

CHARACTERIZATION OF THE BIOSORPTION OF LEAD AND CADMIUM WITH THE RED ALGA (*CERAMIMUM VIRGATUM*)

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In this study *Ceramium virgatum* has been characterized and used for the removal of cadmium and lead from aqueous solutions. The effect of pH, adsorbent dosage, contact time and temperature on adsorption process was studied in batch experiments. Langmuir and Freundlich models were applied to describe the biosorption isotherm of the metal ions by *C. virgatum* biomass. The adsorption data can be well described by Langmuir isotherm. The monolayer biosorption capacity of *C. virgatum* biomass for Pb(II) and Cd(II) ions was found to 56.2 mg/g and 53.1 mg/g, respectively. The mean free energy calculated from Dubinin–Radushkevich isotherm indicated that the biosorption of Pb(II) and Cd(II) onto *C. virgatum* macroalga was taken place by chemical ion-exchange. Kinetics data of both metal ions were best described by pseudo second order model. The thermodynamic studies showed that the adsorption was spontaneous and exothermic in nature. The analysis with Fourier transform infrared spectroscopy indicated that the carboxyl (–C O), hydroxyl (–OH), and amine (–NH) groups are responsible for the binding of the metal ions.

Key words: Langmuir and Freundlich models, biosorption, FTIR analysis, kinetic.

Karakterizacija biopsorpcije olova i kadmija pomoću crvene alge (*ceramium virgatum*). U ovom radu karakterizirana je *Ceramium virgatum* i korištena za ukaljanje kadmija i olova iz vodene otopine. Analiziran je utjecaj pH, količine adsorbensa, vremena kontakta i temperature na adsorpcijski proces. Za opis biopsorpcijske izoterme metalnih iona na biomasi *C. virgatum* korišten je Langmuirov i Freundlichov model. Adsorpcijski podaci mogu se opisati langmuirovom izotermom. Monoslojni kapacitet biopsorpcije na biomasi *C. virgatum* iznosi 56.2 mg/g, odnosno 53,1 mg/g. srednja vrijednost slobodne energije izračunata iz Dubinin-Radushkevich izoterme ukazuje da se biopsorpcija Pb (II) i Cd (II) na makroalgi *C. virgatum* odvija kemijskom ionskom izmjenom. Kinetičke podatke oba metalna iona bolje opisuje model pseudo drugog reda. Termodinamička studija pokazuje da je adsorpcija spontana i egzotermne prirode. FTIR analiz ukazuje na karboksilne (-CO), hidroksilne (-OH) i amino (-NH) grupe koje su slobodne za vezanje metalnih iona.

Ključne riječi: Langmuir i Freundlich modeli, biopsorpcija, FTIR analiza, kinetika.

INTRODUCTION

Rectifying environmental pollutants from industrial wastes and wastewaters is an important environmental problem of global concern.

Environmental pollutants contain organic and inorganic hazardous materials and heavy metals.

Some metal ions are cumulative poisons capable of being assimilated and stored in the tissues of organisms, causing noticeable adverse physiological effects. Lead (Pb) and Cadmium (Cd), are very toxic metal ions, as they are carcinogenic in nature [1]. Cd(II), which is widely used and

extremely toxic in relatively low dosages, is one of the principle heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fraction and destruction of red blood cells [2]. Because of the toxicity and bioaccumulation, Cd is considered as a priority pollutant by the U S Environmental Protection Agency. The permissible limit for Cd(II) as described by WHO is 0.01 mg/dm³. The main anthropogenic pathway through which Cd(II) enters the water bodies is via wastes from industrial processes such as electroplating, plastic manufacturing, metallurgical processes and industries of pigments and Cd/Ni batteries [3]. Pb(II) is the most significant toxin of the heavy metals and its effects are of toxicological and neurotoxic natures which include irreversible brain damage. Inorganic forms of lead typically affect the central nervous system, peripheral nervous system, and hematopoietic, renal, gastrointestinal, cardiovascular, and reproductive systems.

Organic lead toxicity tends to predominate affect the central nervous system. The other hazardous effects of lead are visual disturbances, convulsions, loss of cognitive abilities, antisocial behaviors, constipation, anemia, tenderness, nausea, vomiting, severe abdominal pain, anemia, and gradual paralysis in the muscles [1, 4]. Therefore, the removal of these toxic metal ions from water prior to supplying water for drinking, bathing, etc. is very important and urgent.

Numerous processes such as ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis and electrodialysis have been used for the removal of heavy metal ions from aqueous solution [5]. However, technical or economic factors limit sometimes the feasibility of such processes. Biosorption as a wastewater treatment process has been

found to be an economically feasible alternative for metal removal. Basically, it can be based on the following mechanisms: physical adsorption, ion exchange, complexation and precipitation. Biosorption may not necessarily consist of a single mechanism. In many sorption processes, several mechanisms often act in combination and it is difficult to distinguish between the single steps [6]. Among the different biological substrates studied, algal biomass has received much attention due to the cost saving, low sensitivity to environmental and impurity factors, the possible contaminant recovery from the biomaterial and its elevated adsorption capacity, higher than activated carbon and comparable to those of synthetic ion exchange resins.

Ceramium virgatum is both epilithic and epiphytic, often growing on the stipes and fronds of *Fucus* spp., *C. virgatum* colonizes rock and algal habitats from the midshore in rockpools to the open shore near to low water level and in the shallow subtidal [7]. *C. virgatum* is widespread along the shores of Tunisia, grows well along the Mediterranean Sea coasts.

