

Removal of Cadmium from Aqueous Solution Using Dried Biomass of *Euglena gracilis* var. *bacillaris*[†]

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Abstract: The aim of this work was to evaluate the possibility of applying the dried biomass of *E. gracilis* var. *bacillaris* as a biosorbent for the removal of Cd. Experiments were carried out under conditions of batch systems involving aqueous solutions labelled with ¹⁰⁹CdCl₂. From the kinetics of Cd biosorption, it can be assumed that the Cd removal was a rapid process that achieved the concentration equilibrium of [Cd]_{biomass}: [Cd]_{solution} in the first minutes of the interaction. In individual experiments, the effect of solution pH, initial biosorbent, or Cd concentration was evaluated. According to MINEQL+ speciation modelling, it was found that the biosorption of Cd decreased linearly corresponding to a decrease in the proportion of Cd²⁺ in the solution. The biosorption data were well fitted to the Langmuir model of adsorption isotherm in comparison with the Freundlich model. The maximum biosorption capacity of the dried biomass of *E. gracilis* var. *bacillaris* for the removal of Cd was predicted and reached the value $Q_{max} = 0.13$ mmol/g or 14.1 mg/g (d.w.), respectively.

Keywords: Cd; biosorption; biosorbents; *Euglena gracilis*; adsorption isotherms; speciation



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1. Introduction

Environmental pollution caused by heavy metals is one of the most pervasive problems in the world due to the fact that metals represent non-degradable and persistent contaminants that pose serious risks to both ecosystems and human beings [1]. The discharges of industrial wastewater containing the heavy metals are responsible for the contamination of rivers, lakes, and seas [2]. In the long term, the presence of heavy metals in the food chain [3] may lead to their bioaccumulation in humans, causing health problems [4].

Cadmium (Cd) represents a highly toxic, non-essential, and non-biodegradable heavy metal with a very long biological half-life, ca. 30 years [5]. Cd belongs to the most hazardous Class-I carcinogen and chronic nephrotoxin group [6]. The Agency for Toxic Substances and Disease Registry actually ranked Cd in seventh place within the priority list of hazardous substances based on their frequency of occurrence in the environment, toxicity, and adverse potential to affect human health [7]. Cd shows relatively high physico-chemical similarities with Zn, as an essential nutrient, leading also to significant interactions between these two heavy metals. Earth's crust is rich in Cd sources; however, its prevalence in huge amounts is due to anthropogenic activities, such as electroplating, mining, stabilizing plastics, manufacturing of alloys, cement, pigment, and batteries, fossil fuel combustion, high-phosphate fertilizers, and sewage sludge incineration [8,9]. The maximum contaminant

level for cadmium in drinking water is 5 µg/L, according to the Environmental Protection Agency and the World Health Organization [10,11]. In wastewater and water systems, Cd occurs predominately in the form of Cd²⁺ cations, but it can also be present in the form of inorganic complexes, such as CdCl⁺, CdOH⁺, CdHCO₃⁺, CdCl₃⁻, CdCl₄²⁻, Cd(OH)₃⁻, and Cd(OH)₄²⁻, or organic chelates. However, the most common valence state in the natural environment is Cd²⁺, and the most important factors that control Cd mobility as well as chemical speciation are pH and redox potential [12].

The treatment of industrial wastewater containing heavy metals is a major economic and technical challenge because these contaminants cannot be removed by conventional wastewater treatment [13]. The conventional physico-chemical methods used in wastewater treatment systems and in the removal of heavy metals such Cd include chemical precipitation, adsorption, ion exchange, solvent extraction, and membrane filtration [14]. However, there exist limiting factors in the application of these technologies, such as inefficiency or the higher cost of techniques, energy consumption, incomplete removal of heavy metals, and the formation of potentially toxic by-products [15]. In general, adsorption is a suitable and feasible tool for the removal of metals in comparison to membrane technologies due to its low capital and operating costs and ease of operation, in addition to the potential application of a wide range of solid media for the removal of heavy metals [16].

The use of biomass as an adsorbent has drawn particular interest as microbial biomass can be produced at a low cost and can effectively concentrate heavy metals in the concentration range of 1–100 mg/L [17]. This process, known as biosorption, has the unique advantage that it can be performed in the absence of microbial metabolism, which allows the use of dead biomass, with the consequent economic savings [18]. In biosorption, the heavy metals attached within the cell membrane form a complex, leading to elimination from the environment [19]. Thus, this process is a passive remediation technique involving different mechanisms, such as physical adsorption, ion exchange, complexation, coordination, electrostatic interactions, or microprecipitation [20,21]. Several studies revealed that the presence of functional groups on biosorbent surfaces, such as the hydroxyl, thiol, carboxyl, and amino groups have a crucial role in metals biosorption [14].

