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Determining the Binding Capacities of Cr (VI) and Zn (II) Ions of *Oscillatoria* sp.

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Abstract

This study aimed to determine the removal capacity for Cr (VI) and Zn (II) ions from high concentration of aqueous solutions by using *Oscillatoria* microalgae. In the biosorption process, live and dead *Oscillatoria* cells were exposed for 24 hours to Cr and Zn metals of different concentrations (2.5, 5 and 10 mg/L). In addition, chlorophyll-a analysis have been made to examine the effects on cell metabolism of chromium and zinc metals. The best metal removal percentages was obtained; of chromium ion is 46.74% with dead cells and for zinc ion 82.53% with living cells. Chlorophyll-a analysis shows that when the metals separately applied on *Oscillatoria* cells, chlorophyll-a content of organism increase but when metals together applied decrease of chlorophyll-a content was observed. For this study, Freundlich model best fitted the data for two metal ions with 1/n value <1. This study revealed that *Oscillatoria* cells were an effective adsorbent for removal of the two heavy metals, especially Zn ions from aqueous solutions due to its high efficiency of Zn adsorption. It shows that it is a kind of potential for this heavy metal removal operations.

Keywords: *Oscillatoria*, bioremediation, heavy metal removal, Cr (VI), Zn (II)

1. INTRODUCTION

In recent years, environmental pollution has been increasing steadily due to the increase in consumption by utilizing technologically [1]. At the top of this environmental pollution problem is the pollution of the water with vital importance for the living things by various factors. Industrial activities constitute the biggest share in water pollution. The amount of heavy metals released as a result of industrial activities is rapidly

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increasing every day [2]. Heavy metals are naturally occurring compounds in ground shells and they do not deteriorate and can not be destroyed [3]. Some of these metals are important as kofactor of enzymatic reactions in trace amounts. However, high amounts of these metals can be extremely toxic to living organisms or slow down metabolic reactions [1]. These heavy metals are a serious threat to human and environmental health because of the toxic effect, remain intact in nature for an indefinite period of time, travel through the food chain and accumulate [3]. For this reason, the heavy metal contents of the wastewater must be purified and reduced below the permissible values according to various water quality standards before being given to the environment [4-5]. The remediation of heavy metal pollution are used some methods such as chemical precipitation, coagulation, flocculation, ion exchange, extraction, complex separation, biological processes, electrochemical processes, membrane processes, adsorption [6-8]. With these traditional methods, the metals in the environment can not be completely removed. However, these techniques have some disadvantages like expensive equipment and monitoring systems, the need for excessive chemical and energy, toxic sludge and other waste products [9, 10]. Due to the above reasons, new technologies are being studied on removal of metal ions from aqueous media and different technologies are being developed. One of the methods developed in this regard is the biosorption method. The use of microbial biomass in the removal of toxic heavy metals from water and wastewater is a new low cost alternative metods. The most important advantages of biosorption technology are the use of economical biosorbent materials [11, 12], which are capable of reducing the concentrations of heavy metals in wastewater to very low levels and are easily produced in abundant quantities. In addition, this method effectively removes pollutants even from very dilute water [13], allowing in situ application in polluted areas, bioprocessing technologies are also environmentally, which means that they do not cause a second pollution, high efficiency, no need for supplementary nutrients and the possibility of recovering the metal [14,15]. The living organisms used in this process are microorganisms such as algae, fungi and bacteria [16]. Compared to microbial biomass such as fungi and yeast, the heavy metal biosorption capacity of algae was higher. This is due to the high metal binding capacity of functional groups such as amino, hydroxyl, carboxyl and sulfate found in cell contents of algae. These organism can be used dead or alive in the biosorption process. There are some advantages to using dead biomass compared to living biomass. Dead cells can be stored at room temperature for extended periods, are not affected by metal toxicity, and do not require nutrients [17-19]. In this study, the biosorption capacity of Cr (VI) and Zn (II) ions on dead and live blue-green algae *Oscillatoria* sp. was investigated. At the same time, the effect of heavy metals on chlorophyll-a was investigated and biosorption capacities were determined with Freundlich and Langmuir isotherm models. *Oscillatoria* species are preferred because of their easy availability in nature and their high adsorption capacity.

