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Uranium sorption by native and nitrilotriacetate-modified *Bangia atropurpurea* biomass: kinetics and thermodynamics

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Abstract In this study, the red alga *Bangia atropurpurea* was modified with nitrilotriacetate (NTA) ligand and used for removal of U(VI) ions from aqueous solution using native form as a control system. The modification of *B. atropurpurea* biomass was realized by sequential treatment of algal biomass with glutaraldehyde and NTA ligand. Influence of U(VI) sorption parameters, such as contact time, adsorbent amount, medium pH and ionic strength, initial U(VI) ions concentration, and temperature on the removal performance of both algal biomasses were studied from aqueous solution. The hydroxyl, amino, carbonyl, and carboxyl groups were the main adsorptive groups of the biomasses as observed in FTIR data, and these groups can bind to U(VI) ions via electrostatic interactions. More than 78% of total sorption took place within 40 min, and equilibrium was established about 60 min. Maximum sorption capacities of the native and NTA-modified algal biomasses were found to be 190.2 and 328.8 mg g^{-1}, respectively, at pH 5.5 and at 30 °C. The presence of other ionic species slightly decreased the U(VI) sorption capacity except that in Fe(III) ions. The sorption processes of U(VI) on the algal biomasses were described by the Langmuir and Temkin isotherms and pseudo-second-order kinetic models. The thermodynamic parameters, such as $\Delta H°$, $\Delta S°$, and $\Delta G°$, show that the process is exothermic and spontaneous. It should be stated that the NTA-modified algal biomass has a high potential for the removal of U(VI) ions from aqueous solution.

Keywords Algal biomass · *Bangia atropurpurea* · Rhodophyta · Surface modification · Nitrilotriacetate · Sorption · Uranium

Introduction

Increasing environmental pollution caused by toxic organic and inorganic compounds (such as synthetic dyes, pesticides, drugs, and heavy metals ions) is a topic of great concern. The later heavy metals are dangerous constituents of industrial effluents due to their toxicity to living systems even at low concentrations (Zhao et al. 2016; Shaaban et al. 2017). Uranium is one such metal that is known to pollute the environment through activities associated with nuclear industry, and has both radiochemical and toxicological effects. Toxicity of uranium is closely associated with its solubility (Katsoyiannis 2007; Lee et al. 2014; Bayramoglu et al. 2015; Mona and Kaushik 2015; Birungi et al. 2017; Heidari et al. 2017), and hexavalent uranium species are highly water soluble as compared to tetravalent forms (Sarı and Tuzen 2009; Liu et al. 2013; Bayramoglu and Arica 2017). The normal functioning of the kidney, brain, liver, heart, and reproductive system can be affected by uranium exposure, because, besides being weakly radioactive, uranium is a toxic and carcinogenic metal (Francis and Dodge 1998). Several methods have been reported for removal and recovery of uranium ions from wastewaters such as precipitation, membrane filtration,

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reverse osmosis, evaporation, and sorption (Gottlieb and Husen 1982). The later method has proven to be an effective and convenient technique among all the available methods due to its cost effectiveness, easy operation, and wide choice of adsorbent materials (Wang et al. 2015; Bayramoglu and Arica 2016; Ji et al. 2017). Many natural [such as microbial biomass and their derivatives, alginate, agarose, cellulose] and synthetic adsorbents [such as modified poly(vinyl alcohol), poly(ethyleneimine), poly(acrylic acid), and several acrylate polymers] are also known to interact with metal ions strongly (Camacho et al. 2010; Ahmady-Asbchin 2016; Espinosa-Ortiz et al. 2016). Among them, adsorbents, based on living or nonliving microbial or plant biomass, is a promising potential alternative to conventional adsorbent materials for the removal of organic or inorganic pollutant from solutions (Bayramoglu and Arica 2009). Additionally, the modification of adsorbent materials with functional groups may also improve the adsorbent performance and sorption capacity. Various types of microbial biomass such as algae, fungi, bacteria, and yeast have been modified with various functionality with the aim of finding a more efficient adsorbent (Bai et al. 2010; Yokono et al. 2012; He et al. 2014; Bayramoglu et al. 2015). Algal biomass has proved to be economic material, as algae abundantly grow in natural environments. In addition, algal biomasses possess high metal ion sorption capacities due to the presence of large amounts of polysaccharides, proteins, and lipids on the cell walls, and they contain several numbers of functional groups such as amino, hydroxyl, carboxyl, phosphate, and sulfate, which can act as binding sites for metal ions (Asnaoui et al. 2015; Bampaiti et al. 2016; Nasab et al. 2017). Therefore, various algal biomasses have been used for removal of organic and inorganic pollutants because of the availability of large amounts of algal populations in water environments. Some important algal biomasses including *Chlamydomonas reinhardtii*, *Spirulina platensis*, *Graesiella emmersonii*, and *Scenedesmus quadricauda* were used as adsorbent materials for removal of uranyl ions from aqueous solution (Dixit and Singh 2014; Jena et al. 2015; Jiang et al. 2016; Cheng et al. 2017, Heidari et al. 2017).

In this study, the removal of U(VI) ions on the native and modified algal biomass of *Bangia atropurpurea* from aqueous solution was studied. It is a freshwater red alga and possesses good metal sorption capability due to the existence of several functional groups on its cell surface, and has never been used before for uranium ion sorption. The effect of solution pH, adsorbent dose, initial U(VI) concentration, contact time, and presence of other cations on U(VI) removal was investigated in a batch system. Furthermore, this is the first study to determine the sorption efficiency of NTA ligand-modified *B. atropurpurea* biomass. Also, the reusability and stability of both algal biomass preparations were studied and evaluated. Finally, the equilibrium sorption data were ascertained by Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Temkin isotherm models. The pseudo-first-order, pseudo-second-order, and Elovich kinetic models were used for the determination of the sorption kinetics of U(VI) ions on the algal biomass preparations. The thermodynamic parameters ($\Delta G°$, $\Delta H°$, and $\Delta S°$) were also determined.

Materials and methods

Materials

N-5-(Amino-1-carboxypentyl) iminodiacetic acid (NTA) and glutaraldehyde were obtained from Sigma-Aldrich Chemical Co., USA. The former is the aminopolycarboxylic acid with the formula $N(CH_2CO_2H)_3$ used as a chelating agent for metals, which forms coordination compounds with metal ions such as Fe(III), Cu(II), and U(VI) ions. All other chemicals were of analytical grade from Merck AG (Darmstadt, Germany).

Microorganism and media

Bangia atropurpurea sample was collected from the Manastır stream of Altınoluk, Balıkesir Province, Turkey. It was firstly cleaned with stream water and then washed with distilled water for the removal of particles. The *B. atropurpurea* was isolated from the collected samples by micro-manipulation technique and grown in Bold 1NV liquid medium containing vitamins and essential mineral nutrients (Starr and Zeikus 1993). Cell culture was in minimal base medium at pH 7.0, maintained at 22 ± 1 °C. Illumination was set to a 16 h light, 8 h dark cycle and provided by daylight-type fluorescent tube lamp (20 W; 35 μmol photons m^{-2} s^{-1}) (Yokono et al. 2012). Algal cells at the middle of the logarithmic phase reached in 14 days were harvested by filtration. Algal biomass was dried at 45 °C under reduced pressure in an oven for 48 h. Hereafter, it is denoted as the native algal biomass.