A variety of biosorbents exist (e.g., yeast, fungi, bacteria, plants, microalgae) that show immense potential as effective biosorbents due to their high surface-to-area ratios, ubiquity, and ability to remove heavy metals at relatively dilute concentrations [22,23]. Biosorption of heavy metals, metalloids, or radionuclides using algae biomass has become a valuable technology for industrial wastewater treatment due to its lack of chemical requirements, high efficiency in detoxification of the diluted effluents, and low operation and maintenance costs [24]. In heavy metal biosorption, ion exchange is the principal mechanism in the case of algal biomass, which takes place on the surface wall [25].

The flagellate protist algae-like *Euglena gracilis* is a cosmopolitan organism able to grow under heterotrophic, photosynthetic, or photo-heterotrophic conditions [26]. *E. gracilis* has been found to tolerate and accumulate heavy metals [27]. Its metabolic flexibility [28,29], fast growth, and high biomass production under heterotrophic conditions [30,31] make this algal flagellate a suitable candidate for biosorption of heavy metals [32].

Our previous papers dealt with the biosorption of Cd using the dried biomass of freshwater moss *Vesicularia dubyana* [33], bacteria [34], terrestrial moss *Rhytidiadelphus squarrosus* [35], or activated sludge [36]. In this work, the dried biomass of *Euglena gracilis* var. *bacillaris* was applied to assess its ability to remove Cd from wastewater or contaminated solutions. In individual experiments, in addition to the effect of time, solution pH, biomass, and Cd concentration, or to the prediction of sorption parameters based on Langmuir and Freundlich adsorption isotherms models, the effect of Cd speciation in solution on Cd biosorption was also evaluated.

2. Materials and Methods

2.1. Biosorbent Preparation

The biomass of *Euglena gracilis* var. *bacillaris* was obtained by static cultivation of cells in Hutner's medium [37] for 21 d under permanent illumination (30 $\mu\text{mol photons/m}^2\cdot\text{s}$) and at 26 °C. The medium was sterilized through autoclavation at 121 °C for 20 min. After autoclaving, the pH (3.5) of the medium was adjusted using 1 M HCl. After 21 days of cultivation, the biomass yield was 3.4 g (w.w.) per 1 L of Hutner's medium. *E. gracilis* var. *bacillaris* cells were harvested by centrifugation at 4500 rpm for 5 min and washed 5 times with deionized water to remove any remaining medium. To obtain the defined biomass with a particle size of <300 μm , the biomass was dried at 60 °C for 48 h, mechanically homogenized using a mortar and pestle, and sieved through standardized sieves.

2.2. Batch Biosorption Experiments

All biosorption experiments were carried out in 50 cm^3 Erlenmeyer flasks containing 20 cm^3 of CdCl_2 solution of known concentration in deionized water radiolabeled with known initial activity of $^{109}\text{CdCl}_2$. Stock solution of CdCl_2 (1000 $\mu\text{mol/L}$) was prepared by dissolving a defined amount of CdCl_2 (analytical grade; CAS 10108-64-2; Sigma-Aldrich, St. Louis, MI, USA) into deionized water (0.05 $\mu\text{S/cm}$). For each CdCl_2 concentration, pH adjustment was realized using 1 M NaOH or 1 M HCl solution. Dried biomass of *E. gracilis* var. *bacillaris* (standard amount of biosorbent was 0.01 g/20 cm^3 of CdCl_2 solution) with a particle size < 300 μm was suspended in the prepared CdCl_2 solutions and incubation was carried out on a shaker (250 rpm) at 25 °C. Evaporation of water from the surface of the solution was prevented by sealing the necks of the flasks with parafilm. At the end of the exposure, aliquots were taken from the flasks and the biomass was filtered through syringe filters (13 mm diameter; 0.45 μm permeability). The residual Cd concentration in the solution was calculated through the ^{109}Cd activity determined by scintillation gamma spectrometry. The percentage of Cd removal ($Q\%$) and the biosorption capacity (Q_t) were evaluated with the following equations, Equations (1) and (2):

$$Q\% = \frac{A_0 - A_S}{A_0} \times 100 \quad (1)$$

$$Q_t = (C_0 - C_t) \times \frac{V}{M} \quad (2)$$

where $Q\%$ is the percentage of Cd biosorption (%), A_0 is the initial ^{109}Cd activity in the solution (Bq), A_S is the residual ^{109}Cd activity in the solution (Bq), Q_t is the amount of Cd sorbed on the biosorbent ($\mu\text{mol/g}$; d.w.), C_0 and C_t represent the initial concentration of Cd in solution and the concentration of Cd at the end of the experiment ($\mu\text{mol/L}$), respectively, and V and M are the volume of solution (L) and weight of the biosorbent (g; d.w.).

For the purpose of assessing the effect of Cd speciation on its biosorption by prepared biosorbent, the molar amounts of the disodium salt of ethylenediaminetetraacetic acid (EDTA-Na_2) were added to 20 cm^3 of a solution containing 20 $\mu\text{mol/L}$ of CdCl_2 to obtain the proportions of the Cd^{2+} form in the solution of 0%, 20%, 40%, 60%, 80%, and the maximum achievable amount of Cd^{2+} at pH 4.0. The calculation of the molar addition of EDTA-Na_2 was performed based on the prediction of Cd speciation in the solution using the modelling program MINEQL+ ver. 4.62.3.

