism behind heavy metal toxicity which will help in developing novel biotechnological strategies for bioremediation:

Infra-red analysis (FT-IR)

Different types of vibrational frequencies appeared because different functional groups were shown in FT-IR spectra of the algal bio-adsorbent and are presented in Fig. 2. dealing with phosphate El Sibaiya area east with the three types of algae result in the appearance of the strong, extended (3480 cm^{-1}) and broad adsorption peak belonging to N-H stretching and bending vibrations were appeared with the mother sample compared with the three samples OH group [19]. C-H group appeared only at (2850 cm^{-1}) [20], with (*Scinaria turgid*) while S=O at (1489 cm^{-1}) disappeared with (*Chlorodesmus casonus*) compared with the mother sample and the two others. C-I appeared only with (*Cystoseira myrica*) at (620 cm^{-1}). The stretched peak seen to be shifted in loaded biomass compared to unloaded algal biomass in a sample (*Chlorodesmus casonus*) is attributed to the appearance of C≡C, CH_3 bending [21] as seen in plate 1 this shifted peaks indicate the biosorption of uranium and thorium after [22].

The IR spectrum shows low transmittance of aliphatic and aromatic functionalities between west phosphate sample and the three algal biomass appearance of S-H thiol with sample (*Scinaria turgid & Cystoseira myrica*) at (2400 cm^{-1}), attributed with C-Cl & CH_3 bending appeared with (*Chlorodesmus casonus*) at(1400 cm^{-1}, 870 cm^{-1}) after [23] at the end C=C & C-I appeared with (*Scinaria turgid*) at 950 cm^{-1} and 550 cm^{-1}, the shifting band from C=C 1720 cm^{-1} from the mother sample to CH bending and CH_3 bending at 1640 $cm^{-1}$with (*Cystoseira myrica & Chlorodesmus casonus*) [24] as seen in the plate, However, the present study cuticles are closer in their chemotaxonomic affinity to the ability of algae to biosorb uranium, thorium inside their wall, This was shown by changing the functional groups on the algae as a result of the absorption of the elements uranium and thorium for phosphate ore, so it must be explained that the algae feed on the sample (phosphate) during that it secretes enzymes

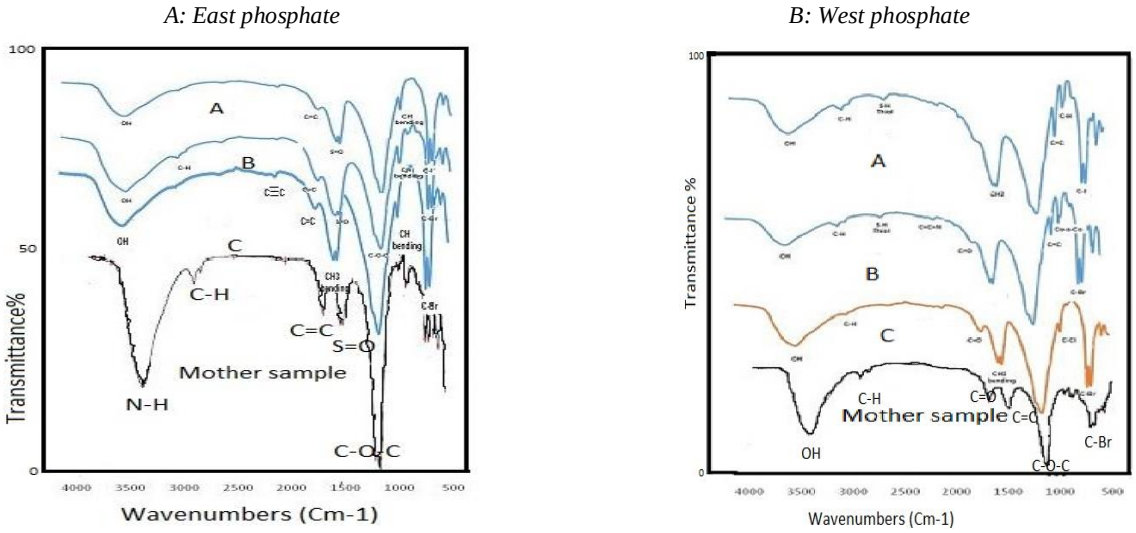

Fig. 2: Vibrational stretches of functional groups of the adsorbate of phosphate east (A) and west (B) in the infrared spectroscopy analysis with the biosorbent materials Scinaria turgid, Cystoseira myrica, and Chlorodesmus casonus. A= Scinaria turgid , B= Cystoseira myrica, C= Chlorodesmus casonus

and substances that change the from of its original nature and this is what was discussed.

