

Effect of Uranium Toxicity on *Spirulina platensis* widespread

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Abstract: *Spirulina* is an organism that grows in both fresh and salt water. It is a type of cyanobacteria, which is a family of single-cell. Just like plants, cyanobacteria can produce energy from sunlight via a process called photosynthesis. *Spirulina* is a biomass of cyanobacteria (blue-green algae) that can be consumed by humans and animals. The two species are *Arthrospira platensis* and *A. maxima*.

Cultivated worldwide, *Arthrospira* is used as a dietary supplement or whole food. [1] It is also used as a feed supplement in the aquaculture, aquarium, and poultry industries.

Spirulina was consumed by the ancient Aztecs but became popular again when NASA proposed that it could be grown in space for use by astronauts.

The effect of uranium on *spirulina* was evaluated. The experimental results showed that uranium has bad effects on *spirulina*

Key words: Uranium; *spirulina platensis*, effects

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I. Introduction

Actually removal of heavy metal ions from waste water can be carried out by various physiochemical techniques such as adsorption (Lee et al., 2012)(Vullo et al., 2008). Biosorption is an alternative cheap, efficient and ecofriendly tool can be applied for this target. In fact some microorganisms, such as bacteria, fungi or algae, are used to remove heavy metals and environmental contaminants (Wang and Chen, 2009). Uranium ions from aqueous solutions can be removed by different biomasses such as fungi, algae and unicellular bacteria (Khani, 2006).

Algal species either in living or in chemically modified form had been employed for the removal of uranium (Lee et al., 2014). However, an improvement in adsorption capacity of microbial biomasses can be carried out by modification with various ligands (Ding et al. 2014). Among algae species, *Spirulina platensis* is a photosynthetic filamentous cyanobacterium that has a biotechnological importance due to its high protein content (about 70%) and its type of lipids (g-linolenic acid) and carbohydrate content that can be applied in nutritional and environmental technology. It was used as bioaccumulator and sorbent of different metals and radioactive ions (Zinicovscaia and Cepoi, 2016).

II. Materials and methods

Materials

All chemicals used in this study were analytical grade and distilled water was used to prepare all the solutions. Uranium nitrate obtained from INC, USA, it was used for the preparation of stock solution (1000 mg L⁻¹). Dry *Spirulina platensis* biomass at room temperature prior to use.

Methods

Instrumentation

The modified and unmodified algal biomass were characterized using a Fourier Transform Infra-red spectrometer (FTIR-Is10, Shimadzu Tokyo, Japan) to establish the functional groups present.

The concentration of metal pollutants in the waste effluent sample was determined using ICP Inductively Coupled Plasma Optical Emission Spectrometer. All pH measurements were measured by using a calibrated pH meter equipped with a standard calomel electrode (SCE) and the adsorption medium pH was adjusted by using 0.1 M HCl or NaOH solutions. Thermostated water bath shaker model C.F.C 3018 was used to shake the samples at the required shaking speed and temperature. Environmental Scanning Electron Microscope (ESEM) with unit was used to show the morphological character of the modified algal biomass and confirm the adsorption of uranium on its surface.

Batch experiments

Adsorption experiments were performed using a batch system. It was carried out at $25 \pm 2^\circ\text{C}$ and shaken at 150 rpm for various time periods, at different pH, algal biomass dosage, uranium concentrations. After adsorption process, the algal biomass was decanted by filtration, and the concentration of U(VI) in the medium was determined by using titration method according to (Daveis and Gray, 1964).

The amount of U(VI) adsorbed per unit of algal biomass (mg U(VI)/g dry biomass) was obtained by using the following equation:

$$q = (C_o - C_e)V / m$$

Where, q is the amount of U(VI) adsorbed onto the unit mass of the algal biomass (mg/g), C_o and C_e are the concentrations of the U(VI) before and after adsorption (mg/L), V is the volume of the aqueous phase (L), and m is the amount of the biomass (g).