2.3. Adsorption Isotherms Modelling

The sorption of sorbates shows an exothermic nature and is significantly affected by temperature changes. Therefore, temperature constancy is an essential requirement for obtaining reproducible results and for the analysis of experimental data by adsorption isotherms. The second requirement for the application of adsorption isotherms is reaching the equilibrium between the specific metal biosorption Q_{eq} (in $\mu\text{mol/g}$) and the residual metal concentration in the solution C_{eq} (in $\mu\text{mol/L}$).

The two-parametric Langmuir and Freundlich isotherm models were used to analyze the data of Cd biosorption by the dried biomass of *E. gracilis* var. *bacillaris*.

The Langmuir isotherm model, which operates on the assumptions that adsorption occurs in a monolayer on the solid, all sites are identical and may sorb only a single molecule, and are independent of adjacent site sorption [38], is given by Equation (3):

$$Q_{eq} = \frac{b \times Q_{max} \times C_{eq}}{1 + b \times C_{eq}} \quad (3)$$

where Q_{eq} is the equilibrium specific metal biosorption ($\mu\text{mol/g}$; d.w.); C_{eq} is the equilibrium concentration of metal in the solution ($\mu\text{mol/L}$); Q_{max} is the Langmuir constant characterizing the maximum biosorption capacity of the biosorbent ($\mu\text{mol/g}$; d.w.); b is the Langmuir constant describing the affinity between metal and biosorbent ($\text{L}/\mu\text{mol}$).

The Freundlich isotherm model is an empirical formulation which assumes heterogeneous surface adsorption [39] and is described by Equation (4):

$$Q_{eq} = K \times C_{eq}^{\left(\frac{1}{n}\right)} \quad (4)$$

where Q_{eq} is the equilibrium specific metal biosorption ($\mu\text{mol/g}$; d.w.); C_{eq} is the equilibrium concentration of metal in the solution ($\mu\text{mol/L}$); K is the Freundlich constant related to the biosorption capacity of the biosorbent for metal (L/g ; d.w.); n is the Freundlich constant characterizing the biosorption intensity (dimensionless constant).

2.4. Scintillation Gamma Spectrometry

For the determination of ^{109}Cd activity in the supernatant aliquots, a gamma-spectrometric scintillation detector, 76BP76/3 (Environet, Třebíč, Czech Republic), with well-type crystal NaI(Tl) was used in combination with data processing software ScintiVision-32 (Ortec, Oak Ridge, TN, USA). A library including γ -photon peaks of radionuclides ^{109}Cd ($E_{\gamma} = 88.04$ keV), ^{137}Cs ($E_{\gamma} = 661.66$ keV), and ^{65}Zn ($E_{\gamma} = 1115.52$ keV) was built to calibrate the energies and efficiencies of the ^{109}Cd activity measurements. Gamma-spectrometric measurement with a counting time of 600 s allowed us to obtain the data with an error < 1.5%.

Standard and experimental solutions were prepared using a standardized $^{109}\text{CdCl}_2$ solution (5.206 MBq/ cm^3 , 50 mg/L CdCl_2 in 3 g/L HCl; $T_{1/2} = 462.6$ d) obtained from the Czech Metrological Institute (Prague, Czech Republic).

2.5. Cd speciation and Statistical Analysis of the Data

Prediction of Cd speciation in the model solutions containing different concentrations of EDTA- Na_2 was carried out using the speciation modelling program MINEQL+ ver. 4.62.3 (Environmental Research Software, Hallowell, ME, USA). This program, within the mathematical iterations, applies the USEPA database of thermodynamic constants and the distributions of individual chemical forms of metals in solution and makes predictions depending on the solution pH, temperature, ionic strength, concentration of cations or anions, and for the carbonate system naturally occurring in equilibrium with atmospheric CO_2 ($p\text{CO}_2 = 38.5$ Pa).

All analytical determinations were performed in triplicate. The graphical presentation of the results and the statistical analysis of the data obtained were performed using the program OriginPro ver. 8.5 (OriginLab Corporation, Northampton, MA, USA).

3. Results and Discussion

As shown in Figure 1a, the kinetics of Cd biosorption by the dried biomass of *E. gracilis* var. *bacillaris* from solutions containing 20 $\mu\text{mol/L}$ CdCl_2 and at pH 4.0 was a rapid process that achieved the concentration equilibrium of $[\text{Cd}]_{\text{biomass}}: [\text{Cd}]_{\text{solution}}$ in the first minutes of the interaction. A Cd removal efficiency of 20% (8.2 $\mu\text{mol/g}$; d.w.) was reached after only 20 min of exposure and did not change after this time.

