Adsorption of uranium(VI) onto *Ulva sp.***-sepiolite composite**

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Ulva sp. and sepiolite were used to prepare composite adsorbent. The adsorption of uranium(VI) from aqueous solutions onto *Ulva sp.*-sepiolite has been studied by using a batch adsorber. The parameters that affect the uranium(VI) adsorption, such as solution pH, initial uranium(VI) concentration, and temperature, have been investigated and the optimum conditions determined. The adsorption patterns of uranium on the composite adsorbent followed the Freundlich and Dubinin–Radushkevich (D–R) isotherms. The Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) models have been applied and the data correlate well with Freundlich model. The sorption is physical in nature (sorption energy, *E* = 4.01 kJ*/*mol). The thermodynamic parameters such as variation of enthalpy ∆*H*, variation of entropy ∆*S* and variation of Gibbs free energy ∆*G* were calculated from the slope and intercept of ln*K_d* vs. 1/*T* plots. Thermodynamic parameters ($\Delta H_{ads} = -22.17$ kJ/mol, $\Delta S_{ads} = -17.47$ J/mol·K, ∆*G*°*ads* (298.15 K) = –16*.*96 kJ*/*mol) show the exothermic heat of adsorption and the feasibility of the process. The results suggested that the *Ulva sp-*sepiolite composite adsorbent is suitable as a sorbent material for recovery and biosorption/adsorption of uranium ions from aqueous solutions.

Introduction

Uranium, a toxic and weak radioactive heavy metal, is relatively widespread in the environment, and as a naturally occurring element it is found at low levels in all rocks, soils and waters.¹ Uranium usually occurs in the hexavalent form as a mobile, hydrated uranyl ion. In developing adsorption techniques for uranium(VI), preconcentration are important, because uranium(VI) plays a role in many nuclear industrial application procedures for waste disposal.2 Uranium adsorption on various solids is important from the purification, environmental and radioactive waste disposal viewpoints.3 Although a large number of studies on uranium adsorption on various adsorbents have been reported $4-9$ only a few of them addressed adsorption kinetics.²

Sepiolite $(Mg_4Si_6O_{15}(OH)_2.6H_2O)$ is a natural clay mineral with formula of magnesium hydro-silicate. Most of the world sepiolite reserves are in Turkey. The special type of sepiolite which is called 'Lületaşı' is used for hand-crafted souvenirs, such as tobacco pipes, chessman and necklaces because of its softness and whiteness. Sepiolite is a natural hydrated magnesium silicate with a wide range of industrial applications derived mainly from its sorptive properties.10 Sepiolite is known to contain a continuous two dimensional tetrahedral sheet but differs from other tetrahedral-octahedral-tetrahedral (T-O-T) layer silicates in lacking continuous octahedral sheets. The tetrahedral basal oxygen atoms invert apical direction at regular intervals coordinating talc-like ribbons. Each talc-like ribbon alternates with channels along the fiber axis. Magnesium fills 90–100% of the octahedral positions.11

The unique fibrous structure allows the penetration of organic and inorganic ions into the structure of sepiolite. Naturally occurring low cost sepiolite as an ion-exchanger, it offers great potential for removing lead from industrial wastewater. Several works related to wastewater treatment using sepiolite have been performed.12 The interaction between some heavy metals including lead and sepiolite has been studied in order to verify the heavy-metal cation sorptiondesorption rates.13 The sorption capacity of sepiolite is restricted to the external surface, which can be enhanced, by chemical¹⁴ and heat treatment.¹⁵ The enhanced surface area of sepiolite is given in the range of 263–350 m²/g in the literature.^{13,16,17}

Biosorption, the process of passive cation binding by dead or living biomass, represents a potentially costeffective way of removing toxic metals from industrial wastewaters.18 Biosorbent may be used as an ionexchange material.19 Researchers typically utilize dead organisms so that the metal uptake is only due to adsorption onto the algae through interactions with the chemical functional groups found on the cell wall. The biosorption of uranium and other radionuclides by algae has received attention. It seems that physicochemical interactions comprise the majority of total uptake. Adsorption occurs through interaction of the metal ions with functional groups that are found in the cell wall biopolymers of either living or dead organisms.20 The cell wall of algal cells is surrounded by a porous threedimensional macromolecular network. Important cell wall components are: peptydoglycan, teichuronic acid, teichoic acid, polysaccharides and proteins,²¹ which display mainly carboxylic, hydroxyl and phosphate groups.22 Most of these molecules are polyelectrolytes that carry charged groups, such as carboxyl, phosphate,

