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Uranium Bio-sorption from its Processed Waste Solution by Green Algae

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Abstract

The present work concerning with studying the potentiality of green algal biomasses namely *Ulva lactuca* Linnaeus (marine green alga) and *Cladophora glomerata* Linnaeus Kützing (fresh water alga) to adsorb uranium from its processing effluents of Gattar Pilot Planet, Eastern Desert, Egypt. The maximum bio-sorption efficiency of uranium was achieved at 1 hr contact time, 1/1000, S/l ratio, 200 ppm uranium as initial concentration, pH 4 at the room temperature using the investigated two green algal biomasses. The optimal bio-sorption values were 147.5and 287.7mg/g for *U. lactuca* and *C. glomerata* respectively. The studied algae were characterized by SEM before and after uranium bio-sorption, which showed different morphological changes such as wrinkling, protuberance and roughness with uranium bio-sorption as well as each algal type had a unique surface structure in its raw form. FTIR was used to distinguish the contributing groups which were variable and involve several mechanisms depending on uranium and algal type. The obtained experimental kinetic data were pseudo-second-order after uranium bio-sorption on *U. lactuca* and *C. glomerata*. The Langmuir isotherm model more fits the data of uranium bio-sorption than the other models (Freundlich, D-R, and Temkin).These indicating that, uranium bio-sorption process on the two green algal masses is physico-chemical monolayer mechanism. The phytochemical analyses clarify the percentage of the main constituents of the algal biomasses as (10.9 and 12,63%) of phenol, (8.3 and 15.9%) of protein and (6 and 10.16%) of carbohydrates for both *U. lactuca* and *C. glomerata* respectively .The loaded uranium was efficiently eluted by 0.1 M HCl. By applying the two green algal biomasses with fixing the optimum concluded conditions on Gatter pilot plant sample, almost of elements and nearly uranium complete concentrations were recovered from the waste water and the water can be safely reused again. However, the uranium was eluted from the concerned algae using 0.1 M HCl, while the other elements were eluted by 0.3 M EDTA and the uranium full recovery needs 3 separation cycles.

Keywords: Uranium biosorption; Fresh and marine green algae: *Ulva lactuca*; *Cladophora glomerata*; Gattar; effluents.

Introduction

Uranium element is widely distributed within the earth's crust and used essentially as a primary fuel for nuclear power reactors. Naturally occurring uranium is composed of about 99.3% 238U, 0.7% 235U and traces of 234U. Utilization of uranium that is recovered from the ground has to be extracted from the ore and converted into a form that can be used in the nuclear fuel cycle [1]. Large amounts of

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uranium–bearing effluent were annually produced from various nuclear-associated activities, such as uranium exploration and processing, manufacture of nuclear weapons, production of nuclear power, and disposal of radioactive waste. The manufacture of fertilizers from natural phosphate ore and their agricultural applications are also responsible for leaking some uranium pollutants into water bodies [2]. Due to widespread applications of nuclear technologies, there are many potential sources of uranium pollution and contamination with a serious danger to the quality of surface and ground waters. Therefore, removal of uranium from aqueous solution by biosorption/ bioaccumulation not only solves the contamination problem but also makes economic recovery possible. Many biosorbents have been used for uranium removal from water such as plant wastes, shrimp shells, different types of fungi and bacteria. In recent years, nonliving biomass of fresh water/ marine algae, took significant thought and used for uranium removal. Currently, algae are considered as alternative natural bio-sorbents technology. They are eco-friendly, economic, and more efficient sustainable resources for chelating and removing hazardous pollutants of aquatic habitats [3, 4]. The high sorption capacity, easy regeneration and low-costs of algae, lesser volume of chemical and/ or biological sludge to be disposed off, give them special interest for the purification of high volumes of waste water with lower concentrations to be removed [5-8], which is difficult and/or expensive to be achieved by conventional metal-removal processes. Many researchers have reported that algal cell walls have a very high capacity for binding with metals due to the presence of polysaccharides, proteins, or lipids on the surface of cell walls, possessing the functional groups viz. aminos, hydroxyls, carboxyls and sulfhydryl, which can act as binding sites for metals [9, 10].

Green algae (chlorophyta) are ubiquitous in fresh and marine habitats. Therefore, they can employ as successful bio-sorbents [11] The current work aims to study an effective eco-friendly technique (biosorption) by using the two marine and fresh water green algal taxa (*Ulva lactuca* and *Cladophora glomerata*) to adsorb and recovery the uranium from its processing effluents of Gattar Pilot Plant , Eastern Desert, Egypt.

Materials and Methods

Materials

All chemicals are of analytical grade and used without further purification. The studied *Ulva lactuca* Linnaeus (marine green alga) was collected from the Egyptian sea shores, Hurghada (the Red Sea shore) while, *Cladophora glomerata*(Linnaeus) Kützing (fresh water alga) was collected from river Nile, Qalubuia governorate. The collected algae washed with tap water then demineralized water to remove epiphytes, epi-fauna, sand, salts and other detritus prior to air drying. The algal taxa were identified and classified. [12, 13]

Bio-sorption Experiments

Loading experiments were performed by shaking 50 ml (200 ppm) uranium aqueous solution with 0.05 gm of interested algal masses in 100 ml Erlenmeyer flasks for one hour at room temperature, except otherwise mentioning. After filtration, the uranium was analyzed by spectrophotometric method [14], using SP-8001 UV-Vis spectrophotometer – Metertech Inc. (200 to 1100 μm), with deuterium lamp (UV range) and halogen lamp (Visible range) as a light source. The studied factors affecting the biosorption process were contact time, pH, initial uranium concentration, solid/liquid ratio and temperature. The ranges of the studied factors

affecting the uranium loading capacity are summarized in table (1).