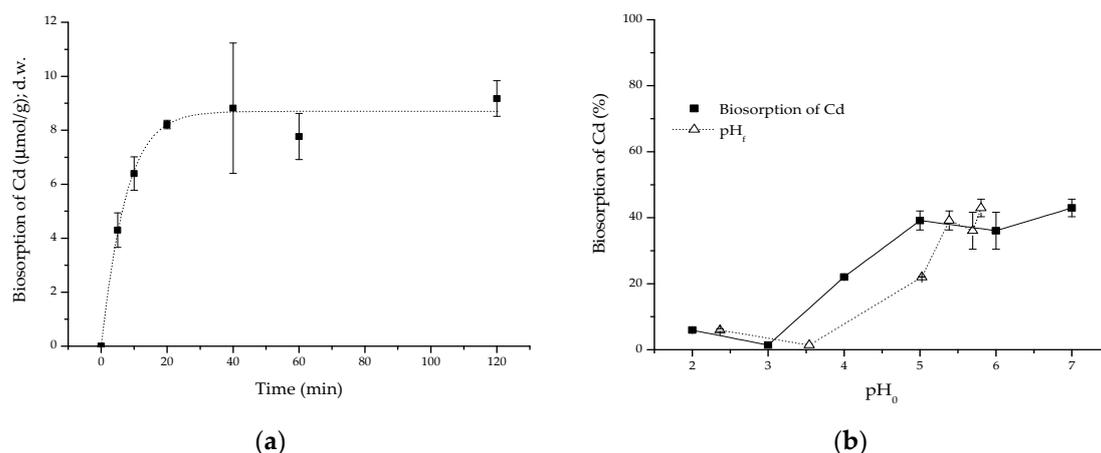


Figure 1. (a) Kinetics of Cd biosorption by dried biomass of *E. gracilis* var. *bacillaris* (biomass concentration $C_B = 0.50$ g/L) from solutions containing $20 \mu\text{mol/L}$ CdCl_2 (radiolabeled with 45.0 kBq/L $^{109}\text{CdCl}_2$) in deionized water, pH 4.0. (b) Effect of initial (pH_0) and final (pH_f) pH values on Cd biosorption by dried biomass of *E. gracilis* var. *bacillaris* (biomass concentration $C_B = 0.50$ g/L) from solutions containing $20 \mu\text{mol/L}$ CdCl_2 (radiolabeled with 44.5 kBq/L $^{109}\text{CdCl}_2$) in deionized water. Exposure of the biomass was carried out on a shaker (250 rpm) for 2 h (effect of pH) and at 25°C . Error bars represent standard deviation of the arithmetic mean of the results of three independent experiments ($\pm\text{SD}$; $n = 3$).

The rapid kinetics demonstrated in this study are confirmed by the results of several other studies. The kinetics of Cd biosorption by the dried biomass of the microalga *Parachlorella* sp. was also studied by Dirbaz and Roosta [40], and they reached the concentration equilibrium after only 20 min. Those authors also found that increased agitation speed had a negative effect on the biosorption efficiency. Also, the time required to achieve the expected equilibrium condition decreased with the increase in the agitation speed. Gu and Lan [41] reported that the biosorption of Pb, Cd, and Zn by the dried biomass of green alga *N. oleoabundans* was rapid, with plateaus achieved within five minutes. At 30 min of contact time, the equilibrium biosorption was achieved for all metals studied.

It is generally known that biosorption kinetics is controlled by several mechanisms, which include (i) bulk diffusion; (ii) external diffusion through a liquid film layer around the biosorbent particles; (iii) intraparticle diffusion; and (iv) reaction rate [42]. It should be noted that by maintaining a well-mixed system with a sufficient agitation speed and avoiding the biosorbent's settling, the contribution to the bulk diffusion can be neglected [43].

In another series of experiments, the effect of the initial pH_0 on Cd biosorption was studied within a range from pH 2.0 to pH 7.0. The applied initial pH_0 value was related to the varying chemical speciation (chemical forms) of Cd as a function of pH. On the basis of speciation modelling realized using MINEQL+ ver. 4.62.3, it was found that at pH = 7 and CdCl_2 concentration $C_0 = 20 \mu\text{mol/L}$, Cd was present, practically, only in the form of free Cd^{2+} cations, and from this value the proportion of the Cd^{2+} form decreased significantly. For example, at pH = 9, the Cd^{2+} form proportion was 92% of the total Cd in solution in addition to the occurrence of CdOH^+ , CdCl^+ , or $\text{Cd}(\text{OH})_2$ forms. It should be emphasized that the total concentration of Cd in solution also plays an important role in this respect, wherein a more significant decrease in the proportion of the Cd^{2+} form can be observed at higher Cd concentrations in solution as a function of pH.