2. MATERIAL AND METHODS

2.1 Organism and culture condition

Oscillatoria cells were obtained from CicCartuja Instituto de Bioquímica Vegetal Y Fotosíntesis Laboratory (Seville, Spain). The alga was grown in 250 mL flasks containing 100 mL BG-11 [20] medium and incubated in an illuminated incubator at 28°C and irradiance at 36 μmol m^{-2} sec^{-1} and magnetic stirring (110 rpm), provided by cool white fluorescent lamps (20 E m^{-2} s^{-1} ± 20%) set on 16:8 h photoperiod. The pH value was adjusted to 6–7 using 1 M NaOH and 1 M HCI. The growth of algae and biomass concentration was monitored by measuring optical density at a wavelength of 660 nm and 730 nm for 30 days. Cells were harvested from the culture by centrifugation. The biomass pellets collected were then washed with distilled water and centrifuged again for the removal of medium.

2.2 Heavy metal concentrations

Stock solutions of the heavy metals K_2CrO_4 and Zn $(NO_3)_2.6H_2O$ were prepared, from which concentrations 2.5, 5 and 10 mg/L of heavy metals was used. All experiments were repeated three times.

2.3 Biosorption studies

Oscillatoria cells were used in the experiment of heavy metal removal using the algal concentrations 2 g. The metal concentration used was 15 mL and the exposure time was 24 h. pH was adjusted to 5 for Cr (VI) and 7 for Zn (II) and incubation was performed at the previous mentioned conditions. After centrifugation at 4000 rpm to separate the biomass, the samples were analysed by ICP-MS (Inductively Coupled Plasma– Mass Spectrometer-Agilent 7700) [21]. The metal uptake loading capacity qe (mg of metal per g of adsorbent) and removal efficiency (RE %) for each sorption system was determined using Eq. 1 and Eq. 2:

$$q = \frac{V(Ci - Ct)}{m} \text{(Eq. 1)}$$

$$RE\ \% = \frac{100*(Ci - Ce)}{Ce} \text{ (Eg. 2)}$$

Where q is the metal uptake (mg/g of biomass); Ci and Ce are the metal concentrations before and after adsorption (mg/mL), respectively; m is the mass of biosorbent used (g) and V is the volume of solution (mL).

2.4 Determinations of chlorophyll-a content

Chlorophyll-a content were estimated in acetone extract according to Parsons and Strickland (1963). For determination of pigment concentrations, 10 mL of culture was filtered using GF/C filters. An aliquot of the sample was centrifuged at 12000 rpm for 5 min and supernatant discarded. The pellet was suspended in 10 mL of boiling acetone at 4°C and stored in dark for 24 h. Pigment content in the filtered extract were determined by the absorbance at 630, 645, 665 and 750 nm in a 1cm quartz cell against a blank of 90% aqueous acetone [22].

2.5 Determination of dry weight

A definite volume (20 g) of algal suspension was filtered through weighted glass fiber (Whatman GF/C). The cells, after being precipitated on the filter study, were washed twice with distilled water and dried overnight in an oven at 105°C. Data were given as mg/mL algal suspension.

2.6 Statistics

All experiments were performed in 3 replicates. The amount of metal ions adsorbed by used biosorbent was obtained by using Langmuir model and Freundlich models [23-25]. The adsorption equilibrium isotherms were evaluated in terms of maximum sorption capacity and sorption affinity. Among the several isotherm equations, two isotherms (Langmuir and Freundlich adsorption isotherms) were investigated, which are widely used to analyses data for water and wastewater treatment applications [26]. Freundlich isotherm model is derived for describing singlecomponent adsorption equilibria on heterogeneous surfaces. Langmuir isotherm represents a single layer and uniform adsorbent without interactions between adsorbed molecules. In the current study, the Freundlich (Eq. 3) and Langmuir (Eq. 4) models were used to determine the concentration of the adsorbed material. If 1/n= 0, the adsorption process is irreversible. If 1< 1/n<0, it is desired. If 1/n>0, it is undesirable [23, 24].

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \text{ (Eq. 3)}$$

q_e: the amount of metal adsorbed (mg/g).

K_F: Adsorption capacity at unit concentration (L/g).

1/n: Intensity of adsorption (L/g).

C_e: the equilibrium concentration of metal ion (mg/L).