The objective of the present work was to assess the potential of *Ceramium virgatum*, for the biosorption of lead and cadmium from aqueous solution. The effects of pH values, contact time, adsorbent dosages and temperature, were studied. During the work program, raw and metal-loaded algal biomasses were tested with Fourier transform infrared spectrometer (FTIR) to evaluate the functional groups that might involve in the sorption of both metal ions.

These results would contribute to a better understanding of the biosorption phenomena and aid in the development of potential biosorbents using locally derived sorbents, which possess high capacities for heavy metal uptake from aqueous solutions.

MATERIALS AND METHODS

Biomass preparation

The raw biomass of *Ceramium virgatum* was harvested from the Cap Zebib beach (North coast of Tunisia). The samples were washed with copious quantities of deionized water to remove extraneous materials as well as release common ions

(e.g., Na⁺ and Ca²⁺) present in seawater. The washed biomass was dried at 60 °C for 48 h. The dried algae biomass was chopped, sieved and the particles with an average of 0.5 mm were used for biosorption experiments.

Reagents and equipments

Stock metal solutions at various concentrations were prepared by dissolving lead nitrate and cadmium nitrate (analytical reagent grade, sigma-Aldrich (Ireland)). The pH of the solution was monitored with a 5500 EUTECH pH Meter using FET solid electrode calibrated with standard buffer solutions by adding 0.1 mol/L HNO₃ and 0.1 mol/L NaOH solutions as per required pH value. The metal concentrations were

measured using an atomic absorption spectrophotometer (Varian – spectra – AA – 55, USA). FTIR spectroscopy was used to detect vibration frequency changes in the algal sorbent. The spectra were collected by an FTS-135 (Bio-Rad) spectrometer within the range 400-4000cm⁻¹ using a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra.

Batch biosorption experiments

Biosorption processes were carried out using batch method. In order to optimize the experimental conditions, the batch studies were performed for different metal concentrations (10-400 mg/L), contact times (5-90 min), pH (2-8), biosorbent dosages from (0.1 to 20 g/L), and temperatures (20-50 °C). The solutions (25 mL of 10 mg/L) including the metal ions and biosorbent were shaken during optimum contact time in an electrically thermostatic reciprocating shaker (Multimatic-55 model, Selecta Company, Spain) at 120 rpm.

After the contents of the flask were filtered through 0.25 μm filters (Double rings, China), the metal concentration of

filtrate was analyzed using AAS. The percent biosorption of metal ion was calculated as follows:

$$\text{Biosorption}(\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i and C_e are the initial and final (or equilibrium) metal concentrations, respectively.

All the investigations were carried out in triplicate to avoid any discrepancy in experimental results with the reproducibility and the relative deviation of the order of ±0.5% and ±2.5%, respectively.

Desorption and regeneration studies

The desorption studies of Pb(II) and Cd(II) from *C. virgatum* was carried out by

using 1M HCl (10 mL) and 1M HNO₃ (10 mL). After determination of metal contents

of the final solutions, the biosorbent was washed with excess of the acid solution and distilled water in order to reuse for next

experiment. Consecutive sorption-desorption cycles were repeated six times to establish the reusability of the biosorbent.

RESULTS AND DISCUSSION

Effect of pH solution

The biosorption capacity of the alga strongly depends on equilibrium solution pH, so characterisation of its effect on adsorption studies is necessary for an accurate evaluation of equilibrium parameters. Therefore, if the metal binding groups are weakly acidic or basic, the availability of free sites is dependent on the pH. The biosorption of Pb (II) and Cd (II)

was studied over a pH range of 2 – 8 and the results are given in Fig. 1. The biosorption efficiency was increased from 60% to 96% for Pb(II) and from 52% to 95% for Cd(II) ion as pH was increased from 2 to 5. The maximum biosorption was found to be 98% for Pb(II) and 96% for Cd(II) ions at pH 5.5.

Therefore, all the biosorption experiments were adjusted at pH 5.5.

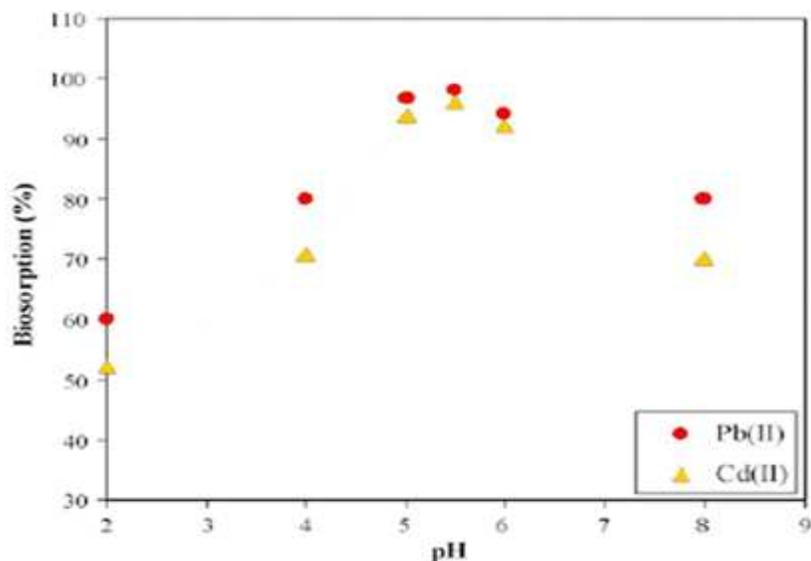


Figure 1. Effect of pH on the biosorption of Pb(II) and Cd(II) onto *C. virgatum* (initial concentration: 10 mg/L; temperature: 20 °C, biomass concentration: 4 g/l)