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hydroxyl or amine.²³ Both clays and fungal biomass have been investigated due to their properties to sorb toxic metals. However, most studies have concentrated on the uptake of metals by either clay minerals or microbial biomass as individual and separate entities.24–31 Only a few studies have been carried out on the sorption properties of mixtures of clay minerals (montmorillonite, kaolinite) and microbial biomass (algae, fungi). $32-34$

In this study, the green macro marine algae, *Ulva sp.* in its natural form and sepiolite were used to prepare a composite adsorbent. The ability of the composite to adsorp uranium in solution was shown as a function of some experimental parameters. Different adsorption isotherms and thermodynamic parameters have been investigated. *Ulva sp.*–sepiolite composite adsorbent is a suitable enhanced barrier material which could effectively prevent migration of very low activity uranium radionuclide. The biosorption/adsorption process based on this composite represent a possible alternative to the conventional uranium separation processes and sites with composite adsorbent suitable as enhanced barrier materials can be considered for future disposal sites for conditioned sludges wastes containing low level radioactive uranium radionuclide only.

Experimental

Chemicals and characterization of sepiolite

The reagents used in the experiments were of analytical reagent (AR) grade (Merck). Distilled water (Millipore Ultra Pure Water System) was used in overall investigations. A solution of 1000 mg/L of uranium was prepared from $UO_2(NO_3)_2$ 6H₂O (Merck) by dissolving the salt in pure distilled water. The stock solution was diluted to prepare working solutions. More diluted solutions were prepared daily as required. The buffer solutions (pH 4, 7 and 9) were used to calibrate the pHmeter. The pH of each test solution was adjusted to the required value with diluted HNO_3 and Na_2CO_3 solutions at the start of the experiment. Reagent blanks were run for every sample solution. Buffering was not used due to unknown effects of buffer compounds on adsorption.

The sample of *Ulva sp*., a species of green marine macro algae (seaweed)*,* was collected by hand from Aegean Sea in Izmir Bay (Turkey) at the depth of 1.0–1.5 m. For the sorption studies, harvested fresh macroalgae samples were rinsed with tap water, washed extensively with distilled water to remove the salts (sodium, potassium, magnesium and calcium) and then

inactivated in an oven at 90 °C for 24 hours. The dry biomass was ground and sieved using the British Standard 120, standard mesh (<125 µm) sieve. This biomass sample was stored in polypropylene container in a desiccator and used to prepare the composite adsorbent.

A commercial sample of the natural sepiolite used in this study was obtained from Eskişehir in Turkey. Sepiolite was washed thoroughly with double distilled water to remove the dirt and other foreign matter. Sepiolite was dry-sieved under open laboratory conditions using the British Standard 120, standard mesh $(\leq 125 \text{ }\mu\text{m})$ sieve and stored in a polypropylene container in a desiccator.

Sepiolite was characterized by X-ray florescence spectrophometry (XRF) and chemical analysis. Chemical composition of sepiolite sample was determined by the usual analytical methods for silicate materials. Chemical analysis: standard wet chemical analysis along with instrumental methods was adopted.³⁵ Al₂O₃, Fe₂O₃, CaO and MgO were analyzed with titrimetric, and $\overline{SiO_2}$ was analyzed with gravimetric methods. Na₂O and $\overline{K_2O}$ were found out by flame photometry. The results of the chemical analyses are presented in Table 1.

The green macro marine algae (seaweed), *Ulva sp*., and clay sepiolite were used to prepare as a composite adsorbent for the biosorptive-adsorptive uranium uptake experiments as described below.