Protein analysis

Uranium and thorium biosorption by microalgae is generally a biphasic process [25, 26]. It occurs in two phases: The first phase is adsorption by extracellular cell-associated materials, for example, polysaccharides and mucilage [27, 29], and cell wall components, for example, carboxy and hydroxyl groups, as well as sulfate and phosphate [30, 34]. Absorption and accumulation is the second phase done inside the cell. This is a slow process involving active transport through the cell membrane into the interior of the cell wall and binding to its proteins and other intracellular components [35]. Ion exchange is considered the principal mechanism of biosorption, which occurs through different functional groups present on the surface of biomass [36, 37]. The mechanism of biosorption usually depends upon the biomass that will be removed to use potentially toxic elements like uranium and thorium [38].

Chlorodesmus casonus

A change occurred in the algal cell surface of *Chlorodesmus casonus* during the handling of phosphate: This change is represented in the analysis of the protein of the dealing cell, which led to a decrease or increase in the different proteins of the algae. We found a group that had an increase as a result of the interaction of the algae and the sample of the phosphate east like glutamic acid, alanine, leucine, tyrosine, phenylalanine, lysine, and NH_4, and another group that had a decrease was represented in aspartic, threonine, serine, glycine, histidine and arginine, and other disappeared as valine and isoleucine with the advent of Proline.

When dealing with the west phosphate area, it was observed that the percentage of some types of cell proteins increased like Serine, glutamic acid, alanine, isoleucine, leucine, tyrosine, phenylalanine, lysine, and NH_4. While other types decreased like threonine, aspartic, glycine, histidine, and arginine, with the emergence of species that were not present inside the cell of the algae as Proline, And the disappearance of the types of interaction results such as Valine as seen in the Tables 1and 4 and Figs. 3 and 6.

Cystoseira myrica

Cystoseira myrica as a type of Phaeophyta protein analysis data after dealing with phosphate east showed us a group of differences in the surface of the algae cell as a result of the difference in protein, where the treatment showed a decrease in the proportion of a group of proteins, which are as follows in aspartic, threonine, valine and tyrosine, While another high percentage was noted like glutamic acid, glycine, alanine, isoleucine, leucine, phenylalanine, histidine, lysine, NH_4, and proline with the disappearance of some group like serine, arginine,

Table 1: Protein analysis data for Chlorodesmus casonus before and after with phosphate west: (µg/mL).

Name	Before	After	Difference
Aspartic	42.21	42.15	-0,06
Threonine	12.455	10.76	-1,695
Serine	8.175	17.91	9,735
Glutamic Acid	37.34	52.66	15,32
Glycine	13.62	12.80	-0,82
Alanine	17.025	35.85	18,825
Valine	3.18	N.D	-3,18
Isoleucine	14.6	25.89	11,29
Leucine	6.445	18.84	12,395
Tyrosine	14.54	51.84	37,3
Phenylalanine	3.02	143.46	140,44
Histidine	9.49	7.36	-2,13
Lysine	12.295	20.98	8,685
NH_4^+	101.105	196.41	95,305
Arginine	26.41	9.20	-17,21
Proline	N.D	55.85	55,85

N.D= Not Detected

Table 2: Protein analysis data for Cystoseira myrica before and after with phosphate west (µg/mL).

Name	Before	After	Difference
Aspartic	40.365	55.88	15,515
Threonine	16.065	12.16	-3,905
Serine	19.12	14.64	-4,48
Glutamic Acid	53.985	69.34	15,36
Glycine	8.24	13.42	5,18
Alanine	32.18	47.30	15,12
Valine	16.765	13.81	-2,96
Isoleucine	11.69	17.69	6
Leucine	44.12	48.02	3,9
Tyrosine	48.805	26.25	-22,55
Phenylalanine	48.545	49.51	0,965
Histidine	7.62	17.37	9,75
Lysine	15.585	29.83	14,245
NH_4^+	83.115	144.80	61,69
Arginine	19.165	N.D	-19,165
Methionine	1.43	N.D	-1,43
Proline	26.19	101.21	75,02

N.D= Not Detected

and methionine. By dealing with *Cystoseira myrica* west and rubbing it with phosphates the results recorded in Tables 2 and 5 and Figs. 4 and 7 showed that some amino acids interacted and increased as aspartic, glutamic acid, glycine alanine, isoleucine, leucine, phenylalanine, histidine, lysine, NH_4 and proline, And the other is a deficiency in a quantity such as a threonine, serine, valine and tyrosine with the disappearance of arginine and methionine.

