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Removal of Cd by dried biomass of freshwater moss *Vesicularia dubyana*: batch and column studies

Anna Šuňovská, Veronika Hasíková, Miroslav Horník*, Martin Pipíška, Stanislav Hostin, Juraj Lesný

Faculty of Natural Sciences, Department of Ecochemistry and Radioecology, University of SS. Cyril and Methodius in Trnava, Nám. J. Herdu 2, SK-917 01 Trnava, Slovak Republic, Tel. +421 33 59 21 452; Fax: +421 33 59 403; emails: anna.sunovska@ucm.sk (A. Šuňovská), v.hasikova@gmail.com (V. Hasíková), hornik@ucm.sk (M. Horník), pipiska@ucm.sk (M. Pipíška), Tel. +421 33 59 21 454; Fax: +421 33 59 403; email: hostin@ucm.sk (S. Hostin), Tel. +421 33 59 21 455; Fax: +421 33 59 403; email: lesny@ucm.sk (J. Lesný)

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ABSTRACT

Adsorption of Cd by dried biomass of the freshwater moss *Vesicularia dubyana* from model solutions under conditions of batch and continuous column systems was studied using γ-spectrometry and $^{109}CdCl_2$ as radiotracer. The Cd adsorption by moss biomass was a rapid process and concentration equilibrium was reached within 60 min of exposure. The efficiency of the adsorption process and removal of Cd from the solutions was significantly dependent on the value of pH (2–8), initial concentration of $CdCl_2$ (20–320 μM) and changes in Cd speciation induced by the presence of Cl^- anions in the solutions. Experimental data of Cd adsorption by designed packed bed column system comprising dried moss biomass at an initial concentration 36 mg/l $CdCl_2$ and flow rate 0.80 ml/min of solution in the column were well described by adsorption kinetic models according to the Clark ($R^2 = 0.981$), Thomas ($R^2 = 0.964$) or Yoon–Nelson ($R^2 = 0.962$) and modified dose–response ($R^2 = 0.954$) models. The suitability of the mentioned models was also evaluated on the basis of differences in the values of root mean square errors, residual sum of squares or corrected Akaike's information criterion. Adsorbed Cd was removed from the dried moss biomass with high efficiency (>92%) by desorption with 0.1 M HCl or EDTA-Na_2 solutions under batch conditions, whereby the desorption efficiency D_{eff} decreased in the order: 0.1 M HCl (93%) ≈ 0.1 M EDTA-Na_2 (92%) > 0.1 M $ZnCl_2$ (85%) > deionized water (20%). The high desorption efficiency in the case of 0.1 M EDTA-Na_2 was also confirmed under conditions of a continuous column system.

Keywords: Cadmium; Adsorption; *Vesicularia dubyana*; Biosorbent regeneration; Speciation; Mathematical modelling

*Corresponding author.

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1. Introduction

Heavy metals and radionuclides in soils and waters are considered as a serious problem worldwide because these elements are toxic, non-biodegradable and can be distributed within the food chain. Cadmium (Cd) is one of the most toxic metals affecting the environment and human health. 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 [1]. First, second and third places in the mentioned priority list belong to arsenic (As), lead (Pb) and mercury (Hg), respectively. Adverse health effects due to Cd are well documented and it has been reported to cause renal disturbances, lung insufficiency, bone lesions, cancer and hypertension in humans [2].

The presence as well as behaviour of Cd in the environment and related health aspects has been reviewed by Kabata-Pendias [3]. Cd enters into the environment mainly through wastewater disposal from electroplating, smelting, mining and metal refining processes, plastic, pigment and battery manufacturing, or application of phosphate fertilizers. Most wastes and wastewaters containing Cd are released into the water systems of lakes or rivers and marine water as well. In the mentioned waters, Cd occurs predominately in the form of Cd^{2+} cations, but it can also be present as several types of complex ions, such as $CdCl^+$, $CdOH^+$, $CdHCO_3^+$, $CdCl_3^-$, $CdCl_4^{2-}$, $Cd(OH)_3^-$ and $Cd(OH)_4^{2-}$, or organic chelates. However, the most common valence state for Cd in the natural environment is Cd^{2+}, and the most important factors that control Cd mobility as well as chemical speciation are pH and redox potential [3].