Figure 1b depicts the relationship between the Cd biosorption by the dried biomass of *E. gracilis* var. *bacillaris* from solutions containing CdCl_2 $C_0 = 20 \mu\text{mol/L}$ and the initial pH_0 value of these solutions, as well as the dependence between the pH_f of the solutions at the end of the experiment and the initial pH_0 value. As can be seen, the highest values of biosorption efficiency for Cd 43% ($16.4 \mu\text{mol/g}$; d.w.) were obtained within the range of pH_0 7.0 to pH_0 5.0 and the lowest Cd biosorption values occurred at initial pH_0 values

of 2 and 3. A similar pattern of Cd biosorption was also described by Demey et al. [42], when they found that Cd biosorption by biosorbent prepared from the biomass of alga *Fucus vesiculosus* was essentially unchanged from pH 5.0 to pH 7.0. Depending on the pH, the functional groups, such as carboxyl and phosphoryl groups, can be protonated or unprotonated. At low pH, these functional groups are protonated, which results in the absence of binding sites for the removal of cationic metal ions, whereas more functional groups would be deprotonated with a pH increase and, thus, increase metal biosorption [44]. As was mentioned, the pH of the solution also has an effect on the metal speciation and zeta potential of the biosorbent as well.

Our results also showed that the initial value of $\text{pH}_0 = 6-7$ decreased towards the equilibrium value of $\text{pH}_f = 5.6$ during the experiments. On the other hand, for an initial $\text{pH}_0 = 4$, the pH value increased towards the equilibrium value of $\text{pH}_f = 5.6$. This phenomenon can be explained by the release of substances from the dried biomass of *E. gracilis* var. *bacillaris* that have the ability to buffer the surrounding environment.

Following the above findings, a series of experiments aimed at evaluating the effect of Cd speciation and the proportion of the Cd^{2+} chemical form on the biosorption of Cd by the dried biomass of *E. gracilis* var. *bacillaris* from solutions containing 20 $\mu\text{mol/L}$ CdCl_2 without or with the addition of different amounts of EDTA-Na_2 was carried out. In a first step, the modelling of the occurrences of the different chemical forms of Cd without or in the presence of EDTA-Na_2 at pH 4 and at 25 °C using the speciation program MINEQL+ ver. 4.62.3 was performed. The concentrations of EDTA-Na_2 added to CdCl_2 solutions were chosen in such molar amounts, to 20 $\mu\text{mol/L}$ CdCl_2 , at which it was possible to achieve the proportion of the Cd^{2+} form in solutions of 0%, 20%, 40%, 60%, 80%, and the maximum achievable amount of Cd^{2+} at pH 4.0. This can be seen in Figure 2a, where a linear decrease in the Cd^{2+} form with increases in the concentrations of EDTA-Na_2 in the solution can be observed in favor of the formation of complexed forms CdCl^+ , Cd-EDTA^{2-} , Cd-HEDTA^- , or $\text{Cd-H}_2\text{EDTA}$. The proportions of the mentioned Cd complexes in the solution decreased in the order $\text{Cd-EDTA}^{2-} \gg \text{Cd-HEDTA}^- > \text{Cd-H}_2\text{EDTA} \geq \text{CdCl}^+$.

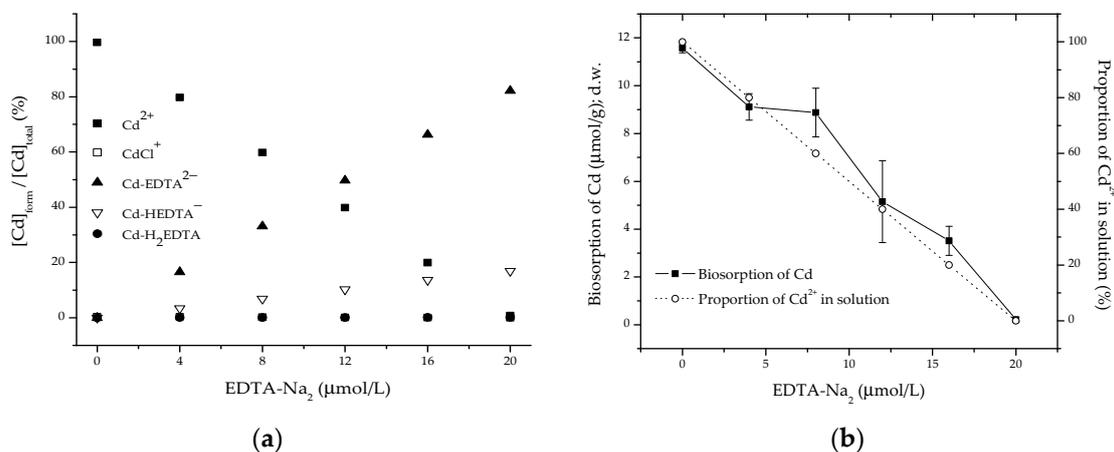


Figure 2. (a) Proportions of chemical forms of Cd in model solutions containing 20 $\mu\text{mol/L}$ CdCl_2 without or with the addition of 4, 8, 12, 16, or 20 $\mu\text{mol/L}$ EDTA-Na_2 . (b) Effect of Cd speciation on Cd biosorption by dried biomass of *E. gracilis* var. *bacillaris* ($C_B = 0.5$ g/L) from model solutions containing 20 $\mu\text{mol/L}$ ZnCl_2 (radiolabeled with 44.7 kBq/L $^{109}\text{CdCl}_2$) without or with the addition of 4, 8, 12, 16, or 20 $\mu\text{mol/L}$ EDTA-Na_2 , pH 4.0. Exposure of the biomass was carried out on a shaker (250 rpm) for 2 h and at 25 °C. Error bars represent standard deviation of the arithmetic mean of the results of three independent experiments ($\pm\text{SD}$; $n = 3$). Cd speciation was predicted using the modelling program MINEQL+ ver. 4.62.3 for pH = 4.0 and 25 °C.