Dry biomass powder (*Ulva sp.*) was mixed with sepiolite at different mole fractions. The mixtures were wetted with pure distilled water and thoroughly mixed. After mixing, the pastes were heated in an oven at 105 ± 5 °C for 6 hours to dry the mixtures. The wetting and drying step were repeated to maximize contact between *Ulva sp.* and sepiolite, thereby improving the composite efficiency. Then the composite of *Ulva sp.*– sepiolite briquette was broken, sieved through \leq 125 µm sieve. The composite was then dried in an electric oven at 105 °C for several hours before using for adsorption purpose and the powder was stored at desiccator.

Uranium(VI) concentrations were determined by UV-Vis spectrophotometer (Shimadzu UV-Vis 1601 Model). The adsorption experiments have been studied by batch technique using a thermostated shaker bath Nüve ST402 Model. The pH of all solution was measured by WTW microprocessor Model pH meter. A Hettich Zentrifügen Universal 16A Model digital centrifuge was used to centrifuge the samples. An Electro-Mag M420 Model oven was used to dry the samples.

Table 1. Chemical analysis of the sepiolite sample (in weight%)

\sim \sim ^∪اد	v TV	H_{max} College	CaO	MgC	า∪ 1.9077 --	nC. $\overline{}$	MnO ₁	m. 11O ²	\bigcap * ⊷
$^{\circ}$ 56.9 . .	.085	0.043	1.40	\sim \sim \sim ن ڪي <u>_</u>	010 U.U.L	0.013	0.0021	0.008	\sim \sim \sim 13.DU

* LOI: Loss of ignition.

Batch experiments

All the adsorption experiments were performed using the composite adsorbent. The prepared composite adsorbent (0.1 g) was suspended in 10 cm³ of $[UO₂(NO₃)₂·6H₂O]$ uranium solution in an polyethylene (PE) flask at selected pH. The flasks were shaken at different temperature for various mixing time. The solution was separated from the solids by centrifugation (5 min at 3500 rpm). Then the residual uranium(VI) ions in aqueous solution were determined spectrophotometrically using TOPO-DBM (trioctyl phosphine oxide and di-benzoyl methane) method at 405 nm using a spectrophotometer.36,37 The amount of adsorbed uranium(VI) was calculated from the difference of the uranium concentration in aqueous solution before and after adsorption. The percent adsorption and distribution constant (K_d) were calculated using the following equations:

$$
\text{Adsorption} \left(\frac{\%}{\text{O}} \right) = \frac{C_i - C_f}{C_i} \times 100 \tag{1}
$$

where C_i and C_f are the concentrations of the metal ions in the initial and final solutions, respectively,

$$
K_d = \frac{\text{Amount of metal in adsorbent}}{\text{Amount of metal in solution}} \cdot \frac{V}{m} \text{ cm}^3/\text{g} \tag{2}
$$

where *V* is the volume of the solution (cm³), *m* is the weight of the adsorbent (g).

Results and discussion

The sorption ability of clay minerals has been thoroughly investigated by several researches. There are many factors that effect the adsorbability of dissolved element including the chemical form of metal, solution pH, time of contact, metal concentration, the presence of competing adsorbates, the amount of sorbent, organic matter, temperatures, particle size and others.^{10,11,38} The ability of composite adsorbent to adsorp metal ions from aqueous solution has been studied at different optimized conditions of pH, concentration of uranium(VI) ions and different temperature. Various adsorption parameters for the effective removal of uranium by using composite adsorbent from aqueous solutions were studied and optimized.

Effect of mixing ratio of Ulva sp. and sepiolite to prepare composite adsorbent

To study the effect of mixing ratio of the components of composite adsorbent on the uranium adsorption, composite adsorbents with various compositions were prepared. The batch adsorption studies were carried out by the prepared composite adsorbents of different mixing ratios. According to the results, the adsorption of uranium as a function of mixing ratio (m/m) is plotted. The adsorption yield $(\%)$ and K_d values are shown in Fig. 1. It was observed that in samples with high *Ulva sp.* content, the amount of adsorbed uranium and K_d were increased. *Ulva sp.*– sepiolite mixing ratio was selected as 1/4 for further experiments.