Scinaria turgid

Scinaria turgid as a type of Radophyta gives different results for the two algae when dealing with phosphate east, where the percentage increased with phenylalanine, And the percentage of amino acids decreased with aspartic, threonine, serine, glutamic acid, glycine, alanine, valine, isoleucine, leucine, tyrosine, histidine, and NH_4 with the disappearance of lysine and arginine and appetence of Proline the same result appeared with phosphate west except tyrosine and histidine disappeared also.

For instance, the cell wall composition is different from one type of microorganisms and the other in the functional groups on the surface of the cell wall, which is responsible for the difference in mechanisms [38, 39]. Apart from the cell wall, extracellular polymer substances secreted by algae are also found to play an important role in biosorption as uranium and thorium as mentioned (40, 41) as seen in the Table 3and 6 and Figs. 5 and 8.

The level of metal toxicity in algae depends on the strength of covalent interaction between the metal and the negatively charged groups on the algal cell surface, this shows the ability of each type of algae to absorb uranium and thorium and the inability to absorb more as a result of saturation, which correspondingly depends on the electro-negativity of the concerned metal or the stability of the chelate compound formed during the interaction of the metal with the ligand molecule which determines the toxicity [42, 44].

Chemical analysis

Microalgal biosensors harboring various algal species, *Chlorodesmus casonus*, *Cystoseira myrica*, and finally *Scinaria turgid* are described as such biosensors for uranium and thorium from the aqueous solutions .in the selected samples of phosphate of Sibaiya west and east, in phosphate of Sibaiya east the percentage of the mother sample for uranium was 67.6 ppm after dealing with

Table 3: Protein analysis data for Scinaria turgid before and after with phosphate west (µg/mL).

Name	Before	After	Difference
Aspartic	93.59	31.80	-61,79
Threonine	33.22	6.79	-26,43
Serine	42.28	10.84	-31,44
Glutamic Acid	125.15	37.60	-87,55
Glycine	25.77	10.35	-15,42
Alanine	110.68	40.97	-69,71
Valine	110.68	26.72	-83,96
Isoleucine	45.05	9.70	-35,35
Leucine	107.13	29.89	-77,24
Tyrosine	99.70	N.D	-99,7
Phenylalanine	127.61	134.19	6,58
Histidine	87.47	N.D	-87,47
Lysine	106.89	7.68	-99,21
NH_4^+	279.41	205.47	-73,94
Arginine	95.35	N.D	-95,35
Proline	N.D	55.07	55,07

N.D= Not Detected

Table 4: Protein analysis data for Chlorodesmus casonus before and after in phosphate east: (µg/mL).

Name	Before	After	Difference
Aspartic	42.21	41.65	-0.56
Threonine	12.455	8.96	-3.495
Serine	8.175	13.24	5.065
Glutamic Acid	37.34	42.65	5.31
Glycine	13.62	10.54	-3.08
Alanine	17.025	29.32	12.295
Valine	3.18	N.D	-3,18
Isoleucine	14.6	N.D	-14,6
Leucine	6.445	14.65	8.205
Tyrosine	14.54	31.8	17.26
Phenylalanine	3.02	45	41.98
Histidine	9.49	3.36	-6.13
Lysine	12.295	18.96	6.665
NH_4^+	101.105	178	76.895
Arginine	26.41	11.09	15.32
Proline	N.D	22.14	22.14

N.D= Not Detected

Table 5: Protein analysis data for Cystoseira myrica before and after in phosphate east.