It was found that the biosorption of Cd decreased linearly corresponding to the decrease in the proportion of Cd^{2+} in the solution given by the increasing concentration of

EDTA-Na₂ as a complexing agent in the solution. At an almost 100% initial proportion of the Cd²⁺ form in the solution, a maximum biosorption of 11.6 μmol/g (d.w.) was observed in this series. At the minimum proportion of Cd²⁺ (0.8%) in the solution, a more than 55-fold lower value of specific Cd biosorption (0.21 μmol/g; d.w.) was determined. Our previous work [33] also confirmed that with an increasing addition of NaCl to the solution, the initial presence of Cd²⁺ in the solution decreased in favor of CdCl⁺ formation, which resulted in a decrease in the Cd biosorption by the dried biomass of the moss *Vesicularia dubyana*.

From this result, it can be concluded that Cd will be biosorbed mainly in the form of free Cd²⁺ cations. This finding is important from the point of view of the application of biosorbents in the removal of heavy metals from real wastewater or contaminated solutions, wherein, due to their heterogeneity in terms of the occurrence of inorganic and/or organic substances, it is necessary to take this fact into account as well.

Figure 3 describes the effect of biomass concentration, C_B , ranging from 0.25 to 2.5 g/L on Cd biosorption by the dried biomass of *E. gracilis* var. *bacillaris* from solutions with an initial Cd concentration of $C_0 = 20$ μmol/L. It was shown that the specific biosorption of Cd expressed in μmol/g (d.w.) decreased with an increasing biosorbent dose, while the removal efficiency (in %) increased slightly and linearly ($R^2 = 0.888$) with increasing biosorbent concentration. A similar observation has been reported by Cheng et al. [45] in the investigation of biosorption of Cd by the dead biomass of *Chlorella vulgaris*, when they confirmed that the removal efficiency of *C. vulgaris* increased from 89 to 95% as the adsorbent dosage was increased from 0.18 to 18 mg, and the biosorption capacity decreased with an increase in algal dose. This decrease can be due to the concentration gradient between the biosorbent and the sorbate–heavy metals; an increase in biosorbent concentration causes a decrease in the biosorption capacity or specific biosorption. Moreover, the increase in the biosorption of metals by increasing the biosorbent dose is due to an increase in the number of active sites and available surface area [46].

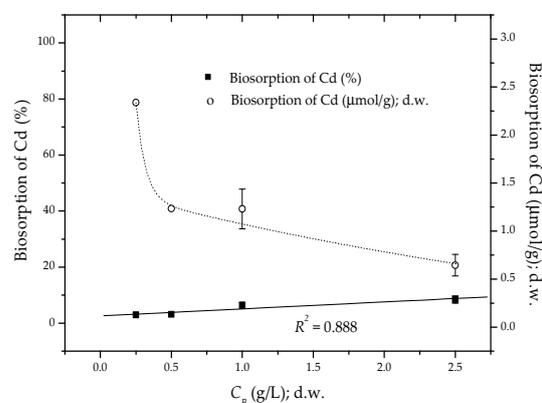


Figure 3. Effect of biomass concentration, C_B , on Cd biosorption by dried biomass of *E. gracilis* var. *bacillaris* from solutions containing 20 μmol/L CdCl₂ (radiolabeled with 44.9 kBq/L ¹⁰⁹CdCl₂) in deionized water, pH 4.0. Exposure of the biomass was carried out on a shaker (250 rpm) for 2 h and at 25 °C. Biosorption of Cd expressed in μmol/g (d.w.) and in % of total Cd in solution. Error bars represent standard deviation of the arithmetic mean of the results of three independent experiments (\pm SD; $n = 3$).

Similarly, the effect of an initial Cd concentration ranging from 1 to 80 μmol/L CdCl₂ on Cd biosorption by the dried biomass of *E. gracilis* var. *bacillaris* was also evaluated. As can be seen from Figure 4, the dependence of the Cd biosorption efficiency (in %) on the initial CdCl₂ concentration did not have a clear pattern. In contrast, however, the specific biosorption efficiency (in μmol/g; d.w.) increased linearly ($R^2 = 0.975$) with increasing initial Cd concentration in solution. Based on this fact, it can be argued that even at the highest concentration applied (80 μmol/L CdCl₂), saturation of the biosorbent was not observed, or active sites remained available on the surface of the biosorbent,

respectively. Montazer-Rahmati et al. [46] characterized the biosorption capacity of marine algae *Cystoseira indica* and *Nizimuddinia zanardini* as a function of the initial concentrations of Cd, Ni, and Pb. They observed that the metal biosorption capacity increases with an increase in the initial metal ion concentration and explained it by the fact that increasing the initial metal concentration provides a larger driving force to overcome all mass transfer resistances between the solid and the aqueous phase, resulting in higher metal biosorption.