In the Langmuir model, q_m and b are Langmuir parameters, which are the maximum adsorption capacity and associated energy, respectively. The equilibrium parameter (R_L) is the basis of the Langmuir isotherm, which is defined by equation, R_L=1/(1+bC_0) [23]. In this equation, C_0 is the initial concentration and R_L is the type of isotherms. 1<R_L<0 is favourable adsorption, R_L>1 is for undesirable adsorption, R_L=1 shows linear adsorption and R_L=0 demonstrates irreversible adsorption [25]. The R_L value was calculated at 50 mg/L of initial metal concentration.

$$\frac{Ce}{qe} = \frac{1}{qmb} + \frac{Ce}{qm} \qquad \text{(Eq.4)}$$

q_m: Langmuir maximum adsorption capacity (mg/g). b: the constant related to free energy of adsorption (L/mg).

3. RESULTS

3.1 Analysis results of the heavy metal uptake (mg/g) and efficiency (%) Cr (VI) uptake (mg/g) and efficiency (%)

The effects of Cr (VI) on *Oscillatoria* sp. was investigated using increasing concentration of chromium from 2.5 to 10 mg/L (Table 1). The metal adsorption capacity by both live and dead algae increased significantly with an increasing initial metal concentration. The metal adsorption value was 5.69, 17.52 and 17.89 mg/g for dead and 0.36, 0.75 and 1.77 mg/g for live algae, when Cr (VI) concentration was 2.5, 5 ve 10 mg/L, respectively. The adsorption efficiency of dead algae was found to be slightly higher (40 %) and significantly different than that of live algae (2 %) using an initial cadmium concentration of 5 mg/L.

Table 1. Cr (VI) adsorption capacity and efficiency by live and dead *Oscillatoria* sp. Data are means (triplicates).

	Live cells		Dead cells	
Cons. (mg/L)	**Adsorption capacity (mg/g)**	**Adsorption efficiency (%)**	**Adsorption capacity (mg/g)**	**Adsorption efficiency (%)**
2.5	0.36	1.96%	5.69	30.36%
5	0.75	2.06%	17.52	46.74%
10	1.77	2.46%	17.89	23.85%

3.2 Zn (II) uptake (mg/g) and efficiency (%)

The efficiency of Zn (II) removal at 2.5, 5 and 10 mg/L concentrations was reported 14.28, 29.81 and 54.20 mg/g by live *Oscillatoria* sp. cells, and 11.27, 14.53 and 12.83 mg/g by dead *Oscillatoria* sp. cells, respectively (Table 2). The maximum Zn removal was 82.53% and 54.18% by live and dead *Oscillatoria* sp. cells at 2.5 mg/L concentration, respectively. The Zn removal decreased at 5 and 10 mg/L concentrations in the two algae.

Table 2. Zn (II) adsorption capacity and efficiency by live and dead *Oscillatoria* sp. Data are means (triplicates).

	Live cells		Dead cells	
Cons. (mg/L)	**Adsorption capacity (mg/g)**	**Adsorption efficiency (%)**	**Adsorption capacity (mg/g)**	**Adsorption efficiency (%)**
2.5	14.28	82.53%	11.27	54.18%
5	29.81	80.96%	14.53	40.07%
10	54.20	74.98%	12.83	17.07%

3.3 Chlorophll-a contents

The effects of chromium and zinc on concentration of chlorophyll derivatives are seen in the Table 3. Chlorophylla concentration was recorded to be decreased simultaneously from an initial value of 1.440 µg/L to 0.0338 µg/L and 0.02 µg/L at the end of the application of chromium and zinc separately and together on live *Oscillatoria* cells, respectively. Zn (II) and Cr (VI) showed a strong inhibition of chlorophyll-a biosynthesis even at the lower concentrations (2.5–5mg/L) on *Oscillatoria* biomass.

Table 3. Effect of heavy metals (Zn and Cr) on the chlorophyll-a content in *Oscillatoria* cultures (μg/L).