Modification of the native algal biomass with NTA ligand

To prepare the NTA-modified algal biomass, the following procedure was applied. The native algal biomass was incubated with glutaraldehyde solution (1.0%, at pH 7.0) in a reactor containing 5.0 g of wet algal biomass. The mixture was placed on an orbital shaker and operated at 150 rpm and at 45 °C for 4.0 h. After this period, the activated algal biomass was washed with distilled water and transferred to an NTA solution (2.0% NTA, at pH 10). Algal biomass mixture was placed again on the orbital shaker and allowed for ligand attachment for 6.0 h in the above given conditions. After this reaction period, the NTA-modified algal biomass was removed from the solution by filtration and washed sequentially with 1.0 M NaCl and with purified water. Finally, it was dried in an oven at 45 °C for 24 h under reduced pressure. Hereafter, it is denoted as the modified algal biomass and stored at room temperature until use. The schematic presentation of the NTA modification reaction of the native algal biomass is presented in Fig. 1.

Sorption of U(VI) ions on the native and modified algal biomasses

The sorption of U(VI) ions on the native and modified algal biomasses was investigated in a batch system. Uranium acetate ($UO_2(CH_3COO)_2$) was used for the preparation of the stock solution (1000 mg L^{-1} in Milli-Q water). A range of uranyl ions (UO_2^{2+}) with different concentrations was prepared from the above stock solution. Sorption experiments were carried out at 25 ± 2 °C while rotated on an orbital shaker at 150 rpm for 2.0 h. After a predetermined time, the algal biomass was removed by filtration, and the concentration of the U(VI) ions in the solution was determined using a previously described spectrophotometric method (Bayramoglu et al. 2015). Briefly, the method was based on the formation of colored complexes of U(VI) ions with sodium salicylate in aqueous solution. A calibration curve was constructed using known concentrations of U(VI) ions. The absorbance of the solution was measured at 468 nm using an UV/visible spectrophotometer (PG Instrument Ltd., Model T80+; PRC).

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

$$q = (C_o – C)V/m \qquad (1)$$

where q is the amount of U(VI) ions adsorbed on the unit mass of the algal biomass (mg g^{-1}), C_o and C are the concentrations of the U(VI) ions at initial and after sorption (mg L^{-1}), V is the volume of the aqueous phase (L), and m is the amount of the biomass (g).

The effect of pH on the sorption rate was investigated in the pH range 2.0–8.0. The medium pH was measured by Boeco microprocess pH meter, Model BT-600 (Germany), and the sorption medium pH was adjusted by using 0.1 M HCl or NaOH solutions at 25 °C, and not controlled during sorption period. To optimize the algal biomass dosage (g L^{-1}), batch experiments were conducted using different amounts of algal biomass (between 0.5 and 3.0 g) in a 1.0-L solution containing 200 mg L^{-1} U(VI) ions, pH 5.5, and at 25 °C. To investigate the influence of ionic strength on U(VI) ion removal, sodium chloride was employed as the background electrolyte and varied between 0.0 and 1.0 mol L^{-1}. The effect of temperature was studied at four different temperatures (i.e., 15, 25, 35, and 45 °C) at pH 5.5. The effect of initial concentration of uranium ions on the sorption rate and capacity was studied by varying the concentration of the U(VI) ions between 10 and 300 mg L^{-1}. After sorption, algal biomass preparations were recovered by filtration, and some of the U(VI) ion-laden biomass preparations were reserved for ζ-potential analysis. All experiments were conducted in triplicate with 20-mg algal biomass preparations. For each set of data reported, standard statistical methods were used to determine the mean values and standard deviations.

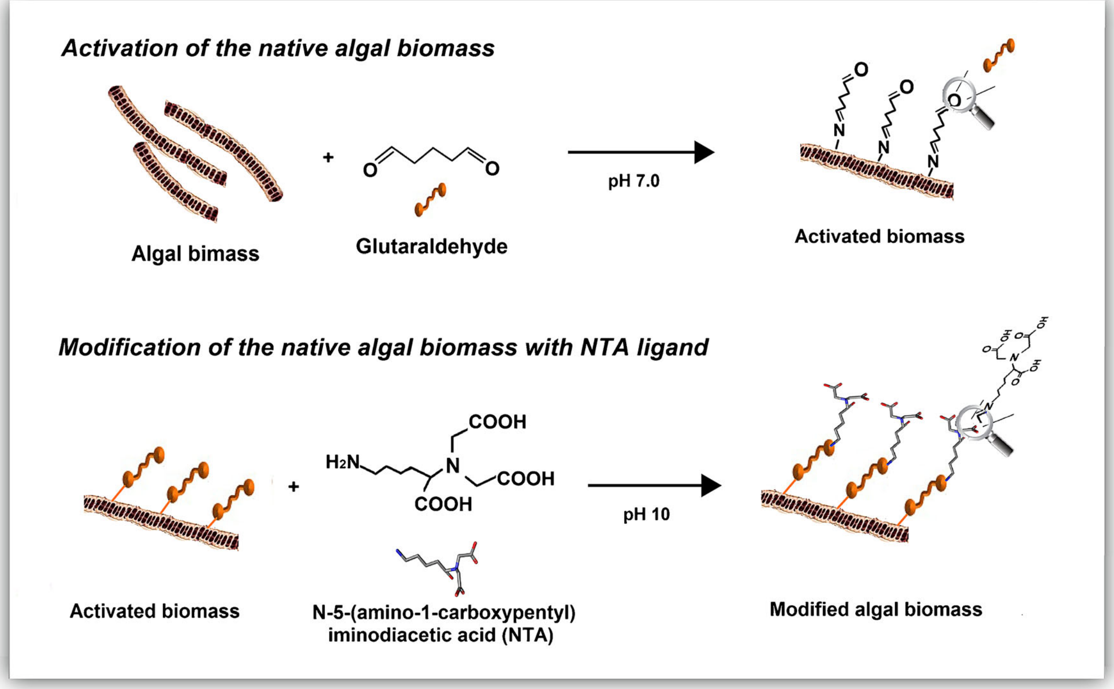

Fig. 1 Chemistry of preparation of modified algal biomass

Effect of different cationic species on U(VI) sorption efficiency

Competitive sorption studies of U(VI) ions on the native and modified algal biomasses in the presence of other cations were investigated in a binary system using a similar procedure described above. These experiments were performed at pH 5.5 and at 25 °C using solutions containing 2 mmol L^{-1} of U(VI), Na, Mg(II), K, Ca(II), or Fe(III) ions. All the used cationic solutions were prepared from chloride salts except that of U(VI) ions.

Elution and regeneration of algal biomass preparations

In order to determine the reusability of the algal biomass preparations, consecutive sorption–desorption cycles were repeated six times by using the same adsorbent samples. Desorption of U(VI) ions was performed by HNO_3 (10 mmol L^{-1}) solution. The U(VI) ion-laden native or modified algal biomass preparations were placed in the desorption medium and stirred at 150 rpm for 2.0 h at 25 °C. The final U(VI) ion concentration in the aqueous phase was determined as described above. After each cycle of sorption–desorption, the algal biomass preparations were washed with 0.1 mol L^{-1} NaCl solution and transferred into fresh U(VI) ion solution for sorption in the succeeding cycle. Desorption ratio was calculated from the amount of U(VI) ions adsorbed on the algal biomass preparations and the final concentration of U(VI) ions in the sorption medium.

Characterization studies

ATR-FTIR spectra of the native and NTA ligand-modified algal biomass preparations were obtained by using an attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectrometer (Nicolet IS 5, Thermo Electron Scientific Instruments, USA). Electro-kinetic properties (zeta potential) of the algal biomass preparations as a function of pH were studied by adding 0.1 g of each algal biomass to 100 mL of purified water. The suspensions were sonicated for 5 min in an ultrasonic bath. The solution pH was adjusted with either 0.1 M NaOH or HCl solutions. The suspension of each algal biomass sample was used to conduct ζ measurement with a Zetasizer instrument (NanoZS, Malvern Instruments Ltd., UK).