Contamination of water systems with heavy metals and their presence in wastewaters represent a challenge for the development of new, alternative, environmentally friendly and economically acceptable remediation methods. Conventional remediation methods for the removal of heavy metals from wastewaters include chemical precipitation, evaporation, coagulation, ion exchange, membrane processing, electrolytic and adsorption technologies [4–6]. The selection of a particular treatment technique depends notably on a variety of factors, e.g. type and concentration of contaminants, effluent heterogeneity and required level of clean up, as well as economic factors [7]. In this context, the requirements of readily available and low-cost materials as adsorbents also play an important role. The mentioned factors represent an open challenge to the scientific community in the research and development as well as application of compounds and materials of biological origin in this regard.

The application of different kinds of biological materials as biosorbents for the removal of heavy metals or radionuclides from wastewaters or contaminated liquids is presented as an alternative approach in adsorption technologies. The technical aspects as well as advantages and constraints of biosorbent application for the remediation of contaminated waters have been described in many reviews [8,9] and monographs [10,11]. Non-viable or dead biomass is preferred rather than vital biomass, and different types of non-living biomass have been studied for their metal adsorption capacities and suitability for adsorption systems involving bacteria [12,13], yeast [14], fungi [15], algae [16,17], water plants or mosses [18,19], plant materials [20,21] and waste products from industrial or agricultural operations [22,23]. The biomass of aquatic plants, algae and terrestrial plants represent biological resources available in large quantities that can be used for the development of potential adsorbent materials [24]. Generally, adsorption processes are affected by several factors. These factors include the properties of the biosorbent and physicochemical characteristics of the solution, such as temperature, pH, initial metal ion or biosorbent concentration and also metal speciation. Many authors have concluded that the application of continuous column adsorption systems has greater advantages than batch adsorption systems, particularly from the point of view of practical realization of wastewater or contaminated liquid decontamination. Therefore, continuous column adsorption studies including biosorbent application need to be performed. Adsorption processes carried out in packed bed columns containing mainly algal, fungal and bacterial biomass have been widely investigated [25–27]. However, applications of freshwater plant or moss biomass in the mentioned adsorption systems have been reported only sporadically in scientific databases [28].

Aquatic mosses have been used in various biomonitoring investigations of surface water pollution as bioindicators, given their wide geographical distribution and lack of well-developed cuticula and vascular tissues that make them sensitive to environmental pollutants [29]. In this context, the biomass of aquatic mosses also represents a potential biosorbent for the removal of toxic metals and radionuclides from contaminated liquids or wastewaters.

In our previous papers, we characterized the adsorption of Co and Sr by freshwater algae and terrestrial moss biomass under batch conditions [30,31] as well as the adsorption of the textile dyes thioflavine T and malachite green by dried biomass of the

microalgae *Chlorella pyrenoidosa* immobilized in polyurethane foam under conditions of continuous column systems [32]. The aim of this work was to quantitatively evaluate the process of Cd adsorption by dried biomass of the freshwater moss *Vesicularia dubyana* in batch and continuous column systems using ^{109}Cd as a radiotracer and γ-spectrometry. In the batch experiments, we studied the effects of time, Cd ion concentration, pH and Cd speciation in the solution on these processes. Also, the possibility of moss biomass regeneration as biosorbent was demonstrated under conditions of batch and continuous column systems.

2. Materials and methods

2.1. Biomass

Biomass of freshwater moss *V. dubyana* was obtained from artificial ponds of Rataj and Son Company (Czech Republic). *V. dubyana* was cultivated in 25% Hoagland nutrient solution [33] under controlled laboratory conditions (22 ± 2°C and a 12 h/12 h light/dark cycle at an illumination of 2,000 lx). Before carrying out the adsorption experiments, the moss biomass was washed three times with deionized water and dried at 60°C for 48 h.