	Separate application		Together application	
Control	1.4404 μg/L			
Cons. (mg/L)	**Cr**	**Zn**	**Cr**	**Zn**
2.5	0.0368	0.0410	0.0001	0.0003
5	0.0305	0.0464	0.0009	0.0029
10	0.0334	0.0438	0.0050	0.0047
Mean	0.034	0.044	0.002	0.003

3.4 Adsorption isotherms study

The results of Langmuir and Freundlich isotherms are presented in Table 4. We concluded that maximum adsorption capacity (q_m) of chromium and zinc calculated from Langmuir isotherm was around 5.6939 (dead cells) and 14.2907 (live cells) mg/g on *Oscillatoria* sp. cells, respectively. According to the correlation coefficient obtained (R^2= 0.99), the adsorption process of *Oscillatoria* sp. algae follows the Langmuir model. K_L in the range between 2 and 6 indicates the undesired chromium and zinc adsorption by the dead and live *Oscillatoria* sp. algae [27]. For live and dead *Oscillatoria* cells, 1/n value was determined between 0.3418-0.8557 and 0.1585-0.1681, respectively. According to Kadirvelu and Namasivayam (2000) [28], n values between 1 and 10 indicate a useful adsorption representative. For a good adsorbent, $0.2<1/n<0.8$ and a smaller value of 1/n indicates better adsorption and formation of rather strong bond between the adsorbate and adsorbent [28] Freundlich isotherm coefficient indicated that the adsorption process does follow this model (Figure 1-4).

Table 4. Compliance of live and dead *Oscillatoria* sp. cells equilibrium data via Langmuir and Freundlich models.

	Langmuir			*Freundlich*		
Adsorbent	**q_m (mg/g)**	**K_L (L/mg)**	**R^2**	**1/n (L/g)**	**K_F (L/g)**	**R^2**
Live	0.360	2.777	0.987	0.855	1.168	0.365
Dead	5.693	6.309	0.999	0.158	0.175	0.754
Live	14.290	2.069	0.994	0.341	2.925	0.008
Dead	11.275	2.925	5.948	0.168	0.088	0.035

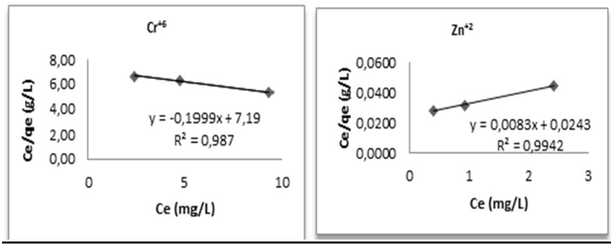

Figure 1. Langmuir adsorption isotherm of live *Oscillatoria* sp. cells.

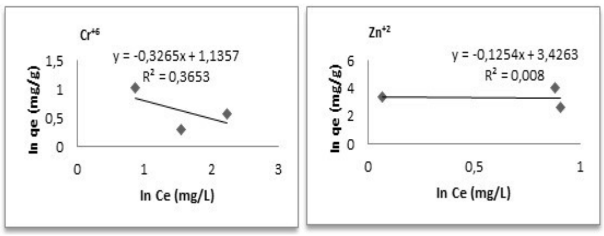

Figure 2. Freundlich adsorption isotherm of live *Oscillatoria* sp. cells.

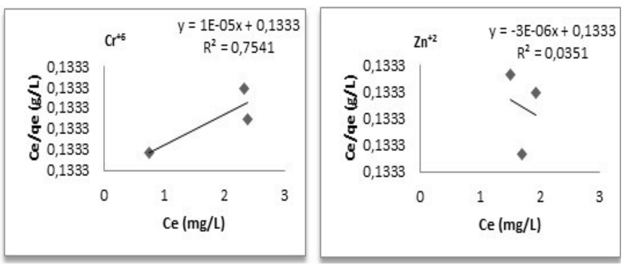

Figure 3. Langmuir adsorption isotherm of dead *Oscillatoria* sp. cells.

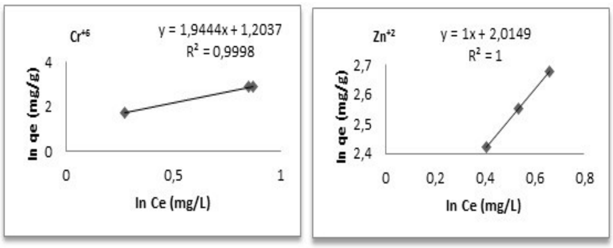

Figure 4. Freundlich adsorption isotherm of dead *Oscillatoria* sp. cells.