The carboxyl group content of the native and NTA-modified algal biomasses were determined by a titration method. Briefly, the algal biomass samples (about 1.0 g) were transferred to NaOH solution (0.2 mol L^{-1}, 20.0 mL) and the medium was incubated in a shaking water bath at 25 °C for 6.0 h. After this period, the final NaOH concentration in the solution was determined with titration of 0.05 M HCl solution. The concentration of carboxylic functions ($-$ COO^- mmol g^{-1}) was calculated using the following equation:

$$[-COO^-] = \left(\left\{[C]_{base} V_{base} \left(2[C]_{acid} V_{acid}\right)\right\}/M\right) 1000 \qquad (2)$$

where $[C]_{base}$ is the concentration of NaOH solution (mol L^{-1}), $[C]_{acid}$ is the concentration of HCl solution (mol L^{-1}), V_{base} is the volume of NaOH solution (L), V_{acid} is the volume of HCl spent in the titration of excessive non-reacted NaOH solution (L), and M is the amount of sample (g).

All experiments were carried out in triplicate under identical conditions for analytical studies. Mean values and standard deviations were calculated. The FTIR and zeta potential measurements were also performed in triplicate. The significance of differences among the obtained results was evaluated with analysis of variance ($p < 0.05$).

Adsorption isotherm models for U(VI) ion sorption

For optimizing the model of the adsorption process for the adsorption of uranyl ions, acquired experimental data were fitted to different sorption isotherm models in order to examine the relationship between sorption and uranyl ion concentration at equilibrium. The relationship between uranium ion sorption capacity and its concentration at equilibrium was tested using four different isotherm models, namely Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Temkin, to correlate of experimental adsorption isotherm data, which were obtained by batch experiments. In general, the Langmuir and Freundlich isotherms are the most commonly used isotherm models for the application of sorbents in water and wastewater treatment. Langmuir isotherm assumes a monolayer formation on a uniform surface and is expressed by the following equation:

$$C_e/q_e = (1/q_{max})(1/C_e) + (1/q_{max}b) \qquad (3)$$

where q_{max} is the maximum sorption capacity (mg g^{-1}), C_e is the equilibrium uranium concentration in solution (mg L^{-1}), and b is the Langmiur constant.

In the Freundlich isotherm model, it is suggested that the adsorption energy exponentially decreases when the adsorption centers are fully occupied. This model describes the adsorption on the heterogeneous surface and the interaction among the adsorbed molecules and is expressed as:

$$\ln q_e = (1/n) \ln C_e + \ln K_F \qquad (4)$$

K_F and n are the Freundlich sorption isotherm constants characteristic of the system and indicate the extent of the sorption and the degree of non-linearity between solution concentration and sorption, respectively.

The Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The linear Dubinin–Radushkevich isotherm (D–R) model equation:

$$\ln q_e = \ln q_D – B_D[\mathrm{RT} \ln (1 + 1/C_e)]^2 \tag{5}$$

where, B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the adsorbent from infinite distance in the solution and q_D is the Dubinin–Radushkevich isotherm constant related to the degree of sorbate sorption by the adsorbent surface (Bayramoglu and Arica 2011; Akar et al. 2013).

Temkin isotherm is based on the assumption that the heat of sorption would decrease linearly with the increase of coverage of adsorbent due to sorbate/sorbent interaction. Linearized Temkin isotherm equation:

$$\mathrm{q_e} = \mathrm{Q_T \ln K_T + Q_T \ln C_e} \tag{6}$$

where $Q_T = RT/ b_T$, b_T is the Temkin constant related to heat of sorption (kJ mol^{-1}), K_T is the Temkin isotherm constant (L g^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature (K). As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (Bayramoglu et al. 2015).

Kinetic models for analyses of U(VI) ion sorption

Kinetic models were used to provide information on the mechanism and process of the adsorption onto adsorbents. In batch adsorption systems, the kinetics are described by models based on adsorption equilibrium parameters such as the pseudo-first-order, the pseudo-second-order, and the Elovich kinetic models. The equations for the models are:

$$\log \left(q_{eq} – q_t\right) = \log q_{eq} – (k_1 \cdot t)/2.303 \tag{7}$$

$$(t/q_t) = \left(1/k_2 {q_{eq}}^2\right) + \left(1/q_{eq}\right) t \tag{8}$$

where q_{eq} (mg g^{-1}) is the experimental amount of U(VI) ions adsorbed at equilibrium, q_t (mg g^{-1}) is the amount of U(VI) ions adsorbed at time t, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the equilibrium rate constants of the pseudo-first- and pseudo-second-order sorption. The constant k_2 is used to calculate the initial sorption rate "h" (mg (g min)$^{-1}$), at $t \rightarrow 0$ by using $h = k_2 q_e$. The application of the pseudo-second-order kinetics by plotting t/q_t versus t yields the second order rate constant k_2.

The Elovich model describes a diffusion step controlling the sorption process. It is generally expressed as follows:

$$q_t = 1/\beta \ln(\alpha\beta) + (1/\beta) \ln t \tag{9}$$

where α and β are the Elovich model constants.

Results

Properties of the native and modified algal biomass preparations

The ATR-FTIR spectra of the native and NTA-modified algal biomass and their U(VI) adsorbed counterpart biomasses were measured by an ATR-FTIR spectrometer (Fig. 2a–c, respectively). Bands at between 3400 and 3300 cm^{-1} are observed in the spectrum of the native algal biomass (Fig. 2a). The broad spectrum of native algal biomass between 3400 and 3300 cm^{-1} should be attributed to the overlapping of the –OH and –NH stretching vibration bands. The peaks at 1657 and 1407 cm^{-1} exhibited characteristics of C = O and –CH stretching vibrations and bending of carbonyl and alkane groups on the algal biomass surface, respectively (Fig. 2a). There is an important band at 589 cm^{-1} representing C–N–C scissoring found in a poly-peptide structure of the algal cell biomass. The peaks at 1029 and 866 cm^{-1} representing C–OH stretching vibrations and =C–H bending, respectively, are due to the several functional groups present on the algal biomass surfaces.

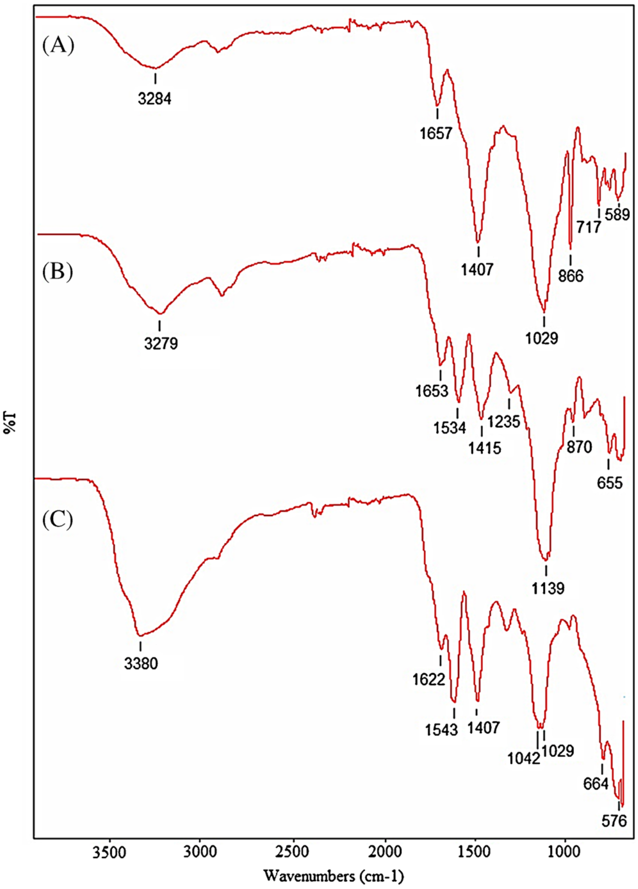

Fig. 2 ATR-FTIR spectra. **a** Native algal biomass. **b** NTA-modified algal biomass. **c** U(VI) ions contacted NTA-modified algal biomass