2.2. Batch adsorption experiments

Analytical grade $CdCl_2$ salt was used as the metal source. Solutions were prepared in deionized water and spiked with a standardized $^{109}CdCl_2$ solution (3.937 MBq/ml, 50 mg/l $CdCl_2$ in 3 g/l HCl) obtained from the Czech Metrological Institute (Prague, Czech Republic). The initial pH 4 was adjusted with 1 M HCl or NaOH solutions. Dried biomass of *V. dubyana* was transferred into Erlenmeyer flasks containing solutions with initial concentrations of $CdCl_2$ of 20, 40, 80, 160 or 320 μM and the exposure to the moss biomass was carried out on a rotary incubation shaker (25°C; 250 rpm). The adsorption kinetics was studied within the time 10–1,440 min. The equilibrium data describing the effect of pH and Cd speciation on Cd adsorption were obtained during 120 min of biomass exposure. At the end of the experiments, the contents of the flasks were filtered to separate the biomass from the solution. The remaining radioactivity from ^{109}Cd in the filtrates and the adsorbed ^{109}Cd radioactivity on the moss biomass were analysed by scintillation γ-spectrometry. From the obtained primary data, the percentage of Cd adsorption $Q_{\%}$ and the specific adsorption Q_S (μmol of metal adsorbed per g of dried moss biomass) were calculated using the following equations:

$$Q_{\%} = \frac{A_B}{A_S} * 100 \quad (1)$$

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

where $Q_{\%}$ is the percentage of Cd adsorption (%), A_B is the ^{109}Cd radioactivity adsorbed on moss biomass (Bq), A_S is the initial ^{109}Cd radioactivity in solution (Bq), Q_S is the amount of Cd adsorbed on moss biomass (μmol/g; d.w.), C_0 and C_t represent the initial concentration of $CdCl_2$ in solution and the concentration of $CdCl_2$ at the end of the experiment (μM), respectively, and V and M are the volume of solution (l) and weight of moss biomass (g; d.w.) in the experiments.

The desorption experiments regarding Cd removal from *V. dubyana* moss biomass were carried out with 0.1 M $ZnCl_2$, 0.1 M EDTA-Na_2 or 0.1 M HCl solutions, and deionized water under the mentioned conditions of the batch experiments. The ^{109}Cd radioactivity leached from the moss biomass into the supernatant was determined and the desorption efficiency D_{eff} was calculated using the following equation:

$$D_{eff} = \frac{A_D}{A_B} * 100 \quad (3)$$

where D_{eff} is the desorption efficiency (%), A_D is the ^{109}Cd radioactivity released from the moss biomass into the supernatant (Bq) and A_B is the ^{109}Cd radioactivity adsorbed on the moss biomass before carrying out the desorption experiment.

2.3. Column adsorption experiments

Column adsorption experiments were performed in a glass column with an inner diameter of 0.8 cm and with freely packed moss biomass (0.05 g; d.w.) up to a bed height of 21 cm and bed volume of 10 ml, respectively. A solution of $CdCl_2$ with known concentration, ^{109}Cd radioactivity and flow rate provided by a Pumpenantrieb 5201 (Heidolph, Deutschland) peristaltic pump was passed through the dried moss biomass in down-flow mode. Samples of the outlet solution (effluent) were collected at regular time or volume intervals by a Frac-920 (GE Healthcare Bio-Science AB, USA) fraction collector and analysed considering the remaining ^{109}Cd radioactivity or value of pH.

γ-spectrometric analysis of ^{109}Cd radioactivity in the moss biomass and $CdCl_2$ solution run through the column allowed the specific Cd adsorption (Q_{SA}) to be determined on the basis of the following equation:

$$Q_{SA} = \frac{A_B * C_T}{M * A_C} \quad (4)$$

where Q_{SA} is the specific Cd adsorption (mg/g; d.w.), A_B is the radioactivity of ^{109}Cd adsorbed on the moss biomass (Bq), C_T is the total amount of Cd in the solution run through the column (mg), A_C is the ^{109}Cd radioactivity in the solution run through the column (Bq) and M is the amount of moss biomass (g; d.w.).