Name	Before	After	Difference
Aspartic	40.365	52.44	12.075
Threonine	16.065	8.9	-7.165
Serine	19.12	N.D	19.12
Glutamic Acid	53.985	70.59	16.61
Glycine	8.24	14.58	6.34
Alanine	32.18	58.25	26.07
Valine	16.765	6.97	-9.79
Isoleucine	11.69	15.72	4.03
Leucine	44.12	50.24	5.43
Tyrosine	48.805	18.41	-30.395
Phenylalanine	48.545	56.24	7.69
Histidine	7.62	24.87	17.25
Lysine	15.585	21.7	6.114
NH_4^+	83.115	123.56	40.445
Arginine	19.165	N.D	19.165
Methionine	1.43	N.D	1.43
Proline	26.19	66.32	40.13

N.D= Not Detected

Table 6: Protein analysis data for Scinaria turgid before and after in phosphate east(ug/mL).

Name	Before	After	Difference
Aspartic	93.59	22.14	71.45
Threonine	33.22	6.98	-26,24
Serine	42.28	14.58	-27.7
Glutamic Acid	125.15	66.35	-58.8
Glycine	25.77	12.47	-13.3
Alanine	110.68	30.87	-64.03
Valine	110.68	46.65	-64.03
Isoleucine	45.05	9.63	-35.42
Leucine	107.13	43.21	-63.92
Tyrosine	99.70	12	-87.7
Phenylalanine	127.61	145.69	18.08
Histidine	87.47	6.89	-80.58
Lysine	106.89	N.D	-106.89
NH_4^+	279.41	180	-99.41
Arginine	95.35	N.D	-95,35
Proline	N.D	33.96	33.96

N.D= Not Detected

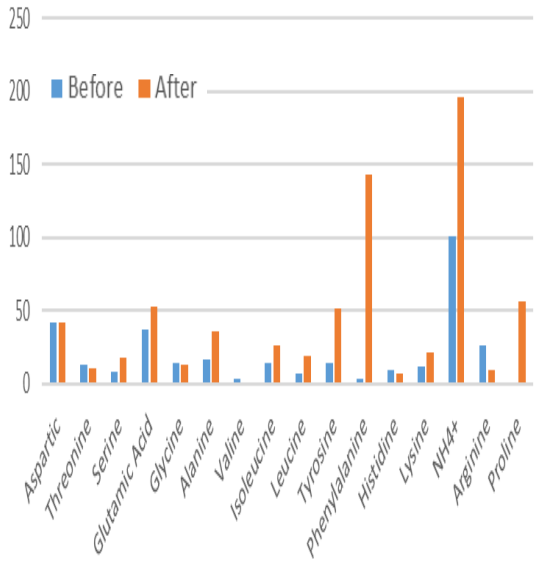

Fig. 3: Protein analysis data for Chlorodesmus casonus before and after with phosphate west: (ug/mL).

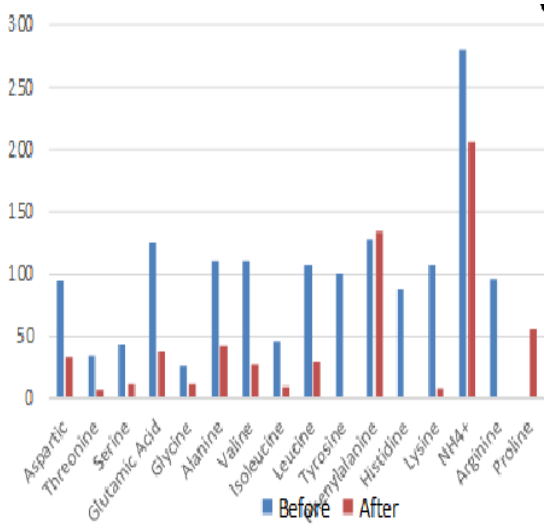

Fig 5: Protein analysis data for Scinaria turgid before and after with phosphate west (ug/mL).

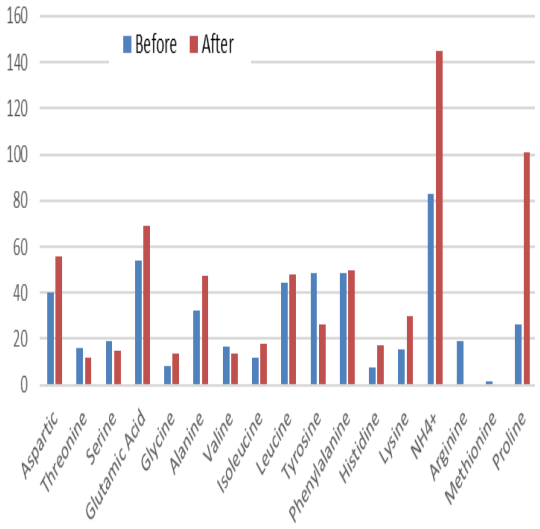

Fig 4: Protein analysis data for Cystoseira myrica before and after with phosphate west (ug/mL).