After covalent modification of algal biomass with NTA ligand via glutaraldehyde coupling reaction, the spectrum of the modified algal biomass shows some changes (Fig. 2b). The changes in the functional groups and surface properties of the algal biomass after modification with NTA ligand are also confirmed by ATR-FTIR spectra. ATR-FTIR spectra of the NTA ligand-modified *B. atropurpurea* biomass confirm the presence of additional carboxyl groups on the modified algal biomass surface and evidence the presence of different characteristic peaks in agreement with the possible presence of hydroxyl, carboxylic, and carbonyl groups. For example, a broad shifted overlapping peak was observed at around 3279 cm^{-1} due to the incorporation of a large number of amine and hydroxyl groups. The presence of absorption peaks in between 1534 and 1139 cm^{-1} also ascertained the incorporation of carboxyl groups on the modified algal biomass. The appearance of new peaks at 1534, 1235 and 1119 cm^{-1} are assigned to N–H bending, C–N stretching and C–O stretching which are due to attached NTA ligand on the algal biomass. In a comparison of the spectra of NTA ligand-modified *B. atropurpurea* biomass with that contacted with U(VI) ions, some shifts in the peak position was observed (Fig. 2c). These changes were due to the interaction of U(VI) ions with carboxyl, amino and hydroxyl groups of the native algal biomass. After interaction of NTA-modified algal biomass with uranyl ions, the most remarkable shifts are observed at around 3450–3000 cm^{-1}, and in the fingerprint region at around 1500–500 cm^{-1} (Fig. 2c). The most remarkable difference among these spectra is at an intensity of 3450–3000 cm^{-1} representing amine and hydroxyl stretching, and the band at around 1622 cm^{-1} represents carbonyl C–O stretching after interaction with uranyl ions. These peaks show the interactions of amine, hydroxyl, and carboxyl groups in the sorption of U(VI) ions. Thus, the FTIR spectra of native and modified algal biomasses revealed that the surface functional groups (such as –COOH, $-NH_2$, and –OH) on the algal biomass preparations are involved in the adsorptive removal of uranium ions.

The determination acidic and basic properties of the native and modified algal biomasses using titration techniques are important due to the involvement of these groups in sorption and bioremediation processes. The acid–base titration studies can produce valuable data for quantitative sorption studies. The amounts of the available total organic acidity of the native and modified algal biomasses were determined by potentiometric titration, as described previously (Bayramoglu and Arica 2016). The total available organic acidity for the native and NTA ligand modified algal biomass was found to be 4.02 and 15.87 mmol g^{-1} dry algal biomass, respectively. After NTA ligand modification, the available carboxyl group content of the algal biomass increased about 3.95-fold compared to the native counterpart.

Electro-kinetic properties of the native and NTA ligand-modified algal biomasses were studied as a function of solution pH (i.e., between 2.0 and 11.0) as reported previously (Arica et al. 2017). The ligand "NTA" as a polycarboxylic acid group was used to increase metal sorption capacity of the algal biomass (Fig. 1). The change in the zeta potential values of the native and modified algal biomasses as a function of suspension medium pH is presented in Fig. 3. As observed in this figure, the zeta potential values for the native and modified algal biomass preparations decreased with increasing solution pH value. It should be noted that the isoelectric point refers to pH value at which zeta potential is zero. The zero zeta potential point values for native and NTA-modified algal biomasses were found to be pH 4.3 and 3.5, respectively. The negative charge density on the native and the NTA-modified algal biomass surface significantly increased with increasing medium pH from 2.0 to 11.0 due to the deprotonation of the carboxyl groups on the algal biomass preparations. The charge density in this pH range changed from − 28.3 to 7.2 mV for native algal biomass. On the other hand, the NTA-modified algal biomass was changed from − 57.6 to 5.9 mV. Note that the zeta potential is also a very important parameter relating to the structure of double electrical layer formed around the adsorbent particles, since it provides information about the ionization state of the functional groups on the sorbent materials, as well as the degree of ionization state and speciation of metal ions.

Effect of contact time on sorption process

The equilibrium sorption time of U(VI) ions on the native and NTA ligand-modified algal biomass from aqueous solution was investigated in a batch system (Fig. 4). The U(VI) ion sorption was found to be a rapid process strictly related to contact time and the saturation levels were obtained after

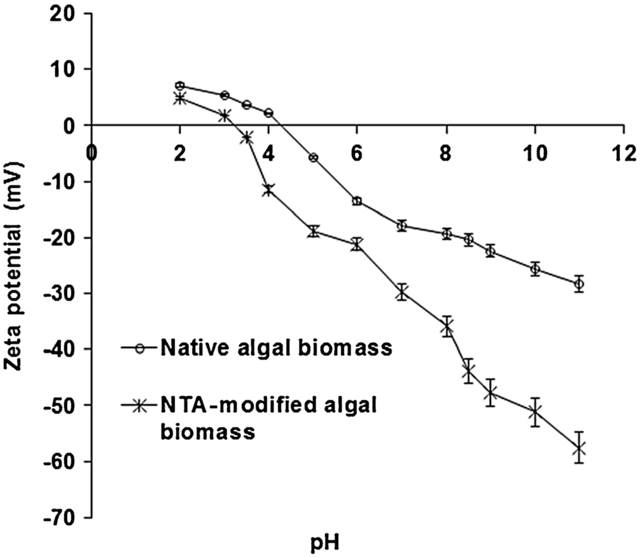

Fig. 3 Zeta potentials of the native algal biomass and NTA-modified algal biomass at different pH values

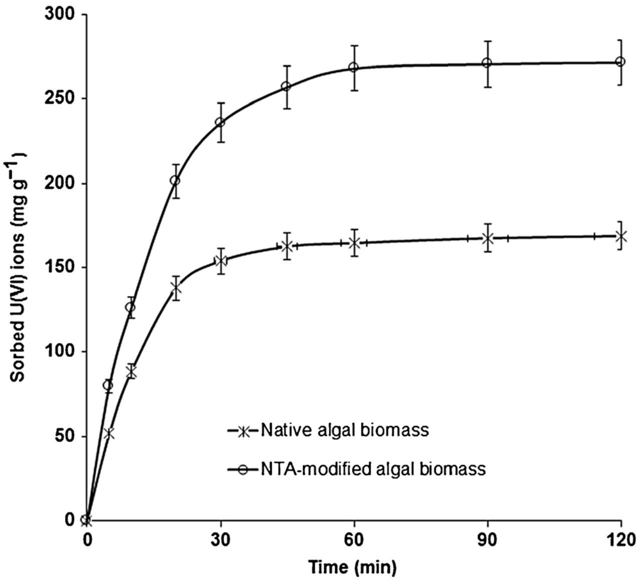

Fig. 4 Effect of contact time on the sorption of the sorption of U(VI) ions algal biomass preparations, (±SD, *n* = 3). Initial concentration of U(VI) 150 mg L^{-1}; amount of biomass 20 mg; volume of the solution 40 mL; temperature 25 °C; pH 5.5; equilibrium time 2.0 h; stirring rate 150 rpm

60 min for both algal biomass preparations. After this period, the amount of adsorbed uranium did not significantly change further with time. Based on this observation, the contact time was used as 120 min for the remaining experiments. The data obtained from the experiments were successfully used further to evaluate the kinetics of the sorption process (Heidari et al. 2017).