Obtained dependencies between the ratio of the Cd concentration in the outlet solution (C_0) to the inlet solution (C_i) and time of exposure t or volume of effluent V_{eff} were described by mathematical kinetic models mainly originating from studies focused on the adsorption of compounds by activated carbon or ion exchange as well as from chromatography [34]. For the evaluation of Cd adsorption by moss biomass under conditions of continuous column systems, the following models were used:

Bohart–Adams model [35]

$$\frac{C_0}{C_i} = \exp\left(k_{BA}C_i t - k_{BA}N_0\frac{Z}{U_0}\right) \quad (5)$$

Thomas model [36]

$$\frac{C_0}{C_i} = \frac{1}{1+\exp\left(\frac{k_{TH}}{F}\left(Q_{\max}M - C_i V_{eff}\right)\right)} \quad (6)$$

Yoon–Nelson model [37]

$$\frac{C_0}{C_i} = \frac{\exp(k_{YN}t - \tau k_{YN})}{1+\exp(k_{YN}t - \tau k_{YN})} \quad (7)$$

Modified dose–response (MDR) model [38]

$$\frac{C_0}{C_i} = 1 - \frac{1}{1+\left(\frac{V_{eff}}{b_{mdr}}\right)^{a_{mdr}}} \quad (8)$$

Clark model [39]

$$\frac{C_0}{C_i} = \left(\frac{1}{1+\left(\frac{C_i^{n-1}}{C_{break}^{n-1}}-1\right)e^{rt_{break}}e^{-rt}}\right)^{1/n-1} \quad (9)$$

where C_0 and C_i are the outlet and inlet metal concentrations (mg/l or mg/ml), k_{BA} is the Bohart–Adams rate constant (ml/mg.min), t is the time (min), N_0 is the bed saturation capacity (mg/ml), Z is the bed height (cm), U_0 is the superficial velocity (cm/min), k_{TH} is the Thomas rate constant (ml/mg.min), F is the flow rate (ml/min), Q_{max} is the maximum adsorption capacity of the biosorbent (mg/g; d.w.), M is the biosorbent weight (g), V_{eff} is the volume of the effluent (ml), k_{YN} is the Yoon–Nelson rate constant (l/min), τ is the time required for 50% adsorbate breakthrough, when $C_0/C_i = 0.5$ (min), a_{mdr} and b_{mdr} are MDR model constants, n is the Freundlich constant, r is the adsorption rate (mg/l min) and C_{break} and t_{break} are the breakthrough concentration (mg/l) and time (min).

Desorption of Cd from *V. dubyana* moss biomass was performed by two-step desorption with deionized water and 0.1 M EDTA-Na_2 under conditions defined in the above-mentioned column adsorption experiments.

2.4. Radiometric analysis

Two γ-spectrometric scintillation well type NaI(Tl) detectors, 54BP54/2-X and 76BP76/3 (Scionix, Netherlands), were used in combination with ScintiVision-32 (Ortec, USA) data processing software for ^{109}Cd radioactivity determinations in moss biomass and solution samples. A library of radionuclides was built by selecting characteristic γ-ray peaks (88.04 keV for ^{109}Cd; 661.66 keV for ^{137}Cs; 1,115.52 keV for ^{65}Zn and 1,173.24 keV for ^{60}Co) for energy and efficiency calibration. γ-spectrometric measurement with a counting time of 600 s allowed the data to be obtained with an error <1.5%.

2.5. Prediction of Cd speciation

The chemical equilibrium modelling software MINEQL+ ver. 4.62.3 was used to predict the Cd speciation in the applied model solutions. This software employs chemical equilibrium models to calculate metal speciation and solubility equilibria in the laboratory or in natural aqueous systems under a variety of conditions including a gas phase with constant partial pressure, pH, temperature, ionic strength and concentrations of cations and anions.

2.6. Statistical analysis

All analytical determinations were performed in triplicate. The statistical significance of differences in the calculated values of Cd desorption from the moss biomass were evaluated by a multiple range test to ascertain differences between individual groups. The level of significance p was 0.05. OriginPro ver. 8.5 (OriginLab Corp., USA), SYSTAT ver. 13 (Systat Software

Inc., USA) and SigmaPlot ver. 12 (Systat Software Inc., USA) programs were used for non-linear regression and statistical analysis of the obtained data.