Slika 1. Utjecaj pH na biosorpciju Pb(II) i Cd(II) na *C. virgatum* (početna koncentracija: 10 mg/L; temperatura: 20 °C; koncentracija biomase: 4 g/L)

The biosorption mechanisms on the biomass surface reflect the nature of the physicochemical interaction of the species in solution and the biosorptive sites of sorbent. At highly acidic pH (pH<2.0), the overall

surface charge on the active sites became positive and metal cations and protons compete for binding sites on cell wall, which results in lower uptake of metal. The biosorbent surface was more negatively

charged as the pH of solution increased from 2 to 5.5. The functional groups of the biomass were more deprotonated and thus available for the metal ions. Especially, carboxyl, amine and phosphate groups are important functional groups involved in

Effect of biosorbent concentration

The biomass concentration is another important variable during metal uptake. At a given equilibrium concentration, the biomass takes up more metal ions at lower than at higher cell densities [9]. It has been suggested that electrostatic interactions between cells can be a significant factor in the relationship between biomass concentration and metal sorption. In this connection, at a given metal concentration, the lower the biomass concentration in suspension, the higher will be the metal/biosorbent ratio and the metal retained by sorbent unit, unless the biomass reaches saturation. High biomass concentrations can exert a shell effect, protecting the active sites from being occupied by metal. The result of this is a lower specific metal uptake, that is, a smaller amount of metal uptake per biomass unit.

Effects of contact time and temperature

Previous work showed that the sorption of heavy metal ions by algae followed a two-step mechanism where the metal ion was physically/chemically uptaken onto the surface of the algae before being taken up biologically into the cell [4]. The first step, known as a passive transport, took place quite rapidly, i.e. within 20-30 min whilst the second biological step or active transport, could take much longer time to complete. In this case, since the alga was dried and biological functions were no longer active, the sorption could only take place on the surface of the cell. Therefore the sorption equilibrium took place quickly

within 20 min and no further sorption was observed thereafter.

biosorption of heavy metals [8]. Decrease in biosorption yield at higher pH (pH >5.5) is not only related the formation of soluble hydroxilated complexes of the metal ions but also to the ionized nature of the cell wall surface of the biomass under the studied pH.

The effect of biomass dosage on the biosorption of Pb(II) and Cd(II) ions was studied using different biomass dosage in the range, 0.1-20 g/L. Results showed that the biosorption yield steeply increases with concentration as the biomass concentration was increased from 0.1 to 4 g/L.

The maximum biosorption percentage reached 98% for Pb(II) and 96% for Cd(II) as biomass concentration was 4 g/L and it was almost same at higher dosages. This trend could be explained as a consequence of a partial aggregation of biomass at higher biomass concentration, which results in a decrease in effective surface area for the biosorption.

Therefore, the optimum biomass dosage was selected as 4 g/L for further experiments.

Therefore, the optimum biomass dosage was selected as 4 g/L for further experiments.

The rate of biosorption is important for designing batch biosorption experiments. Therefore, the effect of contact time on the biosorption of Pb(II) and Cd(II) was investigated. The biosorption yield of Pb(II) and Cd(II) increased considerably until the contact time reached 60 min. Further increase in contact time did not enhance the biosorption yield, so, the optimum contact time was selected as 60 min for further experiments.

On the other hand, the biosorption yield decreased from 98% to 90% for Pb(II)

and from 95% to 88% for Cd(II) as temperature was increased from 20 to 50 °C during the equilibrium time, 60 min. These results indicated the exothermic nature of Pb(II) and Cd(II) biosorption onto *C. virgatum* biomass. A decrease in the biosorption of Pb(II) and Cd(II) ions with

Biosorption isotherms

To find out the mechanistic parameters associated with lead and cadmium adsorption, the results obtained by the adsorption experiments were analyzed by Langmuir and Freundlich models.

The theoretical Langmuir adsorption isotherm model is best known to all the isotherm models, and describes the adsorption of a solute from a liquid solution.

Langmuir adsorption isotherm [10] applied to equilibrium adsorption assuming mono-layer adsorption onto a surface with a finite number of identical sites and is represented as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

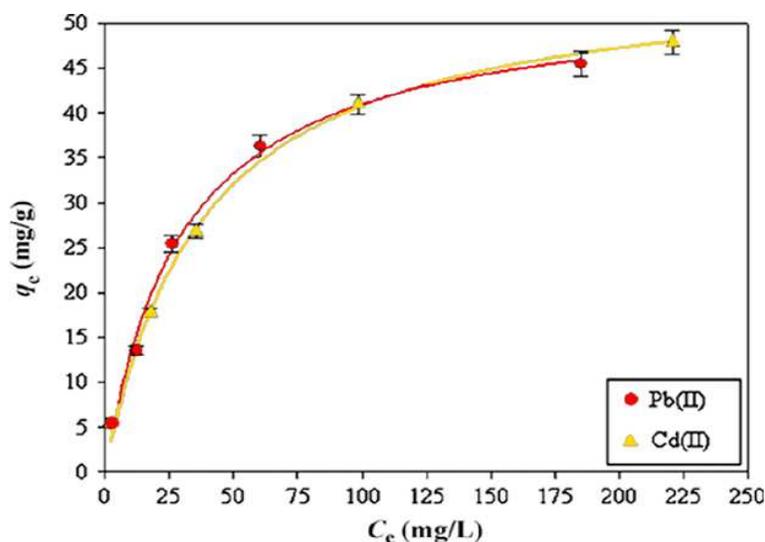


Figure 2. Langmuir isotherm plots for the biosorption of Pb(II) and Cd(II) onto *C. virgatum* (biomass concentration: 4 g/L; contact time: 60 min; pH: 5.5; temperature: 20 °C)