Table (1): The studied factors affecting the loading of uranium using algal biomasses

Factor	Range
Contact time	5, 15, 30, 45, 60 and 120 min.
pH	1, 2, 3,4, 5 and 6
Solid/liquid ratio	1/100, 1/250, 1/500 and 1/1000
Initial concentration	10, 25, 50, 100, 200, 400, 500 and 600 ppm
Temperature	30, 45 and 60

The amount of bio-sorbet metal was calculated as the following: $q = [(C_i - C_f)\ V]/M$

Where;

q:amount of sorbet metal onto the unit amount of the biomass (mg/g)

C_i: initial concentration of the metal in aqueous solution (mg/L).

C_f: final (remained) concentration of the metal in aqueous solution (mg/L).

V: volume of the metal solution (L).

M: biomass weight (g).

The kinetics data were tested on the Lagergren (pseudo-first-order) and Ho and McKay (pseudo-second-order) models [15].

Pseudo-first order model can be obtained from the following equation:

$$log(Q_e - Q_t) = logQ_e - \frac{K1}{2.303}$$

While the Pseudo-second order model can be obtained from the following equation:

$$\frac{t}{Q_t} = \frac{1}{K2Q_e^2} + \frac{t}{Q_e}$$

Where q_e and q_t are the amount of uranium ions sorbet per unit mass of algae at equilibrium and at the time (t), respectively; q_{calc}, k_1 and k_2 refer to the maximum theoretical capacity, the rate constant of pseudo-first and pseudo-second-order, respectively. The goodness of the model may be tested from the consistency of the q_{calc} value with the experimental capacity and the value of regression coefficient (R^2).

The linearized Langmuir, Freundlish, isotherm modelings were applied according to Salima *et al.* [16] and Farah and El-Gendy [17] where:

$C_e/q_e = 1/(Q_e\ K_L) + (1/Q_e)\ C_e$

(C_e) is the element concentration in aqueous solution at equilibrium (mg/L), (q_e) is the experimental amount of adsorbed element at equilibrium (mg/g), (Q_e) is the calculated amount of adsorbed element at equilibrium (mg/g) and (K_L) is the Langmuir constant indicating the adsorption affinity of the binding sites (L/mg) *via* plotting (C_e/q_e) versus (C_e), (Q_e), and (K_L) can be determined from the slope and intercept of the obtained straight line respectively.

Whereas the linearized logarithmic Freundlich equation assumes as:

$$Log\ q_e = Log\ K_F + (1/n)\ Log\ C_e$$

(K_F) is the Freundlich constant indicating adsorption capacity, (n) is the Freundlich constant indicating adsorption intensity.By plotting (Log q_e) versus (Log C_e), (n) and (K_F) can be determined from the slope and intercept of the obtained straight line respectively.

On the other hand Dubinin-Radushkevich (D-R) and Temkin isotherm models were applied according to (Gunay *et al.*,[18] and Dada *et. al.*, [19] where:

$$q_e = (q_s)\exp\left(-K_{ad}\varepsilon^2\right)$$
$$\ell n q_e = \ell n(q_s) - \left(K_{ad}\varepsilon^2\right)$$

Where q_e, q_s, K_{ad} , are q_e = amount of adsorbate in the adsorbent at equilibrium(mg/g); qs = theoretical isotherm saturation capacity (mg/g); K_{ad} = Dubinin–Radushkevich isotherm constant (mol^2/kJ^2).

Whereas the Temkin isotherm equation assumes as:

$$q_e = \frac{RT}{b}\ln(A_T C_e)$$

$$q_e = \frac{RT}{b_T}\ln A_T + \left(\frac{RT}{b}\right)\ln C_e$$

$$B = \frac{RT}{b_T}$$

A_T =Temkin isotherm equilibrium binding constant (L/g),b_T = Temkin isotherm constant, R= universal gas constant (8.314J/mol/K),T= Temperature at 298K, B = Constant related to heat of sorption (J/mol)

Characterization of Algal Biomasses

Some Phyto-chemical Analysis:

Total and fractions of carbohydrates

Total carbohydrates content was determined calorimetrically [20] by UV spectrophotometer, however the fractions of carbohydrates determined [21], using HPLC (Ultimate 3000), at the central laboratory of Desert Research Center, Egypt.

Total proteins

Total proteins content was determined colorimetrically using UV/Visible Spectrophotometer, according to Hartree's modification of Lowry method [22,23] at the central laboratory of Desert Research Center, Egypt.

Total and fractions of phenols

Total phenols content was determined calorimetrically using UV/ Visible Spectrophotometer according to Snell and Snell,[24] and the fractions determined according to Biswas *et al.*, [25] by HPLC (Ultimate 3000), at the central laboratory of Desert Research Center, Egypt.

Amino acids

Fractions of amino acids determined according to AOAC Official Method of analysis [26] by Amino Acid analyzer (Biochrom 30), at Agriculture Research Center.

SEM Images

The dried algal masses were analyzed by Environmental Scanning Electron Microscope model FEI Insect S (ESEM-EDAX) before and after loading of uranium to exanimate the morphological and chemical changes of the surface structure after uranium loading.

Fourier Transform Infrared (FTIR)

The infrared spectrometric analysis (Bruker vector spectrophotometer model FT-IR-22Germany) was performed to characterize the functional groups of the algal samples before and after loading with uranium solution in region of 400 cm^{-1} to 4000 cm^{-1} using KBr binding material sample pellets. The IR analysis was conducted in the Micro Analytical Center, Cairo University. Infra-Red absorption spectra in the mentioned region were recorded.