3. Results and discussion

3.1. Effect of contact time and concentration of $CdCl_2$

Fig. 1 depicts the kinetics of Cd adsorption Q_S (in μmol/g; d.w.) by dried biomass of the freshwater moss *V. dubyana* at different initial $CdCl_2$ concentrations (20–320 μM) and pH 4. It was found that Cd adsorption was a rapid process within the first 60 min and after this time the concentration equilibrium had been reached at all studied $CdCl_2$ concentrations. A similar effect was described by Deng et al. [40] for Cd adsorption by biomass of the algae *Cladophora fascicularis*. The adsorption capacity of the dried moss biomass for Cd increased with increasing initial concentration of $CdCl_2$ due to the higher probability of collisions between Cd and the moss biomass. The maximum adsorption capacities were calculated to be in the range Q_S = 31–287 μmol/g (d.w.).

Generally, adsorption processes are described as ionic exchanges between functional groups (mainly carboxyl, hydroxyl, phosphoryl, amino groups, etc.) on the surface of biosorbents and metal ions [41]. However, vital cells or tissues of higher organisms can also accumulate metal ions by passive or active and non-specific or specific transport systems. Given this consideration, a control experiment with vital moss biomass was carried out under the same conditions as in the experiment with dried biomass. In comparison with the Cd adsorption onto dried moss biomass, the kinetics of Cd uptake by vital biomass under non-growth conditions showed a significantly different trend (Fig. 2). First, a rapid phase identical with the kinetic behaviour of Cd adsorption by dried biomass was observed, but without reaching the concentration equilibrium. This rapid phase of Cd uptake by vital moss biomass was followed by a gradual increase in Cd binding by the moss biomass with time. This fact was also confirmed by achieving a higher Cd uptake by vital biomass (417 μmol/g; d.w.) after 24 h interaction with 320 μM $CdCl_2$ solution in comparison with Cd adsorption by dried biomass (287 μmol/g; d.w.). Similar results were also found by Ngu et al. [42] for Cd, As and Pb uptake by dead and vital biomass of three strains of the *Fusarium* genus.

3.2. Effect of pH and Cd speciation

The decisive parameter in metal ion adsorption is the pH value of the solution, which affects the adsorption capacity of sorbents mainly due to changes in the dissociation of relevant functional groups on the sorbents. In addition to this, the pH also affects the chemical speciation of metals or radionuclides in solution in terms of qualitative and quantitative proportion of different individual chemical forms of metals. To calculate the individual ionic forms of Cd and their abundance in deionized water after adding $CdCl_2$ at defined temperature and pH, the chemical equilibrium modelling software MINEQL+ was applied. We found that at an initial concentration of 320 μM $CdCl_2$ and within the pH range of 2–8, Cd

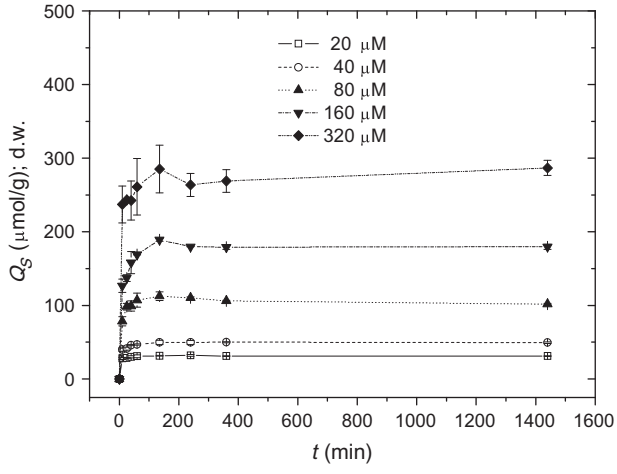

Fig. 1. Effect of contact time and concentration of $CdCl_2$ on Cd adsorption by dried biomass of the freshwater moss *V. dubyana* (0.5 g/l; d.w.) under initial conditions of pH 4.0 and 25°C.