Effect of sorbent dosage

The adsorbent dose determines the capacity of an adsorbent for a given initial concentration of metal ions. As can be seen from Fig. 5, the removal of the uranium ions increased when the dosage of algal biomass sample was changed from 0.5 to 3.0 g L^{-1} at a fixed uranium ions concentration (200 mg L^{-1}). As expected, at constant initial concentration of U(VI) ions, increasing the sample dose provides a greater surface area and larger number of sorption sites and hence enhancement of U(VI) ions removal (Bayramoglu et al. 2015). As observed in Fig. 5, the amount of adsorbed U(VI) ions (mg g^{-1}) on the unit mass of the tested sorbent was increased with an increase in adsorbent dose from 0.5 to 3.0 g L^{-1}. On the other hand, the sorption capacity of the sorbent was decreased with increasing biomass dosage. When sorbent dosage was greater than 1.5 g L^{-1}, the amount of adsorbed uranium ions was nearly unchanged. Thus, the amount of U(VI) ions left in the solution came to be very low and an increase in the number of the accessible sites caused enhancement in the percentage of the adsorbed U(VI) ions on the algal biomasses.

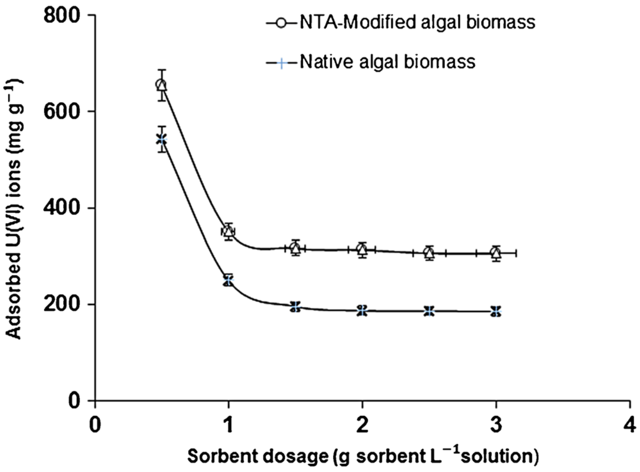

Fig. 5 Effect of sorbent amount on the sorption of U(VI) ions algal biomass preparations, (±SD, *n* = 3). Initial concentration of U(VI) 200 mg L^{-1}; temperature 25 °C; pH 5.5; equilibrium time 2.0 h; stirring rate 150 rpm

Effect of pH on sorption of U(VI) ions on algal biomass preparations

Figure 6 shows the sorption of U(VI) ions at different pH values on the native and NTA-modified algal biomasses. It can be observed that increasing pH from 2.0 to 5.5 had a positive effect on the U(VI) ion sorption capacity for both tested algal biomass. The amount of adsorbed U(VI) ions at equilibrium increased from 68.8 to 168.7 and 91.6 to 271.3 mg g^{-1} for native and modified algal biomasses, respectively, when the pH was increased from 2.0 to 5.5. The UO_2^{2+} ions tend to predominate at pH values below 5.0. In the pH range 5.0–6.0, other cationic species (such as $(UO_2)_3(OH)_5^+$,

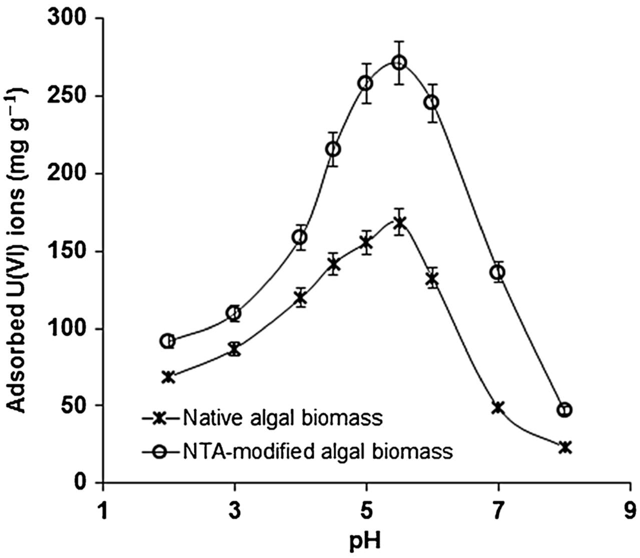

Fig. 6 Effect of pH on the sorption of U(VI) ions algal biomass preparations, (±SD, *n* = 3). Initial concentration of U(VI) 150 mg L^{-1}; amount of biomass 20 mg; volume of the solution 40 mL; temperature: 25 °C; equilibrium time 2.0 h; stirring rate 150 rpm

$(UO_2)_2(OH)_2^{2+}$, and $[(UO_2)_3(OH)]_5^{2+}$ are predominantly found (Krestou 2004; Bayramoglu and Arica 2016; Bagda et al. 2017).

Effect of ionic strength on sorption of U(VI) ions

As presented in Fig. 7, the sorption efficiency decreased with increasing ionic strength of the solutions for both algal biomass preparations. The U(VI) ions sorption capacities of the native and NTA ligand-modified algal biomass decreased 2.3- and 2.9-fold when the NaCl concentration in the sorption medium was 1.0 mol L^{-1}. Thus, the uranyl ions adsorption capacity by both algal biomass preparations decreased significantly with an increasing salt concentration in the solution. The NaCl concentration had a significant effect on the sorption of U(VI) ions. Similar results are reported by others (He et al. 2014; Bayramoglu et al. 2015; 2017).

Effect of initial uranium ion concentrations

The sorption capacities of the native and modified algal biomasses are shown in Fig. 8 as a function of the initial concentrations of U(VI) ions within the solution. The sorption capacity of both algal biomass preparations increased firstly with increasing the initial concentrations of U(VI) ions and reached a saturation values of 250 mg L^{-1}. As can be seen from the figure, the sorption of U(VI) ions at different concentrations between 10 and 200 mg L^{-1} linearly increased and then reached a plateau value at around 250 mg L^{-1}. As can be seen from the figure, the uranium ion adsorption capacity by both native and modified algal biomasses increased significantly with an increasing initial U(VI) ion concentration. Thus, as reported earlier, the initial U(VI) ion concentration had a significant effect on the sorption process (Bagda et al. 2017; Bayramoglu et al. 2015; He et al. 2014).