Elution Experiments

Elution experiments were carried out by shaking 0.05 gm of the loaded two green algal masses (marine and fresh water algae) with 5 ml of eluent in 25 ml Erlenmeyer flasks for 5 min., after filtration the uranium was analyzed. Eluent type, eluent concentration and contact time were studied as the factors affecting the elution efficiency.

Application of Green Algal Biomasses in the Waste Treatment of Gattar Pilot Plant

The waste samples were collected from Gattar pilot planet, Eastern Desert, Egypt. The two green algae *U. lactuca* and *C. glomerata* were used to remove the

uranium from the demonstrated waste according to the observed optimum conditions of the studied factors. The removal percentage of uranium (ppm) was calculated using the following equation:

Removal (%) = (C_i- C_f/ C_i) X 100; where C_i is the initial uranium concentration and C_f is the final uranium concentration after treatment.

Results and Discussion

3.1. Factors Affecting Uranium Bio-sorption Process

3.1.1. Effect of Contact Time upon Uranium Bio-sorption and Bio-sorption Kinetics

The kinetics uniqueness of uranium sorption process is important because it controls the sorption efficiency. The investigational runs measure the effect of contact time upon U sorption were conducted at various time intervals (5 - 120 min) at the conditions: room temperature, uranium ions concentration of 200 mg/L, and the s/l ratio was 1/500, in order to obtain the optimal time required for complete sorption process. The concentration of uranium at the end of each time was used to calculate sorption capacities (q_t) which were plotted against the equilibrium time for kinetic modelling.

The data represented in fig. (1a), indicating that the loading capacity of U increased with increasing the contact time with fixing the other factors, optimized at 60 min shaking time as 68.1 mg/g and 90 mg/g for *U. lactuca* and *C. glomerata* respectively, and then become nearly constant. This can be explained by the uranium bio-sorption is found to be a two stages process, consisting of an initial rapid passive binding of metals to negatively charged sites on the cell walls, followed by a slower active uptake of metal ions in to the cells [27]. The higher rate of bio-sorption in initial stage of bio-sorption could be due to electrostatic interactions, between metal ions and surface ligands on the algal biomass. These binding sites present on surface of the biomass start binding to uranyl ions as soon as they come in contact with each other. As time progresses availability of binding sites reduces, thus reducing the rate of bio-sorption [5]. The obtained results match with the published data [2, 28, 29].

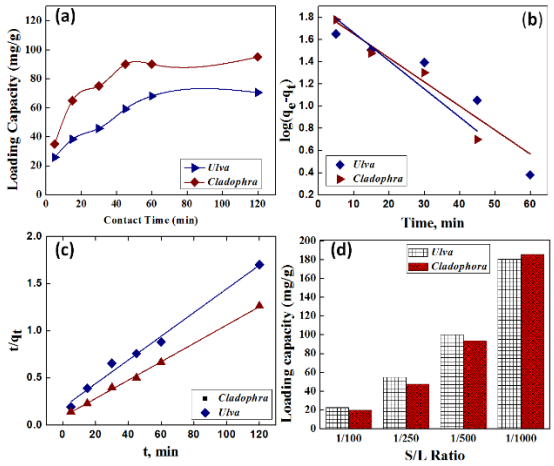

Fig. (1):(*a) Effect of contact time, (b) Lagergren, (c) Ho and McKay for uranium bio-sorption upon the studied algae and (d) Effect of solid/liquid upon uranium bio-sorption upon studied algae.*

Kinetic models were used to test the experimental data to evaluate the controlling mechanism of sorption process. The kinetics data was tested on the Lagergren (pseudo-first-order) and Ho and McKay (pseudo-second-order) models [15]. According to experimental and theoretical kinetic data in table 2, it is obvious that the experimental data obtained were comparable with Ho and McKay than Lagergren model (Fig.1b and c).

Table (2): Kinetic parameters of uranium sorption upon concerned algae according Lagergren and Ho & McKay models

Kinetic model	Parameters	*U. Lactuca*	*C. glomerata*
Pseudo first order kinetics	q_1, (mg/g)	73.7056	68.8494
	K_1 (min^{-1})	0.0498	0.0482
	R^2	0.8981	0.9296
Pseudo second order kinetics	q_2, (mg/g)	79.3651	103.0928
	K_2 (g/mg.min)	0.0009	0.0011
	R^2	0.9888	0.9989

3.1.2.. Effect of pH upon Uranium Biosorption

As shown in fig. (2a), the data represented the effect of pH varied from (1 to 6) on the loading capacity of uranium upon the studied algal biomass with fixing the other factors. The loading capacity gradually increased with increasing the pH value reached its optimum values (90 and 87.5mg/g) at pH 4 for *U. lactuca* and *C. glomerata* respectively. These results are in agreement with the international data [2, 11, 30]. The decreasing in bio-sorption at pH 1.5 could be because at this pH there is a high concentration of H^+ and H_3O^+, which compete with other ions (uranyl) for the binding sites on the surface of the biomass. On the other hand, the reason for increased bio-sorption at pH 4.5 could be due to the presence of ligands like carboxyl, amino, and phosphate on the surface of biomass, which have p*K* values in the range of 3–5. Decrease in the uptake of uranium at higher pH could be due to the formation of uranyl carbonate complexes, as the initial pH of the solution was adjusted with Na_2CO_3, in addition to atmospheric CO_2 which plays a role in the formation of uranyl carbonate complexes above pH 6. At higher pH values the aqueous carbonate competes with surface binding sites for uranyl ions and reduces the availability of uranium for biosorption. Moreover, at higher pH formation of solid schoepite ($4UO_3 \cdot 9H_2O$) takes place which decreases the dissolved uranium concentration in solution, and consequently leads to the reduced sorption of uranium onto the biomass [31].