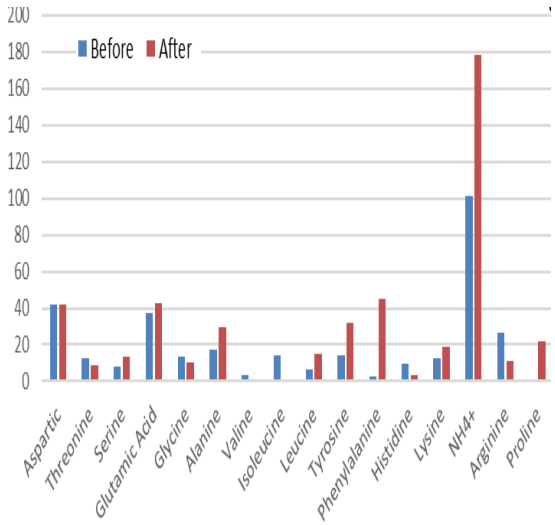

Fig 6: Protein analysis data for Chlorodesmus casonus before and after in phosphate east: (ug/mL).

Chlorodesmus casonus the percentage become 27.60 ppm about 60% biosorption capacity. Using *Cystoseira myrica* as a biosorbent the percentage became 19.2 ppm showing 71.6 % biosorption, *Scinaria turgid* percent became 25ppm in the rate of 63% biosorption, phosphate of Sibaiya west percentage of uranium was 76.4ppm in the mother sample after dealing with *Chlorodesmus casonus* the percent become 28.8ppm about 62.3% biosorption, *Cystoseira myrica* gives a great analysis about 100% complete biosorption for uranium, on the other hand, *Scinaria turgid* give a moderate capacity about 56.8% biosorption, percent of U become 33ppm. Thorium in phosphate east was 16.3 ppm in the mother sample, while in the west sample, it was 23 ppm in the mother sample, dealing with the three types of algae results in complete biosorption in the two samples in a percentage of 100% as described in Tables 7 and 8 and Figs. 9and 10. We can conclude that the chemical analyses discussed by [45, 51]

Table 7: Biosorption of uranium and thorium from phosphate of east area.

	Uranium	% of Biosorption	Thorium	% of Biosorption
mother sample	67.6		16.3	
Scinaria turgid	27	60%	N.D	100%
Cystoseira myrica	19.2	71.6%	N.D	100%
Chlorodesmus casonus	25	63%	N.D	100%

N.D= Not Detected

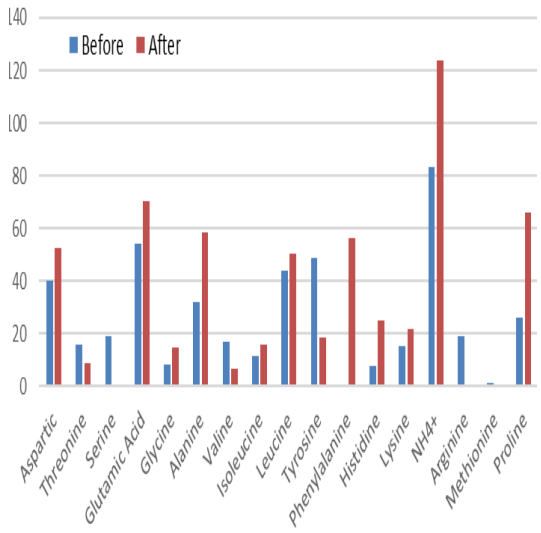

Fig. 7: Protein analysis data for Cystoseira myrica before and after in phosphate east (ug/mL).