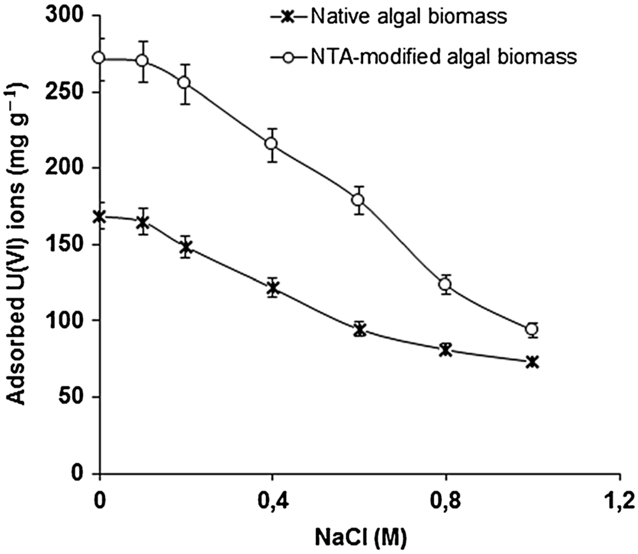

Fig. 7 Effect of ionic strength on the sorption of U(VI) ions algal biomass preparations, (±SD, $n = 3$). Initial concentration of U(VI) 150 mg L^{-1}; amount of biomass 20 mg; volume of the solution 40 mL; temperature 25 °C; pH 5.5; equilibrium time 2.0 h; stirring rate 150 rpm

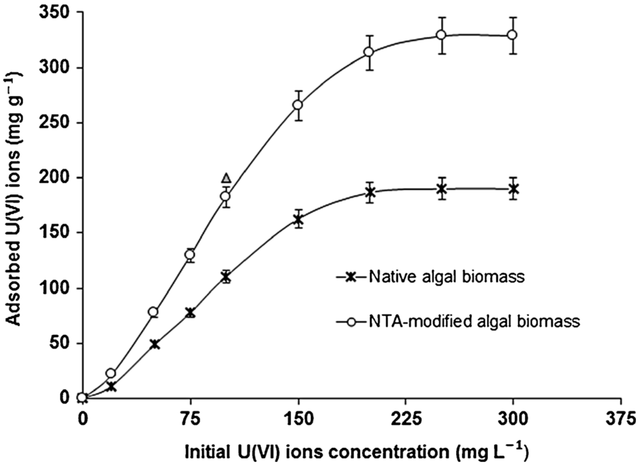

Fig. 8 Effect of initial U(VI) concentration on the sorption capacity of algal biomass preparations, (±SD, $n = 3$). pH 5.5; amount of biomass 20 mg; volume of the solution 40 mL; temperature 25 °C; equilibrium time 2.0 h; stirring rate 150 rpm

The effect of the presence of other cations on the sorption efficiency

The presence of various cations with different valances (i.e., Na, K, Ca(II), Mg(II), or Fe(III) ions) on the uranium ion removal efficiency of algal biomass preparations was studied in binary system using chloride salts of all the tested cations (Fig. 9). As can be seen from the figure, the effect of Na, K, Ca(II), and Mg(II) cations on the sorption of uranium ions, was minimal under the given experimental conditions: Note that these cations are present in high concentrations in wastewaters. On the other

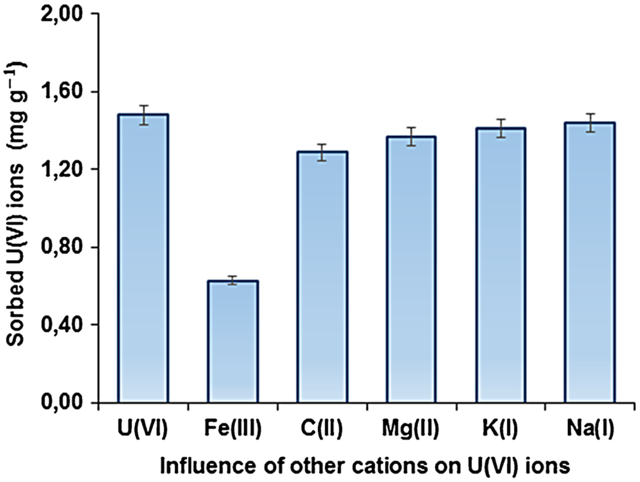

Fig. 9 Influence of presence other cationic species on the sorption efficiency of U(VI) ions (±SD, $n = 3$). Initial concentration of U(VI) 2.0 mmol L^{-1}; amount of biomass 20 mg; volume of the solution 40 mL; temperature 25 °C; pH 5.5; equilibrium time 2.0 h; stirring rate 150 rpm

hand, the presence of Fe(III) cations had a stronger influence on the sorption of U(VI) ions than those of the other tested cations on both algal biomass preparations. The maximum adsorption of iron, uranium, calcium, magnesium, potassium, and sodium onto both algal biomass preparations were determined from the binary mixture and was found to be in the following order: Fe(III) > U(VI) ≫ Ca(II) > Mg(II) > K(I) > Na(I)).

Desorption studies

The use of an adsorbent in wastewater treatment depends not only on the adsorptive capacity but also on how well the adsorbent can be regenerated and reused (Bayramoglu and Arica 2011). Reusability of the native and NTA ligand-modified algal biomass preparations was studied by repeating of sorption–desorption cycles six times using the same adsorbent. After each cycle of sorption–desorption, the adsorbent preparation was washed with 0.1 mol L^{-1} NaCl solution and transferred into fresh uranium ion solution for sorption in the succeeding cycle. The sorption capacities decreased slowly with the number of cycles (data not shown). Additionally, the NTA ligand-modified algal biomass was repeatedly used for sorption and desorption of U(VI) ions, and it was observed that more than 86% sorption capability was maintained after six cycles. It should be noted that the decrease in the sorption capacity of the sorbents could be due to the loss of some functional groups from biomass surface during acid washing process.

Discussion

Modification of biomass surface with various functional groups is a promising strategy for the increase of the metal ion adsorption capacity (Bayramoglu and Arica 2016; Bayramoglu and Arica 2017). In fact, surface metal ion adsorption capacity cannot only be increased but also the adsorbed metal ions can be recovered easily from the modified biomass surface by a suitable eluent under mild desorption conditions. Modification of biomass surface with desired metal chelating ligands could also provide cheap sorbents and can be readily used for the environmental cleanup of metal ion pollution. Additionally, these modified sorbents could not create an environmental pollution problem compared with the resin obtained from petroleum origin. Thus, modification of biomass surface with different ligands could provide to design a desired biosorbent with metal recognition ability and binding specificity (Bayramoglu et al. 2015). In a sorption process, parameters like the contact time, sorbent dosage, temperature, pH, ionic strength, initial concentration of metal ions, and existence of other ions (which may compete with the ions of interest for the active adsorption sites) in the sorption medium may affect the sorption rate and capacity of the sorbent (Bayramoglu and Arica 2009; Cheng et al. 2017). As can be seen from Fig. 4, the adsorption efficiency increased with time until they reached equilibrium at about 60 min, and more than 90% U(VI) ions were adsorbed with 30 min. The adsorption efficiency of the modified algae was higher than that of the native counterpart.

The adsorption efficiency of both algal biomass preparation was also affected by the tested biomass dosage (Fig. 5). The adsorption efficiency decreased from 542.9 to 184.8 mg g^{-1} and from 654.1 to 305.5 mg g^{-1} for the native and modified algal preparation as the dosage increased from 0.5 to 3.0 g L^{-1}. This can be due to an increase in the number of adsorption sites as the biomass dosage increases in the adsorption medium, and the decrease in unit adsorption is basically due to the interactive sites that remain unsaturated during the adsorption process (Bayramoglu and Arica 2017). Similar observations were also reported by other researchers (He et al. 2014; Cheng et al. 2017).