3.1.3. Effect of Solid/Liquid Ratio upon Uranium Bio-sorption

It was found that the loading capacity increased with increasing the solid/liquid ratio and giving its maximum result at 1/1000 (180.6 and 185mg/g) for *U. lactuca* and *C. glomerata* respectively (fig.1d), this may be due to the highest biomass concentration, causing a fast superficial adsorption onto the surface of biomass, which would have resulted in a low metal ion concentration in the solution. At a low metal ion concentration, the metal ion sorbed is low, because of the lower driving force (by a lower concentration gradient pressure). Thus an efficient use of sorptive capacity of the bio-sorbent is not reflected [32]. Moreover the high biomass concentration leads to formation of cell aggregates, which reducing the effective bio-sorption area [33].

3.1.4. Effect of Initial Concentration upon Uranium Bio-sorption

From fig. (2b), the loading capacity increasing with increasing uranium concentration then begin to steady constant at 200ppm (185mg/g) for *U. lactuca* and (280mg/g), at 400 ppm for *C. glomerata*, this can be explained by, as the biomass concentration being constant (1 g/l) the number of binding sites was same. However, the number of uranyl ions increased in parallel with the uranium concentration increase. At low uranium concentrations solution, saturation of biomass by uranyl ions could not be achieved as the number of uranyl ions was smaller than the number of binding sites present on the biomass. Increasing the concentration of uranium in the solution was expected to result in the increase of *q*e, till the saturation of biomass was attained. Once the binding

sites present on the biomass got saturated with the uranium, the availability of binding sites for the uranium decreased. This could explain why the initial stage was fast, and slowed down as the saturation was achieved [29, 32].

3.1.5. Uranium Bio-sorption Isotherms

The sorption mechanism of uranium upon the interested biomasses was evaluated from four sorption isotherm models (Langmuir, Freundlich, D-R, and Temkin) (fig. 2b,c, d and e).The calculated Langmuir constants (k_L and Q_{max}), Freundlich constants (n and k_f), D-R constants(Q_{DR}, K_{ad}, E) and Temkin constants (B, A_T, b_T) as well as the coefficients of correlation (R^2) for all isotherms are represented in table (3). The obtained results when applying Langmuir model revealed that the values of the calculated Q_e (333.33) for both algae and the experimental q_e (325, 310) for *U. lactuca* and *C. glomerata* respectively, are so close which reflect that the biosorption technique consider a good way for uranium adsorption in both low and high concentrations. Whereas the values of Freundlich constant (n) that are greater than unity indicate the ability of the algal biomass to biosorb metals from water [34]. Additionally, the values of the Langmiur correlation coefficient < 0.97 for both *U. lactuca* and *C. glomerata* while the Freundlich correlation coefficient < 0.80 and 0.69 for *U. lactuca* and *C. glomerata* respectively, proving that the Langmuir model more fitting to the data.

The calculated value of apparent energy (E) of adsorption was 4.082 KJ/mol^2 (i.e<5) for both *U. lactuca* and *C. glomerata*. However, the calculated Temkin constants (B) for *U. lactuca* and *C. glomerata* were (64.82 and 63.14) > 25 respectively. These obtained results revealed that the mechanism of the bio-sorption process of uranium on the two green algal masses is physico-chemical mechanism. This result exhibits that sorption of uranium on a monolayer (monolayer coverage) of the biomasses surfaces. It also assumes that the bio-sorption capacity of the used algae increases with increasing the concentration of uranium ions which confirms the mentioned results from the effect of initial concentration on the bio-sorption.

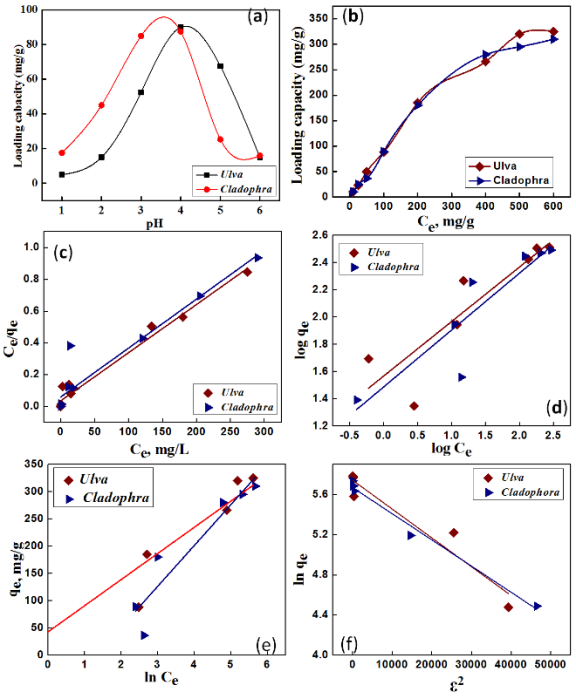

Fig. (2)*:(a)* *Effect of pH upon uranium bio-sorption upon studied algae, (b)* ***e****ffect of equilibrium concentration, (c) Langmuir isotherm,(d) Freundlish isotherms, (e) D-R isotherm (f), Temkin isotherm, upon uranium bio-sorption using studied algae.*