4. DISCUSSION

Many studies have emphasized that biosorption is a lowcost technology and that the use of microalgae for the treatment of metal-bearing wastes is more effective [28-2936]. Bhatnagar and et al. [30] pointed out that microalgae has many mechanisms and some of them unknown what their function is still developing bioremediation technology has emphasized that necessity of re-imaged and modified urgently according to needs and to create a new biological form.

In this study, samples were used both live and dead in order to provide a better comparison in heavy metal removal processes. Studies show that when the same metal is treated with both living and dead cells of the same organism, different findings can be obtained. In example the study with *Oscillatoria* sp. cells Katırcıoğlu and et al. [31], get better removal of Cd (II) with live cells, while Azizi et al. [32] obtained best results with dead cells in their work with the same organism and metal. Das [33], noted that the initial ion concentration plays an important role in determining the adsorption capacity. These two metals are abundant amounts in waste waters. Although the Cr (VI) ion must be found to be very low amount in the water but the Zn (II) ion may be present in small quantities in the water as it is one of the essential metal for living things. Concentration values used in the study have been taken into consideration. As a result of the findings obtained that when the concentration increased, the removal of metals are also increased. These findings are in parallel with other studies [31-33].

Given the previous work, it was reported that the adsorption was completed within a few hours [30,33]. Singh [34], found that absorption of zinc was very rapid in the first 10 minutes of study. Shukla et al. [35] reported that the adsorption for the Cr (VI) ion started within 15 min and the metal was removed up to 96% within 210 min. For this reason, the *Oscillatoria* sp. microalgae exposure to metals was kept constant for 24 hours.

As a result of this study, the best removal for Cr (VI) ion was found with dead cells, increasing the solution concentration gives increasing metal removal. The maximum removal capacity was 17.89 mg/g and the maximum removal percentage was found to be 46.74%. Findings have also been supported by other studies [31-35]. The best removal for the Zn (II) ion was achieved with live cells and the work done with these cells showed that the concentration of zinc was increased by increasing the concentration, and no such correlation was observed in dead cells. The study with dead cells was also found at the highest concentration of 10 mg/L, while the metal removal capacities were close to each other in three concentrations. The maximum removal capacity was found to be 54.20 mg/g, with a maximum removal rate of 82.53%. The data obtained in the bivalent zinc ion correspond to other studies. The environmental factors and the environment in which it is cultivated have been determined by studies that affect the chemical composition of microalgae and which change in the adsorption capacity of heavy metals by changing the chemical composition. Looking at all these, there is a difference in the data obtained in systems where any organism is involved. Factors such as the structure of the organism, content, defense mechanisms for living cells can give different findings even in the same study. As a result of the study, in the removal of Cr ions with live *Oscillatoria* cells, different results obtained with the study of Shukla et al. [35] but similar values were obtained with the study of Jayashree ve et al. [35,40].

In the removal of bivalent zinc, high values were obtained in both with dead cells and live cells. Comparisons within the entire study showed that optimal removal occurred in living cells treated with Zn (II) ions. This can be explained by the fact that the Zn (II) ion is a more elaborate metal in terms of the organism's metabolic needs than the Cr (VI) ion.

When the effect of the application of the metals separately and together is examined on the chlorophylla content of the living organism, the metals are applied individually, there is an increase in the amount of chlorophyll-a in all metal doses, whereas a decrease in the amount of chlorophyll-a is observed when the metals are applied together. When previous studies were examined, Brahmbhatt et al. [36] reported that metal toxicity was considered to be a biomarker and that there was an increase in the amount of alginate chlorophyll exposed to metal compared to the stress-free area. In the same way, Shankar et al. [37] reported an increase in chlorophyll-a in their work with *Oscillatoria* annae cyanobacterium. On the other hand, co-application of metals is thought to have more effect on the cell content of living organisms, which explains the decrease in chlorophyll content. It supports the findings obtained in previous studies [38-39].

When the effect of environmental factors on the study was examined, Shankar et al. [37] reported that the best growth of *Oscillatoria* microalgae was achieved at an optimum temperature of 29 ± 2°C, at approximately 7 pH. In this study, the same values were applied to the samples taken from the culture.

It has been observed in previous studies that the increase in temperature during the biosorption process affects the adsorption capacity positively [32]. For this reason, the temperature was determined to be 29 ± 2°C during the adsorption process. It is supported by this study data that the determined temperature is suitable for adsorption capacity.