The pH of the solution can be considered an important factor affecting heavy metal pollutants due to its impact on the solubility and speciation of metal ions in solution and the surface charge variation of the adsorbent materials. With the increase in pH from 2.0 to 5.5, U(VI) ion sorption increased and the maximum adsorption was observed at pH 5.5 for both tested algal biomass preparations. The adsorption capacity of the modified algal biomass was higher than that of the native biomass all of the tested pH values. For the modification of algal biomass the ligand (i.e., nitrilotriacetic acid, NTA) was covalently coupled on the algal biomass surface via glutaraldehyde coupling. It is an aminopolycarboxylic acid ligand. The ligand has a high affinity to various divalent and trivalent metal ions (such as Ni(II), Cu(II), Pb(II), Fe(III), Ca(II), and U(VI)). The NTA ligand has three carboxyl and an amine group on its molecular structure, and these functional groups can interact with metal ions via ion exchange and/or complexation. For the development of a novel adsorbent, surface modification with functional groups carrying a ligand molecule has been confirmed to be an efficient method (Arica et al. 2017). In this framework, the aminobutyl–NTA ligand was used for surface functionalization of *B. atropurpurea* biomass. It is a freshwater red algae with filaments of multi-seriate structure at maturity. As observed in Fig. 6, a significant increase in the amount of adsorbed uranium ions was observed between pH 2.0 and 5.5 for both algal biomass preparations, and they reached a maximum sorption capacity at pH 5.5. This observation should be due to the electrostatic attractions between these positively charged uranyl ions and the negatively charged native and NTA-modified algal biomass. It should be noted that carboxylic acids have a high affinity for metallic oxides; therefore, the polycarboxyl groups carrying NTA ligand was introduced on the algal biomass surfaces. In this system, the U–OH interact with the carboxylic acid groups of the algal biomass preparations via acid–base interaction yielding U–O–C species with the elimination of H_2O. Additionally, significant decrease in the sorption capacities of the algal biomass preparations for uranium ion at above pH 5.5 could be due to the formation of negatively charged anionic uranyl species such as $(UO_2)_3(OH)_8^{2-}$ and $UO_2(CO_3)^{3-}$ tend to be significant and possibly $[(UO_2)_3(CO_3)^{6-}]$ (Krestou 2004; Bagda et al. 2017). The amount of adsorbed uranium ions on algal biomass preparations should be affected by the chemical state of the uranyl ions in the aqueous solution, and the total charge produced on the surface of the given adsorbents at the studied pH value. At pH 5.5, the uranyl ion species were positively charged, whereas the algal biomass preparations have net negative charge due to the deprotonation of acidic groups (such as carboxyl and phosphate groups) (Liu et al. 2013; Bayramoglu and Arica 2017). These observations are in agreement with previous reports (Bai et al. 2010; He et al. 2014; Asnaoui et al. 2015; Bagda et al. 2017).

Wastewater effluent contains a notable amount of salt which may influence the removal of metals from solutions. Therefore, the effect of ionic strength on U(VI) ion sorption was studied with both algal biomasses. The reduction of the sorption capacity in the presence of NaCl was more pronounced for the NTA ligand-modified algal biomass. The addition of Na^+ and Cl^- ions in the solution can screen the charged sites of the adsorbent preparations and the electric double layers of the adsorbent surface are compressed, leading to a reduction in the electrostatic interactions and, accordingly, resulting in a change in the amount of the uranyl ions adsorbed (Bayramoglu et al. 2015). Therefore, the medium ionic strength is increased, repulsive electrostatic interaction between U(VI) ions and carboxyl functionality of the modified algal biomass surface become dominant. In addition, Rustemier and Killmann (1997) reported that with increasing electrolyte concentration in the medium, the surface charge is screened. Those effects influence the electrostatic interactions between the sorbate and sorbent complex on the surface (Bayramoglu and Arica 2009). Thus, the significant decrease of the binding capacity of the U(VI) ions resulting from the increase of ionic strength could be attributed to the interactions between salt ions and U(VI) and between salt ions and sorbents (Das et al. 2015).

Initial U(VI) ion concentration provides an important driving force to overcome all mass transfer resistance of the metal ions between the aqueous and solid phases. The amounts of uranium adsorbed on the native and NTA-modified algal biomass preparations were found to be 190.2 and 328.8 mg g^{-1}, respectively, under the optimum batch conditions. The modification of algal biomass with NTA ligand leaded in increase in the sorption capacities about 1.72-fold. This can be due to the driving force to overcome the resistance to the mass transfer of U(VI) ions between the aqueous and solid phase, and thus, increased the metal ions sorption. In addition, increasing initial U(VI) ions concentration also increased the number of collisions between metal ions and sorbent, which enhances the sorption process. Thus, the amount of U(VI) ions adsorbed per gram of algal biomass preparation increased with increasing of initial U(VI) ions concentration (Katsoyiannis 2007; He et al. 2014; Espinosa-Ortiz et al. 2016; Ji et al. 2017; Bayramoglu and Arica 2017).

Modeling the sorption isotherm data is essential for predicting and comparing the adsorption performance, which is critical for optimization of the adsorption mechanism pathways, and expression of the adsorbents capacities. Therefore, four isotherm models, i.e., Langmuir, Freundlich, D–R, and Temkin equations, were employed for the analysis of the experimental data. For the solid–liquid systems, the equilibrium of sorption is one of important physical–chemical aspects in the description of sorption behavior. The isotherm model plots are presented for native and modified algal biomass preparations in Fig. S1 and S2, respectively. The isotherm model parameters are determined and presented in Table 1. The higher correlation coefficients of the Langmuir model than those of the Freundlich, D–R, and Temkin equations reveal that the sorption data can be better described by the Langmuir model (Table 1). The monolayer sorption capacities of the native and NTA-

Table 1 Sorption isotherm model constants and correlation coefficients for U(VI) ions on the native and NTA-modified algal biomass preparations

	Sorbents	Model parameters			
		q_{max} (mg g^{-1})	b × 10^3 (L mg^{-1})	R^2	
Langmuir	Native algal biomass	197.1	13.9	0.998	
	NTA-algal Biomass	359.6	49.6	0.994	
		K_F	n	R^2	
Freundlich	Native algal biomass	37.3	1.97	0.822	
	NTA-algal Biomass	26.1	3.22	0.967	
		q_D (mg g^{-1})	$B_D \times 10^3$	R^2	E (kJ mol^{-1})
D–R	Native algal biomass	227.5	2.10	0.987	15.4
	NTA-algal Biomass	233.2	2.86	0.935	26.2
		Q_T (mg g^{-1})	b_T (L mg^{-1})	R^2	
Temkin	Native algal biomass	37.1	15.0	0.961	
	NTA-algal Biomass	71.2	19.3	0.978	

modified algal biomass were calculated from the Langmuir model as 197.1 and 359.6 mg g^{-1}, respectively. The calculated maximum sorption capacity (q_{max} values) of the algal biomass preparations was found to be close compared with the experimental sorption capacity (q_{exp}) values for U(VI) ions. Therefore, the Langmuir isotherm model is suitable to describe the sorption of uranium ions on both algal biomass preparations. As shown in Table 1, values of b were 49.6 L g^{-1} for the modified algal biomass, which was significantly higher than that of the native algal biomass (13.9 L g^{-1}). For the Freundlich model, the magnitude of K_F and n values showed easy uptake of U(VI) ions from aqueous medium with a high sorption capacity of the native and modified algal biomass preparations. Values of $n > 1$ for uranyl ions at 25 °C indicate positive cooperativity in binding and a heterogeneous nature of sorption (Table 1). D–R isotherm was also applied to plots of equilibrium sorption data for the native and modified algal biomasses. Values of D–R constants, q_D and B_D, for the sorption of U(VI) ions on the native and modified algal biomass surfaces calculated from the intercept and slope of the plots are presented in Table 1. Analysis by the D–R model can provide the mean energy of sorption (E). The value of E gives information about the sorption mechanisms: sorption can be described as a physical process when E is between 0.0 and 8.0 kJ mol^{-1} and as a chemical process when E is more than 8 kJ mol^{-1}. The calculated D–R constants and the mean free energy of sorption are shown in Table 1. The E values obtained in the analysis were 15.4 and 26.2 kJ mol^{-1} for native and modified algal biomass, respectively (Table 1). These values are within the energy range of chemical sorption reactions. For the Temkin model, the semi-logarithmic plot of $\ln C$ versus q was employed to generate the intercept value of $\ln K_T$ and the slope q_T. The Temkin constants for sorption of U(VI) ions on the native and modified algal biomasses are presented in Table 1. The correlation coefficient of the model (R^2) for the native and modified algal biomasses was found to be 0.961 and 0.978 for the U(VI) ions, respectively. In Temkin model, the sorption heat of the molecules decreases linearly with the coverage of the surface of the adsorbent owing to existing interactions, and the values of the constants are given in Table 1.