Table (3): Parameters of bio-sorption by Langmuir isotherm, Freundlish isotherm, D-R isotherm, Temkin isotherm, upon uranium bio-sorption using studied algae at room temperature

Isotherm model	Parameters	*U. lactuca*	*C. glomerata*
Langmuir isotherm	Q_L (mg/g)	333.4	333.4
	K_L	0.084034	0.084034
	R^2	0.9752	0.9752
Freundlish isotherm	K_F (mg/g)	53.08844	22.34601
	n	2.996704	2.035831
	R^2	0.8057	0.6945
D-R isotherm	Q_{DR} (mg/g)	311.90542	289.97653
	K_{ad} (mol^2/KJ^2)	3 X 10^{-8}	3 X 10^{-8}
	E (KJ/mol^2)	4.082483	4.082483
	R^2	0.9259	0.9857
Temkin isotherm	B (KJ/mol)	64.823	63.146
	A_T (L/g)	1.93981	0.560011
	b_T	38.22057	39.23561
	R^2	0.8997	0.95

3.1.6. Effect of Temperature upon Uranium Bio-sorption

It was concluded from the data represented in fig (3) that, the temperature has no significant effect on the loading capacity of uranium on the two studied algae. these result was also observed by Baht *et al.*,(2008) [29] in their study on *Catenella repens* for the biosorption of uranium from aqueous medium, they reported that the uranium uptake seemed to be an energy independent mechanism, as it was not affected by temperature across the range of 15–55 ˚C [8].

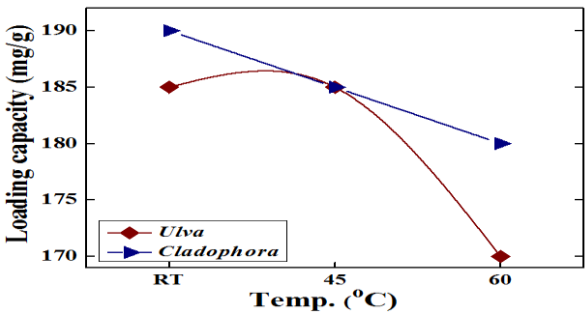

Fig. (3): *Effect of temperature upon uranium bio-sorption upon studied algae*

3.2. Characterization of Algal Biomasses Results

3.2.1. Some Phyto -chemical analysis

Algae in their habitats (fresh or marine) generate in their surfaces various bioactive primary and secondary metabolites (mainly carbohydrates, protein and phenols) for protection and to overcome the heavy metals oxidative stress [35, 36]. So, the phyto-chemical analyses of the algal biomasses throw the light on the importance of these constituents in the biosorption of uranium as well as their fractions. The chemical composition of both *U. lactuca* and *C. glomerata* showed that the percentage of the main constituents were 10.9 (phenol), 8.3 (protein) and 6.0 (carbohydrate) % for *U. lactuca* and 12.63(phenol), 15.9 (protein) and 10.16 (carbohydrate) % for *C. glomerata*. The GC chromatograms showed that the *U. lactuca* alga has two sharp peaks at a retention time 2.65 and 3.0 min corresponded to carbohydrate and phenol fractions respectively, as shown in Fig. (4and 5).The chromatograms of the *U. lactuca* containing phenols (Fig. 4) display three characteristic peaks at a retention time of 2.85, 3.04, and 3.8 for resorcinol, quercetin and kaempferol, with relative areas (84.78, 9.73, 5.49%) respectively, this can be interpreted as the resorcinol is an important fraction can be concluded in the biosorption process. While, the chromatogram of carbohydrate fraction for the same alga displays four characteristic peaks at a retention time of (2.55, 2.7, 3.1, and 3.66) for sucrose, maltose, lactose, and dextrose, with relative areas (4.20, 8.22, 31.84 and 55.74%) respectively, these data was in agreement with that observed by Eduardo *et al.*, 2017 [37], who reported that Sugars or carbohydrates are the main products of photosynthesis, with different distributions in the different algae species. Glucose is often the most present monomer for many species; cellulose, hemicellulose and pectin are present in the cell membranes mainly of green algae. Moreover, Kalin

et al.,(2005) [38], reported that, algal cell wall composed mainly polysaccharids, carbohydrates as cellulose xylan and mannans with negative charge on its surfaces that caving uranium cation.

On the other hand, the GC chromatograms of *C. glomerata* display four characteristic peaks corresponding to phenol fraction at a retention time (3.023, 3.47, 4.75 and5.2) forresorsenol, quercetin, naphthaline and phenantherine, with relative areas (95.78, 1.03, 1.39 and 1.80%) respectively, and GC chromatograms for carbohydrate in *C. glomerata* alga appeared at a retention time of (2.54, 2.7, 3.06 and 3.7) that correspond to sucrose, maltose, lactose, and dextrose with relative areas (15.39, 84.56%) for sucrose and maltose only.

Finally, the analysis of protein fraction was found to contain seventeen types of amino acids with different concentrations (Table 4). The relative high concentrations of sulfonted amino acids such as cysteine and methionine indicating their contribution in the uranium biosorption. Uranium and other metal sequestration by algae may attribute to their sulfated or thiol-containing amino acids and their derivatives [39]. Also, a mixture of different functional groups is responsible for the coordination of uranium mainly influenced under the given experimental conditions by the cell status. Therefore, the amount of uranyl ions complexed to cell walls depends on the number and density of the ligands in the cell walls of *U. lactuca* and *C. glomerata* algae. In which, more than one ligand type (-NH_2, -COOH and –OH) were found on a given cell surface, which results in selective interaction of uranium with the organic ligand at the specified pHs value (i.e. optimum pH 4-5) which is consistent with that early reported [38,40].