Slika 2. Dijagram Langmuirove izoterme za biosorpciju Pb(II) i Cd(II) na *C. virgatum* (koncentracija biomase: 4 g/L, vrijeme kontakta: 60 min.; pH: 5.5; temperatura: 20 °C)

the rise in temperature may be due to either the damage of active binding sites in the biomass or increasing tendency to desorb metal ions from the interface to the solution. The optimum solution temperature was selected as 20 °C for further biosorption experiments.

where q_e is the equilibrium metal ion concentration on the biosorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer biosorption capacity of the biosorbent (mg/g), and K_L is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption.

Nonlinear regression analysis was carried out in Sigma Plot software (Sigma Plot 2001, SPSS Inc., USA) in order to determine K_L and q_m values.

The data obtained with the correlation coefficients (r^2) were listed in Table 1.

The Freundlich adsorption isotherm is an empirical equation based on the adsorption on the heterogeneous surface.

The linear form of the Freundlich adsorption isotherm can be defined by the following equation [11]:

$$q_e = K_f C_e^{1/n} \quad (3)$$

The Freundlich isotherm constant n is an empirical parameter that varies with the degree of heterogeneity and K_f is related to adsorption capacity.

K_f and $1/n$ values were determined using nonlinear regression analysis by Sigma Plot software (Sigma Plot 2001, SPSS Inc.,USA).

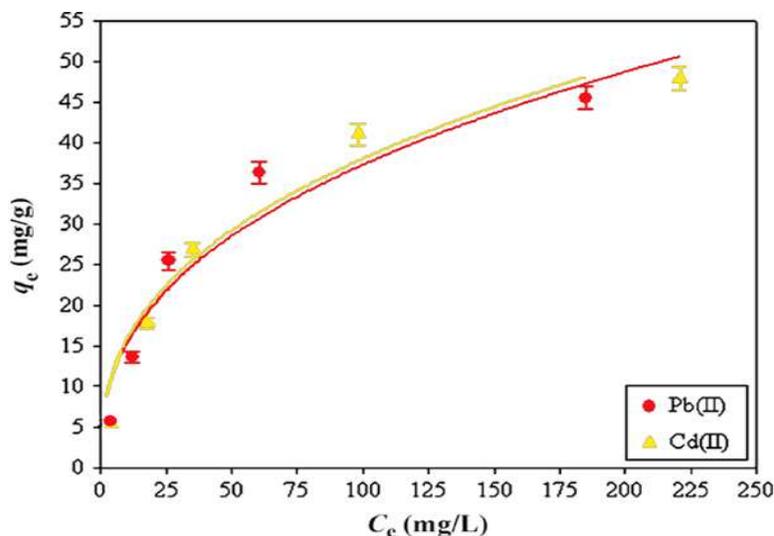


Figure 3. Freundlich isotherm plots for the biosorption of Pb(II) and Cd(II) onto *C. virgatum* (biomass concentration: 4 g/L; contact time: 60 min; pH: 5.5; temperature: 20 °C)

Slika 3. Dijagram Freundlichove izoterme za biosorpciju Pb (II) i Cd (II) na *C. virgatum* (koncentracija biomase: 4 g/L, vrijeme kontakta: 60 min.; pH: 5.5; temperatura: 20 °C)

The values for Freundlich constants and correlation coefficients (r^2) for the adsorption process are also presented in Table 1. The values of n between 1 and 10 (i.e. $1/n$ less than 1) represent a favorable

adsorption. The values of n , which reflect the intensity of adsorption, also reflected the same trend. The n values obtained for the adsorption process represented a beneficial adsorption.

Table 1. Adsorption isotherm parameters for Pb(II) and Cd(II) biosorption onto *C. virgatum*

Tablica 1. Parametri adsorpcijske izoterme za biosorpciju Pb(II) i Cd(II) na *C. virgatum*

<i>Metals</i>	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	K_L (L/mg)	r^2	K_f (mg/g)(L/mg) ^{1/n}	1/n	r^2
<i>Cd(II)</i>	53.1	3×10^{-2}	0.992	6.54	0.38	0.942
<i>Pb(II)</i>	56.2	2×10^{-2}	0.997	6.26	0.39	0.965

Table 1 shows that the experimental data are better fitted to Langmuir ($r^2 = 0.997$ and 0.992 for Pb(II) and Cd(II), respectively) than Freundlich ($r^2 = 0.965$ and 0.942 for Pb(II) and Cd(II), respectively) adsorption isotherm.

The equilibrium data were also subjected to the Dubinin–Radushkevich (D–R) isotherm model to determine the nature of biosorption processes as physical or chemical. The D–R sorption isotherm is more general than Langmuir isotherm, as its derivation is not based on ideal assumptions such as equipotent of the sorption sites, absence of steric hindrance between sorbed and incoming particles and surface homogeneity on microscopic level [12]. The linear presentation of the D–R isotherm equation [13] is expressed by

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (4)$$

where q_e is the amount of metal ions adsorbed on per unit weight of biomass (mol/L), q_m is the maximum biosorption capacity (mol/g), β is the activity coefficient related to biosorption mean free energy (mol²/J²) and ε is the Polanyi potential [$\varepsilon = RT \ln(1 + \frac{1}{C_e})$].