III. Results and Discussion

The changes in the functional groups and surface properties of the algal biomass are presented in (Fig.2.(b) and (c) respectively). A new sharp intense peaks at 2360 and 2342 cm^{-1} were observed that could be attributed to C=N stretching vibration. By the addition of biomasses the intensity of the band at 2360 decreased and the band at 2342 disappeared confirming the change in the functional groups on algal biomass surface after modification.

FTIR spectra of native and modified algal biomasses also revealed that the surface functional groups (such as $-\text{COOH}$, $-\text{NH}_2$, and $-\text{OH}$) on the tested biosorbents were involved in U(VI) biosorption. It also confirms that the algal cell wall structural polymers such as lipids, carbohydrates, and proteins were possibly included in the biosorption process through hydroxyl, carboxyl and amino groups that might be enriched by modification improving the biosorption capacity. deprotonate and become negatively charged resulting in an enrichment of the modified algal biomass surface with negative charges improving biosorption capacity of modified algal biomass (Movileanu et al., 2000).

Dead biomass (heat, acid, and/or chemically treated) had great biosorption capacity, might be due to the uncovering of mask binding sites. The two principle mechanism involved in biosorption appear to be the ion exchange where ions such as Na^+ , K^+ , Mg^{2+} and Ca^{2+} became displaced by heavy metals ions, and the complexation between metal ions and various functional groups such as carboxyl, amine and hydroxyl that can interact with heavy metal ions (Donat et al., 2009; Bayramoglu and Arica, 2011).

Vijayaraghavan et al., 2018 showed that carboxyl groups were the dominant anionic functional group involved in uranium adsorption of marine unicellular cyanobacterium *Synechococcus elongatus* BDU130911, which validates an ionic interaction between the biomass and uranium, a cationic metal.

Effect of U(VI) Spirulina platensis dry biomasses

Initial pH plays an important role in the adsorption of uranium ion from the aqueous medium. It influences both the binding sites present on the surface of algal biomass and the speciation of uranium ion in the aqueous medium (Rippka et al., 1979; Bayramoglu and Arica, 2009).

Ghasemi et al., 2011 that showed the optimal pH for adsorption of uranium ions by *Cystoseira indica* was at pH 4.0 and Bhat et al., 2008 who reported that pH 4.5 was the best for uranium removal by *Catenella repens*, a red alga also Erkaya et al., 2014 showed pH 4.5 the optimal pH for *Chlamydomonas reinhardtii*. The reason for maximum adsorption of uranium at pH 4.0 could be due to dissociation of groups on the surface of the biomass like amino, carboxyl and hydroxyl groups resulted more negative charges and lower numbers of competing hydrogen ions resulting in greater metal sorption capacity, However further increase in pH result in precipitation of U(VI) in the form of hydroxide complex due to lower polarity of metal decreasing metal adsorption ability of modified biomass (Kumar et al., 2007).

Effect of algal biomass dosage

increase in U(VI) removal. the incremental U(VI) removal became less significant, therefore, of modified algal biomass was used in further U(VI) removal studies. The increase in algal biomass dose resulted increase the functional groups and surface area enhancing adsorption capacity of modified algal biomass (Ilhan et al., 2004).

Effect of contact time on adsorption of uranium

The change in contact time from results in an increase in U(VI) removal of the experimental duration the adsorption decreased progressively during of contact with the uranium ions, this may be due to the break of the bonds between the algal cell and the uranium ions, similar results were reported by (Abd El Monsef et al., 2014).

Effect of initial uranium ion concentration on adsorption of uranium The adsorption rate increased with increasing initial concentration of U(VI) from 10-500 mg L⁻¹, this increase was related to collisions between U(VI) and the modified algal biomass which is attributed to the fact that concentration is the driving force for metal ions adsorption (Ihan et al., 2004), significant increase in uranium removal which may be attributed to the saturation of the binding sites (Benhima et al., 2008).