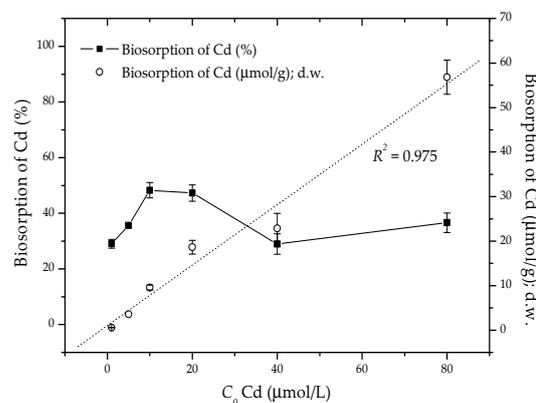


Figure 4. Effect of initial Cd concentration on Cd biosorption by dried biomass of *E. gracilis* var. *bacillaris* (biomass concentration $C_B = 0.50 \text{ g/L}$) from solutions prepared in the form of CdCl_2 (radiolabeled with $47.5 \text{ kBq/L } ^{109}\text{CdCl}_2$) in deionized water, pH 4.0. Exposure of the biomass was carried out on a shaker (250 rpm) for 2 h and at $25 \text{ }^\circ\text{C}$. Biosorption of Cd expressed in $\mu\text{mol/g}$ (d.w.) and in % of total Cd in solution. Error bars represent standard deviation of the arithmetic mean of the results of three independent experiments ($\pm\text{SD}$; $n = 3$).

Due to the fact that the biosorption of Cd by the dried biomass of *E. gracilis* var. *bacillaris* was a rapid process that achieved the concentration equilibrium of $[\text{Cd}]_{\text{biomass}} : [\text{Cd}]_{\text{solution}}$ within 20 min of exposure at constant temperature, it was possible to carry out a mathematical description of the data obtained in the study of the effect of the initial concentration of CdCl_2 in solution on the biosorption of Cd. For these purposes, the adsorption isotherms according to the Langmuir and Freundlich models in their nonlinear forms were applied. The description of the data obtained using a nonlinear regression method is shown in the plot of Figure 5. The relationship between the biosorption capacity, Q_{eq} , and Cd concentration in solution, C_{eq} , at equilibrium showed that the biosorption of Cd increased with the equilibrium concentration of Cd in solution, progressively, until the biosorbent’s saturation. Experimental data were slightly better fitted by the Langmuir adsorption isotherm ($R^2 = 0.999$) than the Freundlich adsorption isotherm ($R^2 = 0.997$). The Langmuir isotherm model implies a monolayer adsorption of the metals on the surfaces of biosorbents. The parameters predicted from the Langmuir and Freundlich models of adsorption isotherm, such as the maximum biosorption capacity, Q_{max} , Langmuir affinity constant b , Freundlich constants K and n , are summarized in Table 1.

Table 1. The obtained parameters of adsorption isotherms according to Langmuir and Freundlich models. Details of the experiment are described in Figure 4.

Langmuir Adsorption Isotherm			Freundlich Adsorption Isotherm			
$Q_{max} (\mu\text{mol/g})$	$b (\text{L}/\mu\text{mol})$	R^2	$K (\text{L/g})$	$1/n$	n	R^2
125 ± 8	0.0163 ± 0.0017	0.999	2.96 ± 0.49	0.753 ± 0.044	1.33 ± 0.08	0.997

To compare the ability of the dried biomass of *E. gracilis* var. *bacillaris* to remove Cd from model solutions, in Table 2 we summarized the Q_{max} values obtained by other authors when different biosorbents derived from macro- or microalgal biomasses were applied as biosorbents for Cd removal from single-component solutions. From the comparison,

it is clear that for Cd biosorption, we did not obtain comparable data with those of other authors applying the different types of algal biomasses as biosorbents. These vastly different biosorption capacities for the same heavy metal by the same biosorbent or algal biomass are compatible with a commonly observed phenomenon. The biosorption capacity of algal biomass is dependent on many parameters, including the medium and condition of algal cultivation, the physiological state when algae were harvested, the condition of the drying process, as well as the biosorption conditions, such as the pH, metal concentration, incubation time, and biosorbent dose [47].

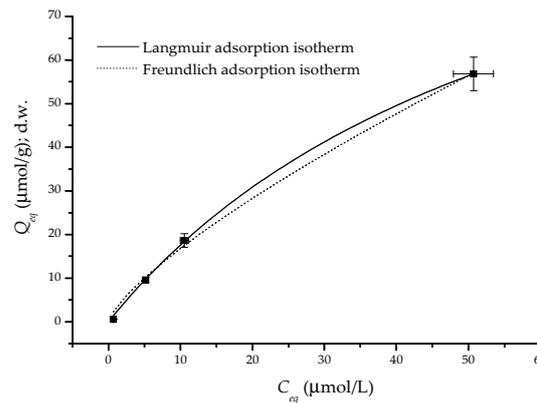


Figure 5. Description of Cd biosorption by dried biomass of *E. gracilis* var. *bacillaris* (biomass concentration $C_B = 0.50$ g/L) using adsorption isotherms according to Langmuir and Freundlich. Details of the experiments are described in Figure 4. Error bars represent standard deviation of the arithmetic mean of the results of three independent experiments (\pm SD; $n = 3$).