Summing up, the achieved results from the phyto-chemical analysis prove that the relative high rate of uptake in the case of *C. glomerata than U. Lactuca* is due to the higher concentrations of carbohydrates, proteins and phenols, as well as their fractions. These results are confirmed by that obtained previously in the experimental work. In conclusion, there is a potential for using these algal biomass in industrial processes to uptake uranyl from aqueous streams.

Table (4): Fraction amino acids concentration, (%), of the concerned algae

Amino acid	*U. Lactuca*	*C. glomerata*
Aspartic (ASP)	1.35	1.21
Therionine (THR)	0.62	0.55
Serine (SER)	0.60	0.47
Glutamic (GLU)	1.23	1.68
Glycine (GLC)	0.73	0.66
Alanine (ALA)	1.13	0.88
Valine (VAL)	0.72	0.89
Isoleucine (ILE)	0.47	0.46
Leucine (LEU)	0.77	0.82
Tyrosine (TYR)	0.31	0.32
Phenylalanine (PHE)	0.61	0.53
Hisitidine (HIS)	0.19	0.16
Lysine (LYS)	0.49	0.58
Argnine (ARG)	0.62	0.62
Proline (PRO)	0.45	0.49
Cysteine (CYS)	0.26	0.34
Methionine (MET)	0.28	0.26

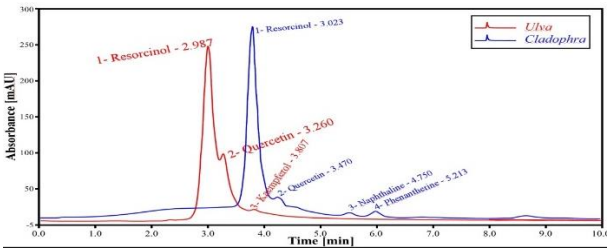

Fig. (4): *Fraction phenols concentration of the concerned algae*

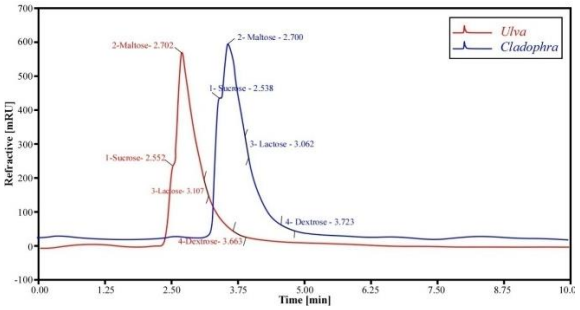

Fig. (5): *Fraction carbohydrates concentration of the concerned algae*

3.2.2. Scanning Electron Microscopy (SEM) analysis

As seen in figs. (6&7), the difference in the morphological surface structure of the two studied algae is clearly appears. The raw marine alga *U. lactuca* (fig. 6a) possess a papillary surface and has honey comb structure supplying a large exposed surface area for bio-sorption, whiles the fresh water pure alga *C. glomerata* (fig. 7a), is relatively flat texture with detectable linear lines. On the other hand the uranium loaded *U. lactuca* surface seems to be wrinkled and the matrix layers of the cell wall are seen to shrink and stick(fig. 3 b).However the loaded *C. glomerata* surface becomes rough(fig. 7 b). This may be due to strong cross- linking of chemo-sorption between uranium particles and the algal cell wall [41]. Additionally, as seen from EDS spectra shown in fig. (6 and 7), as well as the other characteristic peaks of the bio-sorbent, the uranium peak is detected at about 3 keV which corresponds to 89.5 and 82.5wt% for *U. lactuca* and *C. glomerata* respectively. These results are confirmed by the published data [11].

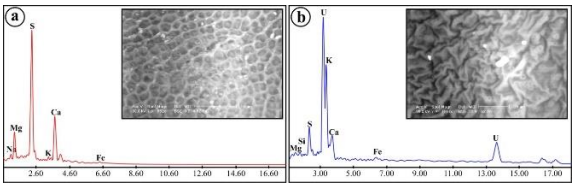

Fig. (6): *EDAX chart represented the marine green alga U. lactuca (**a**), before uranium bio-sorption and (**b**), after uranium bio-sorption*

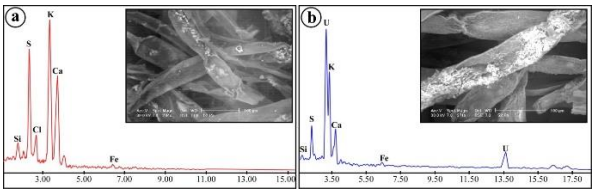

Fig. (7): EDAX chart represented the fresh water green alga *C. glomerata* algae (**a**), before uranium bio-sorption and (**b**), after uranium bio-sorption

3.2.3. Fourier Transform Infrared (FTIR) analysis

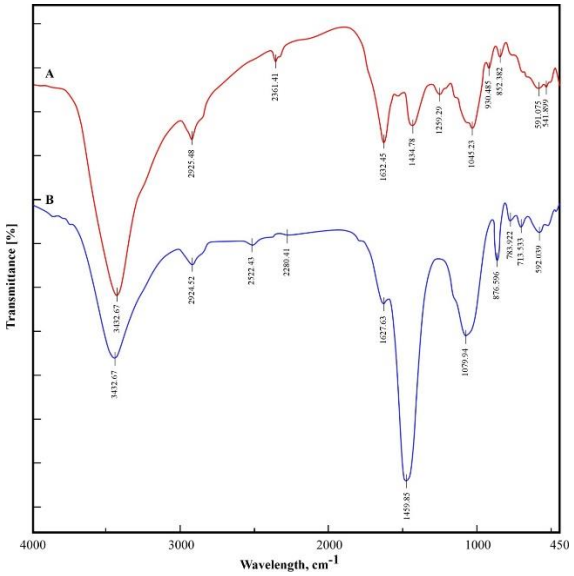

Fig. (8): *FT-IR spectrum of marine green alga U. Lactuca before (B), and after (A), uranium bio-sorption*