Effect of the initial pH

In order to establish the effect of pH on the sorption of UO_2^{2+} ions onto composite adsorbent, the batch sorption studies at different pH values were repeated in the range of 2.0–5.0. Figure 2 shows the effect of pH on sorption. As can be seen from the figure, the maximum adsorption of UO_2^{2+} ions on the composite adsorbent was observed at pH 4.5. As seen in Fig. 2, the adsorption of uranium decreases from 84.7 to 82.3% with an increase in pH of the solution from 2.5 to 3.5 and then increases to 85.7% at pH 4.5. The composite adsorbent has a maximum sorption at pH 4.5.

Various hydroxo complexes of uranium may form when the pH increases from an acidic value to a neutral value. The relative proportion of these species is determined by the pH and total uranium concentration. Repartition of the hydroxo complexes is determined by the following equilibrium:39

 $UO_2^{2+} + 2H_2O \leftrightarrow UO_2(OH)^{+} + H_3O^{+}$ (pK: 5.8) $2UO_2^{2+} + 4H_2O \leftrightarrow (UO_2)_2(OH)_2^{2+} + 2H_3O^+$ (pK: 5.62) $3\text{UO}_2^{2+} + 10\text{H}_2\text{O} \leftrightarrow (\text{UO}_2)^2 + (\text{OH})_5^{2+} + 5\text{H}_3\text{O}^+$ (pK: 15.63)

Fig. 1. Effect of *Ulva sp.*–sepiolite mixing ratio (*m*/*m*) on the adsorption of uranium (U concentration: 200 µg/cm³, pH: 3.0, *T*: 30 °C, contact time: 24 h, *m*: 0.1 g, *V*: 10 cm3)

Fig. 2. Effect of pH on adsorption of U(VI) on the composite adsorbent ([U]: 100 μ g/cm³), *m*: 0.1 g, *V*: 10 cm³, *t*: 24 h, *T*: 30 °C)

The uranium biosorption mechanism was affected by the solution pH through the hydrolysis of uranyl ions in aqueous solution. At low pH value, the uranium is present in the solution mainly in the form of free UO_2^{2+} ions; the uranium biosorption mechanism was affected by the pH of the solution through the hydrolysis of uranyl ions in aqueous solution. At low pH value, the uranium is present in the solution mainly in the form of free UO_2^{2+} ions, and it was competing with protons for the binding sites on the biomass.

Variations in pH affect both the solution speciation and the preferred type of the sorption sites on the sepiolite surface in the composite adsorbent. The main species present in the solution at pH 3.0 is UO_2^{2+} (major) and $UO₂OH⁺$ (minor).⁴⁰ With increasing pH the uranyl unit becomes more hydrolyzed and forms oligomeric solution species. The formation of surface sorption complexes can be kinetically favored in comparison to hydrated uranyl precipitates.⁴¹ SYLWESTER et al.⁴² observed that at pH 3.2–4.0 the uranyl ion preserves its structure portion and undergoes an ion-exchange process.

The effect of initial uranium concentration

The sorption of U(VI) was studied as a function of U(VI) concentration. The U(VI) concentration was varied from 25 to 250 μ g/cm³. Figure 3 illustrates the effect of the initial uranium concentration on adsorption.

The uranium(VI) adsorption increased in the initial concentration range from 75 to 200 μ g/cm³ and slightly decreased after 200 µg/cm3.

Desorption of adsorbed uranium from the composite adsorbent

After adsorption of uranium on composite adsorbent, the composite adsorbent was treated with different desorptive solutions to recover the adsorbed uranium from composite. Desorption of uranium from loaded composite adsorbent was studied as a function of desorptive solution. The results are shown in Table 2. Composite adsorbent showed lower desorption yield using NaOH, NaNO₃, EDTA, H₂O compared to the other desorptive solutions. $1\overline{M}$ HNO₃ represents relatively high desorption yield for uranium. Other desorption parameters were changed to increase the desorption yield.

Sorption isotherms

The sorption data have been subjected to different sorption isotherms namely Freundlich, Langmuir and Dubinin–Radushkevich (D–R). The data do not fit the Langmuir isotherm.