The constants of pseudo-first-order, pseudo-second-order, and Elovich equations were calculated from experimental data and presented in Table 2. As seen in this table, the correlation coefficients (R^2) obtained from the pseudo-second-order model were found to be above 0.987 for the algal biomass preparations making them larger than those of the pseudo-first-order and Elovich models (Ho and McKay 2002). The results obtained from the pseudo-second-order model described the best among applied the models. The calculated sorption capacities (q_{eq}) using the pseudo-second-order model agreed with the corresponding experimental sorption capacities of the algal biomass preparations (Table 2).

The temperature of the sorption medium could be important for energy dependent mechanisms in pollutant removal by algal biomass preparations. Energy-independent mechanisms are less likely to be affected by temperature since the processes responsible for sorption are largely physico-chemical in nature. The sorption of uranium by the native and NTA-modified algal biomasses appears to be temperature dependent (from 15 to 45 °C) and the maximum binding capacity values were increased as the temperature increase indicating the process was endothermic in nature for both algal biomass preparations (Table 3). The reason for the increase in uranium sorption on the used adsorbents at high temperatures could be attributed to increase in the interaction between uranyl ion species and functional groups on the sorbent surfaces because of an increase in the energy of the system.

The following equations have been used to determine the thermodynamic parameters such as enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS).

$$\Delta G = -RT \ln K_a \tag{10}$$

$$\ln K_a = -\Delta G/RT = -\Delta H/RT + \Delta S/R \tag{11}$$

where R is the gas constant (8.314 J mol K^{-1}), T represents the absolute temperature (K), and K_a ($b = K_a$) is the association

Table 2 Kinetic parameters for sorption of U(VI) on the native and NTA-modified algal biomass preparations

	Sorbents	Model parameters				
		$q_{e,exp.}$ (mg g^{-1})	$q_{e,\ cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	
First-order	Native algal biomass	190.2	81.1	70.3	0.987	
	NTA-algal biomass	328.8	224.8	115.2	0.978	
		$q_{e,exp.}$ (mg g^{-1})	$q_{e,\ cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	h × 10^{-2} (g mg^{-1} min^{-1})	R^2
Second-order	Native algal biomass	190.2	196.2	14.3	0.55	0.997
	NTA-algal biomass	328.8	348.8	18.4	0.56	0.987
			A (mg g^{-1} min^{-1})	b × 10^2 (g mg^{-1})	R^2	
Elovich	Native algal biomass		0.45	3.60	0.886	
	NTA-algal Biomass		0.97	6.70	0.931	

K_a = sorbed U(VI) ions on the sorbents at equilibrium (mg g^{-1}) /U(VI) concentration in solution at equilibrium (mg L^{-1})

Table 3 The distribution and sorption constants and the thermodynamic parameters for U(VI) ions sorption on the native and NTA-modified algal biomasses at different temperatures

Sorbents	T(K)	q_{exp} (mg g^{-1})	$K_a \times 10^{-3}$ (M^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
Native algal biomass	288	177.4	5.24	−20.5		
	298	190.2	13.0	−23.4	71.8	0.320
	308	195.3	27.8	−26.2		
	318	198.6	94.7	−30.3		
NTA-algal biomass	288	287.6	3.4	−35.5		
	298	328.8	6.2	−39.8	61.4	0.338
	308	350.4	9.3	−42.4		
	318	357.6	11.7	−45.6		

coefficient which can be calculated by using Langmuir Eq. (3). The values of ΔH^{o} and ΔS^{o} were determined from the slope and intercept of the van't Hoff plot of ln K_a versus $1/T$. The values of the thermodynamic parameters are presented in Table 3. The negative values of ΔG suggested that the sorption process was spontaneous, and the decreasing of ΔG with the increasing of temperature indicated that the sorption was more favorable at high temperatures. The positive values of ΔH^{o} confirmed the endothermic process for the sorption of U(VI) ions, consistent with the increase of sorption capacity as temperature increased. The positive value of ΔS^{o} suggested that the increasing randomness between the solid/solution interface during the sorption process.

The biomass preparation of *B. atropurpurea* had great ability to remove metal ions from aqueous solution, similar to other algal species reported (He et al. 2014; Bayramoglu et al. 2015; 2017). As reported earlier, the different affinity may be caused by the physical properties of metal ions, including ionic radius, electron configuration, electronegativity, and charge density (Liu et al. 2013). The surface of the algal biomass preparations has weak acidic groups, such as carboxyl, phosphate, carbonyl and hydroxyl, and the alkali metal ions can interact very little or no significant sorption interference with these groups. Therefore, the tested alkali metal ions did not significantly affect the sorption of U(VI) ions by algal biomass preparations (Bayramoglu et al. 2015). On the other hand, Fe(III) metal ions show high affinity to oxygen rich compounds (Pearson 1963). Thus, the presence of Fe(III) cations showed detrimental effect on the removal efficiency of the uranium ions on the algal biomass preparations (Fig. 9). According to the theory of hard and soft acids and bases defined by Pearson, the oxygen atoms of the carboxyl and phosphate groups on the algal biomass preparations can be classified as hard bases. These atoms coordinate preferentially with metal ions classified as hard acids such as Fe(III) cations. This explains why the algal biomass preparations had higher affinity for the used trivalent Fe(III) ions compared with U(VI) ions.

In conclusion, preparation of novel adsorbent materials is a key factor for applying sorption-based technologies designed to removal of metals and toxic organic compounds. In this study, the uranium (VI) sorption capacity of the NTA ligand-modified algal biomass was characterized and compared with data obtained for native counterpart. ATR-FTIR analysis indicated that several surface groups of algal biomass preparations were involved in the U(VI) ions sorption. The presented method could be used to modify other natural and synthetic materials. The sorption data showed that the U(VI) sorption capacity of the NTA-modified algal biomass presented a higher U(VI) removal performance. The result of sorption isotherms was suitable by Langmuir isotherm model and the sorption kinetic follows pseudo-second-order kinetic model which suggests a chemical sorption process. In particular, the NTA modified algal biomass could be used as an efficient sorbent system for the treatment of metal and organic pollutants containing wastewater. In the binary system, the presence of Fe(III) had a stronger influence on uranium sorption than those of the presence of other cations. The strong sorption site for Fe(III) ions likely involves interactions with polycarboxylate groups of the NTA ligand. Presumably, the larger ionic radii of U(VI) ions can allow for such interactions, as opposed to a smaller Fe(III) ions suggesting. Finally, the modified algal biomass can be successfully used in separation and pre-concentration processes of many pollutants and in the treatment of industrial effluents containing U(VI) ions.

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