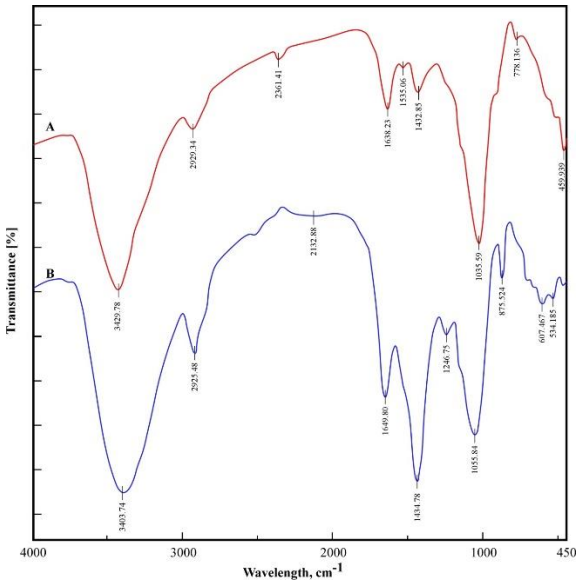

Fig. (9): *FT-IR spectrum of fresh water green alga C. Glomerata before (B), and after (A), uranium bio-sorption*

The FTIR spectra of the studied algal biomasses before and after uranium biosorption are presented in Fig. (8 & 9) and table (5), the obtained data revealed that there are many essential functional groups participating in the biosorption process can be discussed briefly as:

The bands at 3432.67cm^{-1} and 3403cm^{-1} observed in raw *U. lactuca* and *C. glomerata* algae respectively may be ascribed to (–NH) and (-OH) stretching vibrations of alcohols and phenols [2], indicating the presence of (OH) and (NH_2) group on the cell surface of the two studied algae [42,43].

The bands at (2522-3132 cm^{-1}) in the raw algal masses *U. lactuca* and *C. glomerata* respectively which shifted to (2361cm^{-1}) explained by combination of amino acids (2500-2000cm^{-1}) which are included in uranium bio-sorption [44,45].

The bands at (1079-1055cm^{-1}) in the blank samples of the two studied algae *U. lactuca* and *C. glomerata* respectively shifted to (1025-1035) in the loaded samples could be due to (C-O) of alcoholic group [46] and they are a characteristic peaks of polysaccharides as the structural component of the algal masses [2, 47, 48], and their shift proving its important role in the uranium bio-sorption.

The appearance of new band in the uranium loaded alga *U. lactuca* at 930cm^{-1} confirm the existence of UO_2 group, this result was previously observed [49,50] who stated that the fully hydrolyzed uranyl ions show bands at 961cm^{-1}further more, the bands around 920cm^{-1}mainly represent the υ_3 (UO_2) mode of complexed uranium.

The band at 875.59 cm^{-1}shifted to 852.1cm^{-1}and the bands at 783.59 and 713.97 before U bio-sorption are disappeared after U bio-sorption this attributed to the functional group like –OH, –NH_2 and –COOH were involved in the bio sorption process, The attraction between U (VI) ions and the surface group of bio-sorbent could be carried out via ion exchange and complex formation depending on pH value of the solution [11].

The bands at (592& 534) in the two algal masses shifted to (541 and 459) after uranium bio-sorption by *U. lactuca* and *C. glomerata* respectively could be due to existence of C-N-S group which included in the bio-sorption mechanism [51]. In addition, Mahdy (2011) [52]**,** reported that the spectra in the range (669-544 cm^{-1}**)** may be atributad to stretching vibrations of CO-SO_2-Ogroups**,** so the appearance of nearly close bands for the two studied algae in the present work indicating the participating of sulfonate groups in the uranium bio-sorption.

The current FTIR study of the raw and loaded algal biomasses concluded that, carboxyl, amino, sulfhydryl, and sulfonate are the main chemical groups, which are involved in metallic cation biosorption [31,38]**,** these groups are part of the algal cell wall structural polymers namely, polysaccharides (sulfated polysaccharides), proteins, and peptide-glycans.

Table (5): FTIR frequencies for algal biomasses before and after uranium biosorption

Functional groups	**Raw*U. lactuca***	**Loaded*U. lactuca***	**Raw*C. glomerata***	**Loaded*C. glomerata***
OH groups	3432	3432	3403	3429
CH Stretching methyl or Methylene groups	2924	2925	2925	2929
C=O carboxylic	1627	1632	1649	1638
C-O carboxylic	1459	1434	1434	1432
C-O alcoholic	1079	1045	1055	1035
UO_2group	---	---	---	930
C-N-S group	592	591-541	607-534	459

3.3. Elution Results

3.3.1. Effect of Eluent Type upon Uranium De-sorption from the loaded green Algae

Many eluent types were studied such as the H_2O, mineral acids (HCl, H_2SO_4 and HNO_3), EDTA and acidified NaCl solution. Concerning the potentiality of these eluents to desorb the maximum amount of loaded uranium upon the algal biomasses, it was observed that, the elution efficiency enhanced by using the three mineral acids and the acidified NaCl giving the maximum value with HCl at 57 and 60 % for *U. Lactuca* and *C. Glomerata* respectively, (fig. 10 a). However less efficiency by using EDTA solution reaching 18.5 and 20 % for *U. Lactuca* and *C. Glomerata* respectively, and non-efficient process with distilled water.