Freundlich isotherm: The Freundlich adsorption isotherm was tested in the following linearized form:

$$
\log C_{ads} = \log K_f + 1/n \log C_e \tag{3}
$$

by plotting $\log C_{ads}$ vs. $\log C_e$. C_e is the equilibrium activity of metal ions and *Cads* is the surface activity for metal ions on the solid surface. Both K_f and *n* are constants, being indicative of the extent of adsorption and the degree of non-linearity between solution and concentration, respectively. The result is presented in Fig. 4. The sorption data is obeyed well to the Freundlich isotherm. From the slope and intercept of the straight portion of the plot the values of Freundlich parameters, i.e., $1/n$ and K_f are computed: $1/n = 0.27$ and K_f = 7.86·10⁻⁸ mmol UO²⁺ g⁻¹. These values signify the sorption intensity and sorption capacity, respectively.

The numerical value of $1/n<1$ indicates that the sorption capacity is only slightly suppressed at lower equilibrium concentration and suggests multiple binding sites, with the sites of highest strength binding the sorbate first. Alternately, $1/n>1$ can mean that bound sorbate molecules interact in such a way that the binding strength is increased as more sorbate binds.^{43,44} The value *n* between 2 and 10 shows good adsorption. The Freundlich sorption isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. This isotherm does not predict any saturation of the sorbent by the sorbate thus infinite surface coverage is predicted mathematically, indicating a multilayer sorption of the surface.⁴⁴

Fig. 3. Variations of K_d and adsorption (%) versus initial uranium concentration (pH: 3.0, *m*: 0.1 g, *V*: 10 cm3, contact time: 24 h, *T*: 30 °C)

Table 2. Desorption yields of some desorptive solutions

Elution solution	Desorption, %
1M HNO ₃	85.4
1M NaOH	56.8
IMEDTA	18.4
$1M$ NaNO ₃	15.6
H ₂ O	11.3

Fig. 4. Freundlich sorption isotherm of uranium on composite adsorbent

Dubinin–Radushkevich (D–R) isotherm: The sorption data have been applied to the D–R model based on the heterogeneous surface of the adsorbate as in Freundlich isotherm in order to distinguish between physical and chemical adsorption. The linearized form of the D–R isotherm may be written as:

$$
\ln C_{ads} = \ln X_m - \beta E^2 \tag{4}
$$

where C_{ads} is the amount of metal ions adsorbed on per unit weight of adsorbent, X_m is the maximum sorption capacity and β is the activity coefficient related to the mean sorption energy and *E* is the Polanyi potential which is equal to:

$$
E = RT \ln (1+1/C_e) \tag{5}
$$

where *R* is the gas constant $(kJ \cdot mol^{-1} \cdot K^{-1})$ and *T* is the temperature (K). The saturation limit X_m may represent the total specific micropore volume of the sorbent. The sorption potential is independent of the temperature but varies according to the nature of the sorbent and sorbate.⁴⁵ The slope of the plot ln C_{ads} versus *E* gives β $(mol²/J²)$ and of the intercept yields the sorption capacity, X_m (mg/g). The sorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces having same sorption potential. This sorption potential is independent of the temperature but varies according to the nature of the sorbent and sorbate. The mean sorption energy (E) is given by $E = 1/\sqrt{-2}B$.

The plot of ln C_{ads} vs. E^2 as shown in Fig. 5 is a straight line. From the slope and intercept of this plot the values of $\beta = -3.010 \cdot 10^{-8} \text{ mol}^2/\text{kJ}^2$ and X_m = 3.01·10⁵ mmol UO₂^{+/}g have been estimated. The mean sorption energy (E) is given by $E = 1/\sqrt{-2\beta}$. The numerical value of the mean sorption energy is in the range of $1-8$ kJ·mol⁻¹ and $9-16$ kJ·mol⁻¹ forecast the physical adsorption and chemical adsorption, respectively.⁴⁶ The value of E is calculated to be $E = 4.01 \text{ kJ/mol}^{-1}$ and evaluated in the range of $1-8$ kJ·mol⁻¹ for composite adsorbent. The value of *E* is expected for physical adsorption. It is assumed to be heterogeneous (marine algae and sepiolite) in the structure of composite.