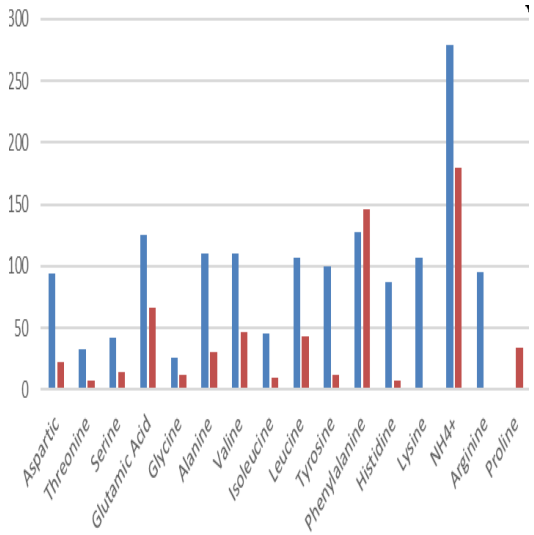

Fig. 8: Protein analysis data for Scinaria turgid before and after in phosphate east (ug/mL).

may be caused by several mechanisms: (a) the change of functional groups of biologically important molecules (e.g., enzymes and transport systems for essential nutrients and ions). (b) The displacement of essential metal ions from bio-molecules and functional cellular units.

This may result in the modification and inactivation of enzymes as well as disruption of cellular and organelle membrane integrity [46, 49], this shows the link between protein analysis and IR in terms of changing the enzymes and functional groups of the algae as a result of its saturation with the largest possible amount of uranium and thorium. Therefore, we must say that algae can absorb these elements until they are saturated and reach the maximum biological absorption capacity from uranium and thorium as mentioned by [22]. Toxic metals like uranium and thorium resistance in microalgae may result from the ability to prevent uptake (avoidance). Heavy metals with high amounts may be made metal resistance metals inside tissues (tolerance), during the uptake (absorption) and accumulation of the metal ions inside the cell an active process appeared inside microalgae cells via micronutrient transporters [50].

CONCLUSIONS

This study deals with the treatment of the El Sibaiya phosphates area with the three types of algae to absorb uranium and thorium. The treatment led to changes inside the cell represented by the analysis of amino acids, where groups appeared like Proline and other groups disappeared like Valine with an increase in the percentage of some of them and decreased in other groups, and the IR analysis showed differences after treatment, such as S-H thiol, CH bending and CH_3 bending, The level of metal biosorption on algae cell surface depends on the strength of covalent interaction between the metal and the negatively charged groups on algal cell surface so we can conclude that *Cystoseira myrica* belonging to Phaeophyta is a best for biosorption for uranium and thorium in both phosphate

Table 8. Biosorption of uranium and thorium from phosphate of west area.

	Uranium	% of Biosorption	Thorium	% of Biosorption
mother sample	76.4		23	
Scinaria turgid	33	56.8%	N.D	100%
Cystoseira myrica	N.D	100%	N.D	100%
Chlorodesmus casonus	28.8	62.3%	N.D	100%

N.D= Not Detected

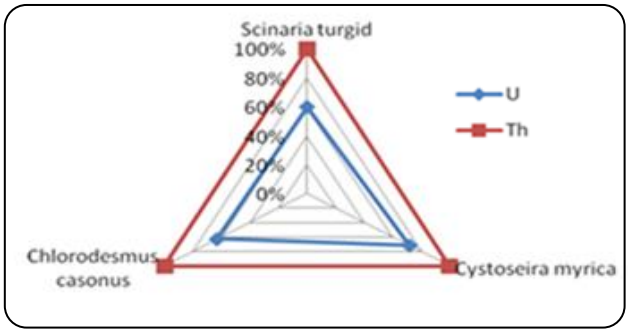

Fig. 9: % of biosorption of uranium and thorium from phosphate of the east area.

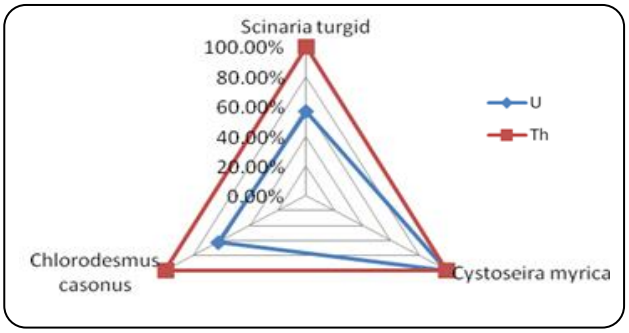

Fig. 10: Biosorption of uranium and thorium from phosphate in the west area.

El Sibaiya area west and east, This phosphate-free of uranium and thorium can be used for many aspects such as the phosphate fertilizer industry) which contain nitrogen, phosphorus, and potassium, are the largest group of plant fertilizers and are essential for healthy plant growth in different proportions and are also called compound fertilizers.

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