3.3.2. Effect of Eluent Concentration

It was clear from fig.(10 b) that the elution efficiency increased with increasing the HCl eluent concentration to 0.4M reaching 57 and 54 % for *U. Lactuca* and *C. Glomerata* respectively, however, the more favorable concentration was 0.1M (57.5 and 60 % for *U. Lactuca* and *C. Glomerata* respectively,) in order to economic considerations. In case of EDTA solution the maximum efficiencies are 16.5 and 18.5 % for *U. Lactuca* and *C. Glomerata* respectively, at 0.1Mwith fixing the solid/liquid ratio and the contact time.

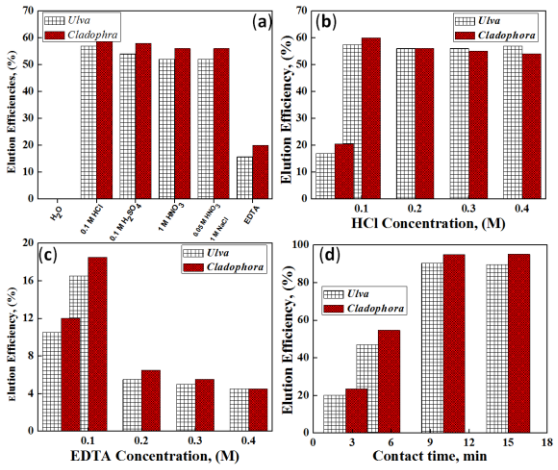

Fig. 10 ***(a)*** *Effect of eluent type upon uranium elution from the loaded algae, (b) effect of eluent concentration HCl, (c) EDTA upon uranium elution from the loaded algae, and (d)* ***e****ffect of contact time upon uranium elution from the loaded algae*

3.3.3. Effect of Contact Time

Many time intervals were studied (2.5, 5, 10, and 15 min) with the previous two interested eluents. Fig.(10 d), showing that the equilibrium achieved at 10 min with elution efficiency of 91 and 95 % to *U. Lactuca* and *C. Glomerata* respectively, for HCl. It was concluded from all studied factors that the mineral acids such as diluted H_2SO_4, HNO_3 and HCl, were effective in uranium desorption and the biomass damage caused by the acid elution was negligible and the obtained results are in agreement with the published data [53]. The biomass weight loss during the acidic desorption process was less than 5 %. The biomass was also protonated at the same time and was ready for the next run of uranium biosorption [54]. The regeneration of algal biomasses appropriate for further consideration is achieved.

4. *Applicability of Green Algae upon Real Uranium Waste Solution*

Table (6): chemical composition of Gattar waste liquor before and after bio-sorption experiments using the concerned algae

Metal Conc., ppm	Gattar waste solution	*U. lactuca*			*C. glomerata*		
		Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3
SO_4	3890	2589	935	840	2150	755	570
K	95	84	36	13	82	34	12
Ca	198	110	100	8	110	102	4
Fe	1620	750	80	6	740	80	10
Zn	65	34	7	5	35	5	5
Cu	15	14	6	2	12	4	nil
Ni	12	10	4	2	7	2	nil
Th	25	25	23	nil	25	23	nil
U	60	60	58	7	60	56	3
Mn	115	72	36	9	70	32	10
Pb	12	10	7	4	7	2	2
Cd	6	4	3	nil	2	2	nil

The obtained results (Table 6), prove that due to high concentrations of iron and sulfate in the Gattar pilot planet waste sample, the uranium uptake starts after two cycles using the two green algae *U. lactuca* and *C. glomerata* at 1/1000 S/L ratio and 60 min stirring as optimum adsorption conditions. About 99 % of the loaded uranium was eluted using 0.1 M HCl and 10 min. contact time while the other elements such as iron, calcium, zinc, copper,…etc were eluted by using 0.3 M EDTA and 10 min. contact time. The algal biomasses were washed with water to regenerate and can be reused. By applying these conditions almost of elements and nearly uranium complete concentrations were recovered from the waste water and the water can be reused again in Gattar pilot planet or may be used in agriculture in safe environment.

The obtained results prove that, both *U. lactuca* (marine algae) and *C. glomerata* (fresh water) showed more or less the same picture of high bioaccumulation abilities for uranium and heavy metals. These results are in agreement with the published data [55]. *C. glomerata* generally tolerates and flourish in heavy metals polluted aquatic habitats [56]. This due to its effective scavenging phytochemical compounds [57] and to its morphological structure which gives it highest exposed surface area. However, *C. glomerata* has branched, lamellate wall filament [58], whereas *U. lactuca* has mono-layer flattened leaf like form [59].

Conclusion

The present work demonstrated the possibility of applying an eco-friendly and economically low-cost method to recover nuclear and economic elements. Also, purification of waste solution of Gattar pilot plant treat waste water from Gattar pilot planet using two green algae *Ulva lactuca* Linnaeus and *Cladophora glomerata* Linnaeus Kützing. The obtained results were very promising, as more than about 98% of uranium and some other elements such as iron, calcium and manganese were recovered by applying the previously mentioned optimal conditions such as 1/1000 solid/liquid ratio and 60 min. time. The uranium was eluted from the concerned algae using 0.1 M HCl, while the other elements were eluted by 0.3 M EDTA and the uranium full recovery needs 3 separation cycles.

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