Thermodynamic studies

The influence of temperature variation was examined on the sorption of U(VI) on composite adsorbent from $1M HNO₃$ solution using 24 hours equilibration time and 0.1 mg composite adsorbent/10 cm³ of sorptive solution from 293 to 308 K. Thermodynamic parameters were calculated for this system by using the following equation:43,47

$$
\ln K_d = (\Delta S^\circ / R) - (\Delta H^\circ / RT) \tag{6}
$$

where K_d is the distribution coefficient, ΔH , ΔS and *T* are the enthalpy, entropy, and temperature in Kelvin, respectively and *R* is the gas constant. The plot of

 $\ln K_d$ against $1/T$ for U(VI) is shown in Fig. 6. The values of enthalpy (∆*H*) and entropy (∆*S*) were obtained from the slope and intercept of $\ln K_d$ vs. $1/T$ plots, which were calculated by a curve-fitting program. Gibbs free energy (∆*G*) was calculated by using the following equation:

$$
\Delta G = \Delta H - T \Delta S \tag{7}
$$

The values of the thermodynamic parameters for the sorption of U(VI) on composite adsorbent are given in Table 3.

Fig. 5. Dubinin–Radushkevich (D–R) sorption isotherm of uranium on composite adsorbent

Fig. 6. Influence of temperature on the thermodynamic behavior of adsorption of uranium on composite adsorbent (pH: 3.5, *m*: 0.1 g, *V*: 10 cm3, [U]:150 ppm, contact time: 24 h)

Table 3. Thermodynamic parameters for the adsorption of uranium(VI) on composite adsorbent

	ΔS_{ad} , J·mol ⁻¹ ·K ⁻¹	ΔG . kJ·mol ⁻¹				
ΔH_{ad} , kJ·mol ⁻¹		293 K	298 K	303 K	308 K	
-22.17	-1747	-17.05	-1696	-16.88	-16.79	

The negative value of enthalpy change, ∆*H*, show the adsorption of uranium is exothermic. The value of ∆*G* for these processes becomes less negative with increasing temperature which shows that sorption is less favored at high temperatures as shown in Table 3, indicating that the reaction is spontaneous and more favorable at lower temperature. The negative value of adsorption entropy is a harmonious result with the general information of decreasing entropy when ions pass solid phase from solution. Fixation or immobilization of uranium ions as a result of adsorption is attributed to a decrease in the degree of freedom of adsorbate ions which gives rise to a negative entropy change.47 The resultant effect of complex bonding and steric hindrance of the sorbed species eventually increases the enthalpy and entropy of the system.

Conclusions

The results of this study indicate that the composite adsorbent prepared from *Ulva sp.*–sepiolite can be successfully used for the hexavalent uranium recovery from aqueous solutions under the optimized conditions. Composite adsorbent consisted of *Ulva sp.* and sepiolite are an effective adsorbent for the recovery of uranium from aqueous solution. Sepiolite is cheap and can be found at several localities in Turkey and macro marine algae, *Ulva sp.,* are easily found at Aegean Sea.

Taking into account the results, we have considered it of great interest to assess the ability of locally available sepiolite and green macro marine algae (*Ulva sp.*) to prepare a composite for the adsorption of uranium(VI) from aqueous solutions in the batch technique and optimization of conditions for its adsorption and desorption.

Biosorption+adsorption by composite adsorbent thus demonstrated itself to be a useful alternative to conventional systems for the recovery of uranium in solutions. The adsorption of uranium onto composite adsorbent follows Freundlich and D–R isotherms. The value of *n* is 3.70, indicating a favorable adsorption process. The temperature variations have been used to evaluate the values of ∆*H*, ∆*S* and ∆*G*. The negative value of ∆*H* indicates that the adsorption of uranium on composite adsorbent is an exothermic process. The negative value of ∆*G* showed spontaneous nature of adsorption. The value of sorption energy, *E*, gives an indication about the nature of sorption.

The experimental results show that $HNO₃$ is a successful solution for desorption of uranium. Of the five desorptive solution examined, nitric acid solution appeared the most promising because it can effect near complete uranium recovery.

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