The D–R isotherm model well fitted the equilibrium data since the R^2 value was found to be 0.991 for Pb(II) biosorption and 0.993 for Cd(II) biosorption (Fig. 4). From the intercept of the plots, the q_m value was found to be 9.5×10^{-4} mol/g for Pb(II) biosorption and 10.1×10^{-4} mol/g for Cd(II) biosorption. The biosorption mean free energy (E , kJ/mol) is as follow:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (5)$$

The E (kJ/mol) value gives information about adsorption mechanism, physical or chemical. If it lies between 8 and 16 kJ/mol, the adsorption process takes place chemically and while $E < 8$ kJ/mol, the adsorption process proceeds physically [14].

The mean biosorption energy was calculated as 10.3 and 10.1 kJ/mol for the biosorption of Pb(II) and Cd(II) ions, respectively.

These results suggest that the biosorption processes of both metal ions onto *C. virgatum* biomass could be taken place by chemical ion-exchange mechanism because the sorption energies lie within 8 – 16 kJ/mol. [15]

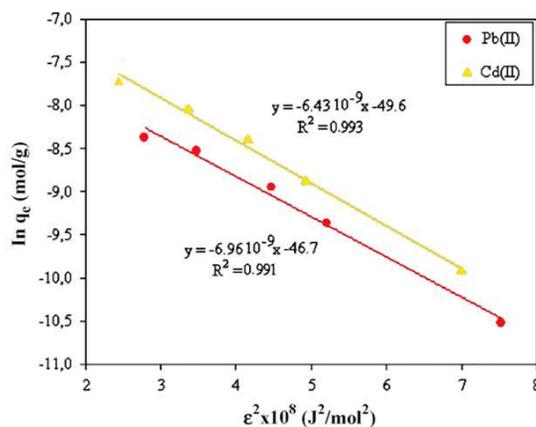


Figure 4. D–R isotherm plots for the biosorption of Pb(II) and Cd(II) onto *C. virgatum* alga (pH: 5.5; biomass concentration: 4 g/L; contact time: 60 min; temperature: 20 °C)

Slika 4. Dijagram D-R izoterme za biosorpciju Pb(II) i Cd(II) na *C. virgatum* (pH: 5.5; koncentracija biomase: 4 g/L; vrijeme kontakta: 60 min.; temperatura: 20 °C)

Adsorption kinetics study

The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid–solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process [16]. The results obtained from the experiments were used to study the kinetics of metal ion adsorption.

The rate kinetics of metal ion adsorption on *C. virgatum* biomass was analyzed using pseudo-first order [17] and pseudo-second order [18].

The conformity between experimental data and the model predicted values was expressed by correlation coefficients (r^2).

The pseudo-first order kinetic model was proposed by Lagergren [15, 17]. The integral form of the model generally expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_t and q_e (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the equation (min^{-1}).

Results obtained by applying the first-order Lagergren model to the experimental data were given in Table 2.

Experimental data were also tested by the pseudo-second order kinetic model which is given in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \quad (7)$$

where k_2 ($\text{gmg}^{-1} \text{min}^{-1}$) is the rate constant of adsorption, q_2 is maximum adsorption capacity (mg g^{-1}) [19]. The values of k_1 , q_e and k_2 , q_2 were obtained from the slopes and intercepts of plots of $\log(q_e - q_t)$ versus t and t/q_t versus t at different temperatures.

The linear plots of t/q_t versus t for the pseudo-second order model for the biosorption of Pb(II) and Cd(II) ions onto the alga biomass at 20–50°C were shown in Figs. 5a and 5b, respectively.

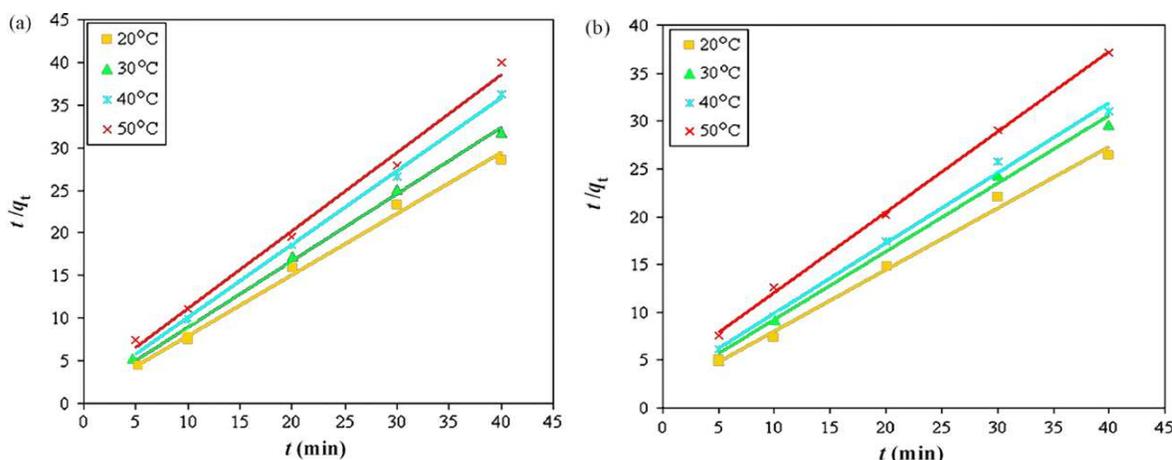


Figure 5. Pseudo-second-order kinetic plots at different temperatures: (a) for Pb(II) biosorption (b) for Cd(II) biosorption (pH: 5.5, biomass concentration: 4 g/l, contact time: 60 min, initial concentration: 10 mg/L)

Slika 5. Dijagram kinetike pseudo drugog reda na različitim temperaturama za biosorpciju (a) Pb (II), (b) Cd (II) (pH: 5.5; koncentracija biomase: 4 g/L; vrijeme kontakta: 60 min.; početna koncentracija: 10 mg/L)

The Pseudo-first-order and pseudo-second-order parameters for the biosorption of Pb(II) and Cd(II) onto *C. virgatum*

biomass at different temperatures were given in Table 2.