The latter mixture shaken then filtered. The remaining U(VI) concentration in the supernatant was measured to evaluate the desorption percentage and then used for the next sorption-desorption cycle. It showed high efficiency

In the present study, different isotherm models were applied to describe interactions between the U(VI) and quercetin-NaOH modified algal biomass. Modeling of the experimental isotherm data has been done using the Langmuir (Langmuir 1919), Freundlich (Freundlich 1906) and D-R (Dubinin and Radushkevich 1947). The Langmuir model can be described by the following linearized equation:

$$C_e/q_e = (1/q_{max}) C_e + (1/q_{max}) b \quad (1)$$

where q_{max} is the maximum adsorption capacity (mg/g), C_e is the equilibrium U(VI) concentration in solution (mg/L), and b is the Langmuir constant.

The Freundlich isotherm can be expressed as follows:

$$\ln q_e = \ln K_F + 1/n \ln c_e \quad (2)$$

where K_F is the Freundlich constant and n is adsorption intensity, respectively.

The D-R isotherm can be expressed as follow:

$$\ln q_e = \ln q_m - K \varepsilon^2 \quad (3)$$

where q_m is the theoretical monolayer adsorption capacity (mg/g), K is the constant of the sorption energy (mol²/J²). ε is Polanyi potential $\varepsilon = RT \ln (1 + 1/C_e)$, where T is the solution temperature (K) and R is the gas constant and is equal to 8.314 J/mol·K. E (kJ/mol), can be calculated from D-R parameter K [$E = (-2K)^{-1/2}$].

The Langmuir isotherm model well fitted to experimental data since its R^2 value was 0.998 than other two models. Also, theoretical maximum adsorption capacity was nearest to experimental data. It indicates to homogeneous and monolayer biosorbent surface. Physical adsorption is considered since E value obtained from D-R model

Kinetics of adsorption

Pseudo-first-order and Pseudo-second-order models were applied to examine the rate-controlling mechanism of adsorption process (HO and McKay, 1998). The Pseudo-first-order rate equation is given as

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t$$

where q_e (mg/g) is the amount of metal ion adsorbed at equilibrium,

and q_t (mg/g) is the amount of adsorbed metal ion

adsorbed at time t where k_1 is the first-order adsorption rate constant (min⁻¹).

pseudo-second-order equation is given as

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

where k_2 is the second-order adsorption rate constant

(g mg⁻¹ min⁻¹) and q_e is the adsorption capacity calculated

by the pseudo-second-order kinetic model (mg/g).

Its correlation coefficients (R^2) was higher and its calculated adsorption capacities ($q_{e,cal}$) agree with the corresponding experimental adsorption capacities ($q_{e,exp}$) indicating that U(VI) adsorb by chemical or surface complexation mechanism rather than mass transport. As seen from isothermal models Both physical and chemical adsorptions may occur on the algal biomass surface at the same time (Bayramoglu et al., 2015).

Thermodynamic

The effect of temperature on U(VI) adsorption was investigated at three different temperatures at optimized conditions. It was found that U(VI) adsorption increase with increasing the temperature indicating the endothermic nature of the process which could be attributed to increase on probability of interaction between functional groups on algal biomass surface and U(VI). The thermodynamic parameters of U(VI) adsorption on

$$\ln K_c = -\Delta H^\circ / RT + \Delta S^\circ / R$$

$$\Delta G^\circ = -\Delta H^\circ - T \Delta S^\circ$$

Where, $K_c (=q_e/C_e)$ equilibrium constant in molar unit, (ΔH°) enthalpy change, (ΔS°) entropy change, and (ΔG°) Gibbs free energy change the biosorption process was feasible and spontaneous as showed by negative value of Gibbs free energy change (ΔG°). Furthermore, the positive values of ΔH° and ΔS° suggested the endothermic nature of the process and the increase in randomness at the solid-solution interface during U(VI).

IV. Conclusions

Uranium has bad effects on spirulina .

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