Table 2. Comparison of Q_{max} values quantifying Cd biosorption by biosorbents derived from macro- or microalgal biomasses.

Biosorbent	Maximum Biosorption Capacity Q_{max}		Reference
	(mmol/g); d.w.	(mg/g); d.w.	
<i>Fucus vesiculosus</i> (brown macroalgae)	1.27	143	Moreira et al. [48]
<i>Scenedesmus quadricauda</i> (green microalgae)	1.20	135	Mirghaffari et al. [49]
<i>Sargassum polycystum</i> (brown marine macroalgae)	0.93	105	Jayakumar et al. [50]
<i>Fucus vesiculosus</i> (brown macroalgae)	0.87	97.8	Demey et al. [42]
<i>Parachlorella</i> sp. (green microalgae)	0.76	86.1	Dirbaz and Roosta [40]
<i>Sargassum filipendula</i> (brown marine macroalgae)	0.42	47.2	Verma et al. [51]
<i>Neochloris oleoabundans</i> (green microalgae)	0.39	43.9	Gu and Lan [41]
<i>Chlorella vulgaris</i> (green microalgae)	0.19	21.4	Gu and Lan [44]
<i>Cystoseira indica</i> (brown marine macroalgae)	0.17	19.6	Montazer-Rahmati et al. [46]
<i>Chlorella vulgaris</i> (green microalgae)	0.15	16.7	Cheng et al. [45]
<i>Euglena gracilis</i> var. <i>bacillaris</i>	0.13	14.1	This work

4. Conclusions

In this work, the possibility of applying the dried biomass of *E. gracilis* var. *bacillaris* as a biosorbent for the removal of Cd from aqueous solutions was evaluated through batch biosorption experiments.

The kinetics of Cd biosorption by the dried biomass of *E. gracilis* var. *bacillaris* from solutions containing 20 $\mu\text{mol/L}$ CdCl_2 and at pH 4.0 showed that it was a rapid process that achieved the concentration equilibrium of $[\text{Cd}]_{\text{biomass}}: [\text{Cd}]_{\text{solution}}$ in the first minutes of the interaction. The highest values of biosorption efficiency for Cd, 43% (16.4 $\mu\text{mol/g}$; d.w.), were obtained within the range of pH₀ 7.0 to pH₀ 5.0, and the lowest Cd biosorption values occurred at initial pH₀ values of 2 and 3. Attention has separately been focused on the effect of Cd speciation on its biosorption. According to MINEQL+ speciation modelling, a linear decrease in the Cd^{2+} form with increases in the concentration of EDTA- Na_2 in the solution was observed in favor of the formation of complexed forms CdCl^+ , Cd-EDTA^{2-} , Cd-HEDTA^- , or $\text{Cd-H}_2\text{EDTA}$. It was found that the biosorption of Cd decreased linearly, corresponding to decreases in the proportion of Cd^{2+} in the solution given by the increasing concentration of EDTA- Na_2 as a complexing agent in the solution. At an almost 100% initial proportion of the Cd^{2+} form in the solution, a maximum biosorption of 11.6 $\mu\text{mol/g}$ (d.w.) was observed in this series. At the minimum proportion of Cd^{2+} (0.8%) in the solution, a more than 55-fold lower value of specific Cd biosorption (0.21 $\mu\text{mol/g}$; d.w.) was determined. The specific biosorption of Cd, expressed in $\mu\text{mol/g}$ (d.w.), decreased with a biosorbent dose increasing from 0.25 to 2.5 g/L, while the removal efficiency (in %) increased slightly and linearly ($R^2 = 0.888$) with an increasing biosorbent concentration. The obtained biosorption data were well fitted to the Langmuir model of adsorption isotherm in comparison with the Freundlich model. Also, from the Langmuir model of adsorption isotherm, the maximum biosorption capacity of the dried biomass of *E. gracilis* var. *bacillaris* for the removal of Cd was predicted and reached the value $Q_{\text{max}} = 0.13$ mmol/g or 14.1 mg/g (d.w.), respectively.

From the obtained results, it can be concluded that dried biomass of *E. gracilis* var. *bacillaris* could be used as a cost-effective, efficient, and environmentally friendly biosorbent for the removal of Cd from wastewater or contaminated water. However, limiting factors for the utilization of this type of biosorbent include their relatively low selectivity and stability, especially in terms of their regeneration or their reuse over long periods of time. Also, an important issue is their further treatment after use as hazardous waste. In particular, solidification or controlled incineration is expected. In some cases, controlled incineration could lead to the recovery of precious metals.

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