Table 2. Pseudo-first-order and pseudo-second-order parameters for the biosorption of Pb(II) and Cd(II) onto *C. virgatum* biomass at different temperatures

Tablica 2. Parametri pseudo prvog i pseudo drugog reda za biosorpciju Pb (II) i Cd (II) na biomasi *C. virgatum* pri različitim temperaturama

Temperature (°C)	$q_{e,exp}$ (mg / g)	Pseudo-first-order			Pseudo-second-oder		
		k_1 (1 /min)	$q_{e1,cal}$	r^2	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e2,cal}$	r^2
Pb(II)							
20	1.42	$4.3 \cdot 10^{-2}$	0.46	0.956	0.25	1.56	0.992
30	1.38	$4.0 \cdot 10^{-2}$	0.44	0.806	0.23	1.41	0.992
40	1.34	$3.4 \cdot 10^{-2}$	0.41	0.867	0.21	1.37	0.995
50	1.30	$3.1 \cdot 10^{-2}$	0.40	0.973	0.19	1.20	0.999
Cd(II)							
20	1.40	$4.5 \cdot 10^{-2}$	0.58	0.785	0.61	1.41	0.993
30	1.36	$4.4 \cdot 10^{-2}$	0.53	0.888	0.57	1.28	0.998
40	1.32	$2.4 \cdot 10^{-2}$	0.48	0.965	0.47	1.18	0.999
50	1.28	$1.9 \cdot 10^{-2}$	0.44	0.893	0.43	1.09	0.992

When the correlation coefficients of models were compared, second order equation has a greater r^2 values. In addition, the theoretical $q_{e2,cal}$ values were closer to the experimental $q_{e,exp}$ values. In the view of

these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Pb(II) and Cd(II) onto *C. virgatum* in contrast to the pseudo-first-order model.

Thermodynamic parameters

Thermodynamic parameters such as Gibbs free energy change ΔG^0 , standard enthalpy change ΔH^0 and standard entropy change ΔS^0 were also found out to give more information about the nature of sorption process [20].

The thermodynamic parameters were calculated by the following equations

$$\ln k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (\text{Van't Hoff equation}) \quad (8)$$

$$\Delta G^0 = -RT \ln k_c \quad (9)$$

where $K_c = (q_e / Ce)$ is the adsorption equilibrium constant, T is absolute temperature (K), R is gas constant.

When $\ln K_c$ versus $1/T$ is plotted (Fig. 6), ΔH^0 and ΔS^0 values can be computed from slope and intercept of the van't Hoff equation. The calculated parameters were given in Table 3.

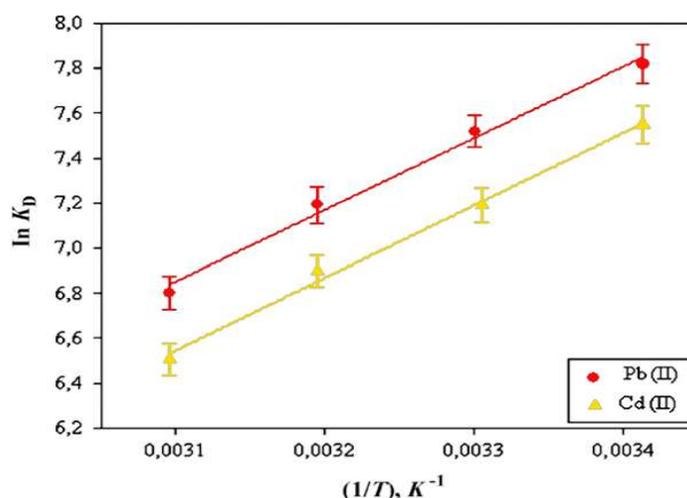


Figure 6. Plot of $\ln K_D$ vs. $1/T$ for the estimation of thermodynamic parameters for biosorption of Pb(II) and Cd(II) onto algal species *C. virgatum*

Slika 6. Dijagram ovisnosti K_D o $1/T$ za proračun termodinamičkih parametara biosorpcije Pb(II) i Cd(II) na vrsti alge *C. virgatum*

The negative ΔG^0 values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in

ΔG^0 value with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures.

Table 3. Thermodynamic parameters for Cd(II) and Pb(II) biosorption onto *C. virgatum***Tablica 3.** Termodinamički parametri za biosorpciju Pb(II) i Cd(II) na *C. virgatum*

Metal ion	T (K)	ΔG^0 (kJmol ⁻¹)	ΔH^0 (kJmol ⁻¹)	ΔS^0 (Jmol ⁻¹ k ⁻¹)
<u>Cd(II)</u>	293	-18.4	-26.8	-28.6
	303	-18.1		
	313	-18.0		
	323	-17.5		
<u>Pb(II)</u>	293	-19.1	-26.5	-25.2
	303	-18.9		
	313	-18.7		
	323	-18.3		

The negative ΔH^0 is indicator of exothermic nature of the biosorption and also its magnitude gives information on the type of biosorption, which can be either physical or chemical.