One of the important factors in adsorption processes is the pH range. Several studies have shown that mild acidic pH values are more suitable for metal adsorption [31-36]. The dependence of metal uptake on pH is related to the competition between protons and metal cations on the surface of the absorption medium. These different chemical interactions between cell surfaces and metal can result in different retention capacities for metal ions at various pHs [7]. Dabbagh et al. [38] reported that the optimum pH for strontium metal was 9 ± 0.3 while the previous studies evaluated, the pH ranges for chromium and zinc metals were determined to be 5.0 and 7.0, respectively. When the adsorption capacities are evaluated, the chromium (VI) ion is less biosorbent than the zinc (II) ion can be attributed to the working pH values. At lower pH, the cell surface charge is positive and H_3O^+ ions show a rate-reducing effect by competing with positive metal cations to bind to the cell. At pH values on the isoelectric points of the cells, the cell surface has a net negative charge. The ionic state of ligands such as carboxyl, phosphate, imidazole and amino groups accelerate the binding of metal cations to biomass [7].

Langmuir and Freundlich biosorption isotherms were used in the evaluation of the study findings. These isotherms used to describe biosorption have previously been used in many studies [31, 39]. According to Nakiboğlu [39] regarding the evaluation of isotherms, it has been reported that in some cases this adsorption can not be explained by Langmuir isotherm, even though C_e coefficient value increases. In such cases, more Freundlich isotherm coefficient values are used to define the adsorbance. For Freundlich isotherms, the lower the value of 1/n, the more absorbance bonds are formed. When the findings obtained are evaluated, it is seen that the study is better explained by Freundlich isotherm.

5. CONCLUSION

The goal of this work was to explore the potential use of *Oscillatoria* sp. biomass as a low-cost sorbent for the removal of Cr (VI) and Zn (II) heavy metal ions from aqueous solutions. Batch experiments showed that the dead and live

Oscillatoria sp. cells have a remarkable ability to take up Cr (VI) and Zn (II) heavy metal ions, respectively. Only 2.6 % of the world's water reserves are composed of fresh water. A large part of this is found in glaciers in the polar regions, only 0.02% of which form lakes and rivers. The limited amount of water resources that can be contained is polluted by various pollutants from day to day. The heavy metals from industrial wastes come at the expense of the polluting water resources. Biologically available heavy metals accumulate in tissues, causing different levels of negativity in living organisms. The heavy metal accumulation in the aquatic ecosystem continues from the first ring of the nutrient chain to the upper steps of the nutrient chain. For this reason, microalgae in the first part of the food chain are widely used for the assessment of heavy metal toxicity. In this study, different concentrations of chromium and zinc metals, which are quite common in wastewater, are classified as a microalgae, *Oscillatoria* sp. has been investigated, significant contributions have been made to the findings literature. It is once again seen that pH is an important parameter as a result of this study. When previous studies examined, it is known that different pHs affect the removal capacity when applied to live or dead samples of the same metals. Accordingly, it may be advisable to evaluate pH over a wide range during subsequent studies for the same organism and metals. It is also known that the initial ion concentration plays an important role in determining the adsorption capacity. The metals used in the study were selected by looking at the parameters that should be found in the clean waters. The chromium (VI) ion is toxic to living organisms even at very low levels in the water, while the zinc (II) ion, another metal, is a metal that enters organisms in vigorous quantities. For this reason, it is suggested to extend the construction intervals for further studies.

This study with *Oscillatoria* sp. microalgae has shown that chromium (VI) and zinc (II) ions are effective biosorbents in removing water from water under the determined conditions. However, the *Oscillatoria* sp. is a kind of microalgae that requires more care than other types of algae to cultivate and maintain the culture. It is advisable to consider this for other studies. As a result of this and similar studies in the literature, it has been shown that the biosorption method can be an effective method of removing heavy metal ions from water and wastewater environments. Many organisms are used in the biosorption process, but studies show that microalgae have more removal capacity in these processes. Microalgae are found more easily than other biosorbents and are easily cultured in inexpensive environments. At the same time, much biomass removal can be achieved with these biosorbents. With these organisms, it is possible to develop more effective and cheap treatment systems and to protect existing water resources.

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