Therefore, the ΔH^0 values showed that the biosorption processes of Pb(II) and Cd(II) ions onto *C. virgatum* biomass were

taken place via chemisorption. The ΔS^0 parameter was found to be -25.2 J/mol K for Pb(II) biosorption and -28.6 J/mol K for Cd(II) biosorption.

The negative ΔS^0 value suggests a decrease in the randomness at the solid/solution interface during the biosorption process. [15, 21]

FTIR analysis

The functional group is one of the keys to understand the mechanism of metal binding on the algal surface. FTIR was used

to analyze the functional groups in the fresh-dried algal biomass.

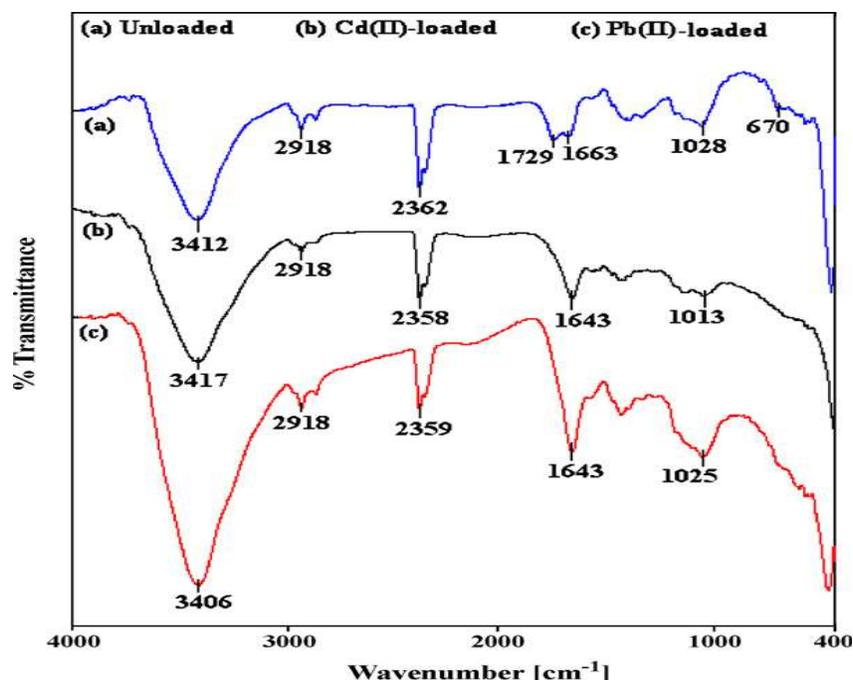


Figure 7. FTIR spectrum of pristine, Pb(II)-loaded and Cd(II)-loaded biomass *C. virgatum*
Slika 7. FTIR spektar Pb(II) i Cd(II) vezanih na biomasu *C. virgatum*

Fig. 7 shows the FTIR spectra of pristine and metal-loaded biomass samples. The peak at 3412 cm^{-1} was due to bounded hydroxyl ($-\text{OH}$) or amine ($-\text{NH}$) groups. The peak at 2918 cm^{-1} can be assigned to the $-\text{CH}$ groups of unloaded biomass sample. The peaks at 1729 cm^{-1} were attributed to stretching vibration of carboxyl group ($-\text{CO}$).

The band observed at 1028 cm^{-1} was assigned to C–O stretching of alcohols and carboxylic acids. Some bands in the fingerprint region could be attributed to the phosphate groups. The asymmetrical stretching vibration at 3412 cm^{-1} was shifted to 3406 and 3417 cm^{-1} after the biosorption of Pb(II)-loaded and Cd(II), respectively.

The changes in $-\text{OH}$ adsorption peak of indicated that the hydroxyl group had been changed from multimer to monopolymer or even dissociative state [22]

which showed that the degree of the hydroxyl polymerization in biomass was decreased by binding of Pb(II) and Cd(II). It offered more opportunity for Pb(II) and Cd(II) to be bound to the hydroxyl or amine groups. The carboxyl peak at 1729 cm^{-1} was observed at 1643 cm^{-1} for both Pb(II) and Cd(II)-loaded biomass. The peak of C–O group was shifted to 1025 cm^{-1} after Pb(II) sorption and 1013 cm^{-1} after Cd(II) sorption.

These results indicated that the free carboxyl groups changed into carboxylate, which occurred during the reaction of the metal ions and carboxyl groups of the biosorbent. Moreover, the ion-exchange process occurred when the metal ions in the solution was transferred from solution to biomass and chemical bonds were formed between the metal ions and the carboxyl ($-\text{CO}$), hydroxyl ($-\text{OH}$), and amine ($-\text{NH}$) groups of the biomass.

Comparison of Pb(II) and Cd(II) removal with different adsorbents reported in literature

The adsorption capacity of *C. virgatum* biomass for the removal of Pb(II) and Cd(II) have been compared with that of different adsorbents reported in literature

and the values of adsorption capacities have been presented in Table 4. The values are reported in the form of monolayer adsorption capacity.

Table 4. Comparison of adsorption capacity of *C. virgatum* biomass for Pb(II) and Cd(II) with that of other adsorbents

Tablica 4. Usporedba kapaciteta adsorpcije biomase *C. virgatum* za Pb(II) i Cd(II) s ostalim adsorbensima

Adsorbents	Biosorption capacity (mg/g)		Reference
	Pb(II)	Cd(II)	
Calcite	19.92	18.52	Yavuz et al., 2007.
Olive cake	19.53	10.56	Doyurum et al., 2006.
Wheat bran	62	21	Farajzadeh et al., 2004.
Cystine-modified biomass	45.9	11.6	J. Yu et al., 2007.
<i>Mucor rouxii</i>	35,7	8,5	G. Yan et al., 2003.
<i>C. virgatum</i>	56.2	53.1	Present study

The experimental data of the present investigations are comparable with the reported values in some cases.

The adsorption capacity varies and it depends on the characteristics of the individual adsorbent, the extent of

surface/surface modification and the initial concentration of the adsorbate. However, it can be noteworthy that the *C. virgatum* alga has important potential for the removal of Pb(II) and Cd(II) ions from aqueous solution.

Desorption efficiency and regenerability

The regeneration of the biosorbent is one of the key factors for assessing of its potential for commercial applications.

Two different desorption agents, 1M HCl (10 mL) and 1M HNO₃ (10 mL), were

used to recover the Pb(II) and Cd(II) ions from the biosorbent.

Higher than 95% of the adsorbed Pb(II) ions were desorbed from the biosorbent. 1M HNO₃ (10 mL) was selected

as desorption agent for Pb(II) and Cd(II) ions from the biosorbent due to the attaining the best regeneration using this solution. On the other hand, the reusability of the

biosorbent was also tested during six consecutive biosorption-desorption cycles (Fig. 8).

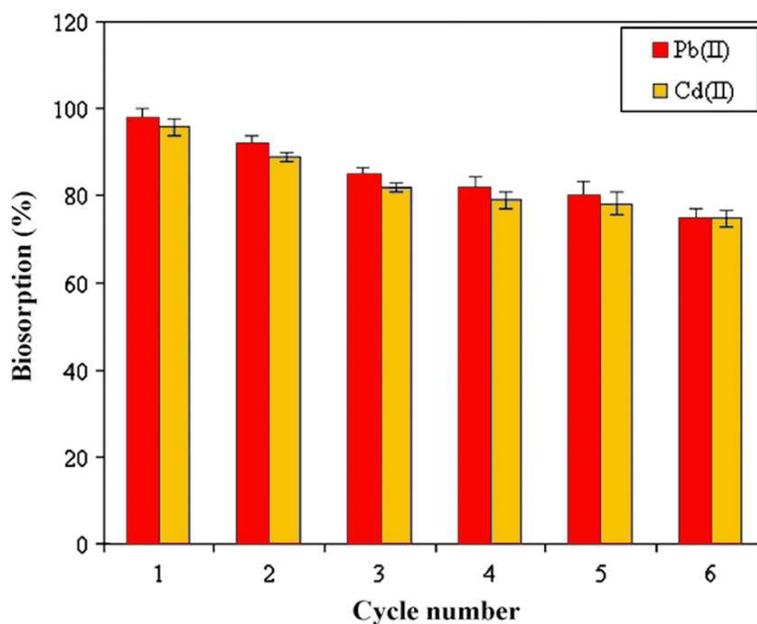


Figure 8. Reusability of *C. virgatum* algae with repeated sorption–desorption cycle (pH: 5.5, biomass concentration: 4 g/l, initial concentration: 10 mg/L)

Slika 8. Višekratno korištenje alge *C. virgatum* s ponovljenim ciklusom sorpcija-desorpcija (pH: 5.5; koncentracija biomase: 4 g/L, početna koncentracija: 10 mg/L)

The lost in the biosorption capacity of the biomass for both metal ions was determined to be 5%. This might be due to the ignorable amount of biomass lost during the adsorption-desorption process. These

results indicated that the *C. virgatum* biomass offers potential to be used repeatedly in Pb(II) and Cd(II) biosorption studies without any detectable loss in the total biosorption capacity.

CONCLUSION

In this study, batch adsorption experiments for the removal of Cd(II) and Pb(II) from aqueous solutions have been carried out using algal biomass (*C. virgatum*). The adsorption characteristics have been examined at different pH values, contact time, adsorbent dosages and temperature.

The Langmuir adsorption isotherm models were better fitted to represent the experimental data.

The monolayer adsorption capacity of *C. virgatum* biomass for Pb(II) and Cd(II) ions was obtained to be 56.2 and 53.1 mg/g, respectively. From the D–R isotherm model,

the mean free energy was calculated as 10.3 kJ/mol for Pb(II) biosorption and 10.1 kJ/mol for Cd(II) biosorption, indicating that the biosorption of both metal ions was taken place by chemical ion-exchange.

Experimental data obtained from rate kinetics were better described by pseudo-second order model than pseudo-first order model as evident from correlation coefficient values (r^2). The calculated thermodynamic parameters (ΔG^0 , ΔH^0 and ΔS^0) showed that the biosorption of Pb(II) and Cd(II) ions onto *C.virgatum* biomass was feasible,

spontaneous and exothermic under examined conditions. It was proven that the carboxyl ($-\text{CO}$), hydroxyl ($-\text{OH}$), and amine ($-\text{NH}$) groups are responsible for the binding of the metal ions. The reusability of the biosorbent was good after six consecutive sorption-desorption cycles. This work illustrated an alternative solution for the management of the unwanted biological materials where *C.virgatum*, one of the fast-growing marine algae, could be, to some extent, utilized as a biosorbent for the removal of heavy metals from the low strength wastewater.

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