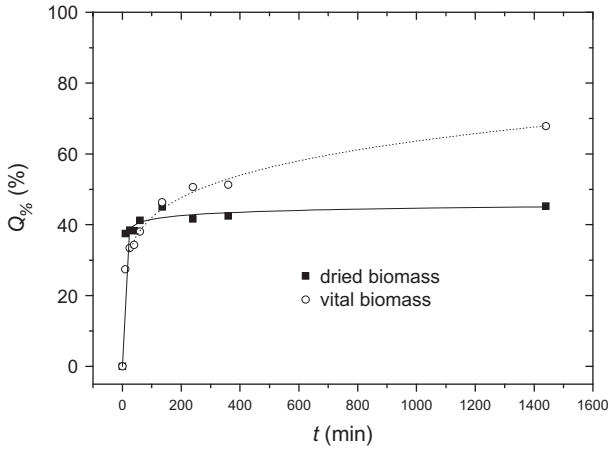

Fig. 2. Kinetics of Cd uptake by dried and vital *V. dubyana* moss biomass (0.5 g/l; d.w.) from a 320 μM $CdCl_2$ solution under initial conditions of pH 4.0 and 25°C.

occurred predominantly in the form of Cd^{2+} ions (>95%) with smaller amounts of the $CdCl^{+}$ form. However, values of pH > 8 resulted in a gradual decrease of Cd^{2+} form proportion on account of $CdOH^{+}$ and $Cd(OH)_2$ formation.

From Fig. 3, it can be seen that the maximum Cd adsorption Q_S 280 μmol/g (d.w.) was found within the range of initial values of pH_0 4–8. A 65% decrease in Cd adsorption was observed at pH_0 3 and the minimal Cd adsorption Q_S 3 μmol/g (d.w.) was calculated at an initial value of pH_0 2. Similar results were reported by Bunluesin et al. [24] for Cd adsorption by the aquatic plant *Hydrilla verticillata*. They found that Cd adsorption was negligible under very acidic conditions (pH 1), whereas Cd adsorption reached the equilibrium concentration within the range of pH 3–9. This difference was explained by the competition effect of H^{+} ions, which inhibit Cd adsorption at pH < 3. A similar tendency was described by Huang et al. [43] with the same biomass. Sari and Tuzen [44] found by FT-IR spectroscopic analysis that moss biomass *Hylocomium splendens* contained different functional groups on the surface, such as carboxyl, hydroxyl or amino groups, which are responsible for binding metals from solutions. Moreover, the participation of these functional groups in metal adsorption can be dependent on the pH of the solution [45].

Fig. 3 also depicts the dependence of Cd adsorption on the final value of pH_f obtained at the time when adsorption equilibrium was reached. The dried moss biomass showed a significant buffering capacity in the solution across the pH range obtained at the end of the adsorption experiments. The initial value of pH_0 2–6 increased during the experiment to a final value pH_f 7, while in the case of pH_0 8, the pH decreased to pH_f 7. It can be expected that functional groups on the surface of the moss biomass (e.g. carboxyl or phosphoryl groups) play an important role in this phenomenon.

As we mentioned, the software MINEQL+ was used for the calculation of Cd speciation in the model solutions. We found that Cd in the range of pH 4–7, at 25˚C and a concentration of 320 μM $CdCl_2$ in deionized water occurred preferentially in the form of Cd^{2+} ions (>95%) with a smaller proportion of the $CdCl^{+}$ form. Based on this consideration, it can be concluded that an increasing Cl^{-} ion concentration in the environment will increase the proportion of $CdCl^{+}$ complexes. For this reason, we performed experiments focused on studying the effect of changes in Cd speciation given by the presence of different NaCl concentrations on the level of Cd adsorption by dried moss biomass. We found that increasing the NaCl concentration decreased the proportion of the Cd^{2+} form from 99 to 46%, predominantly on account of the $CdCl^{+}$ form (Fig. 4). The mentioned decline in the Cd^{2+} form in solution resulted in lower adsorbed amounts of Cd. At concentrations of 20, 200 or 2,000 μM NaCl, when changes in Cd speciation were negligible (max. 10%), a minimal decrease in Cd adsorption was also observed. However, at a concentration 20,000 μM NaCl, there was a 46% decrease in the proportion of the Cd^{2+} form to the total amount of Cd in the solution and a 40% decrease in Cd adsorption. From these results it can be concluded that metal speciation will play a decisive role in adsorption

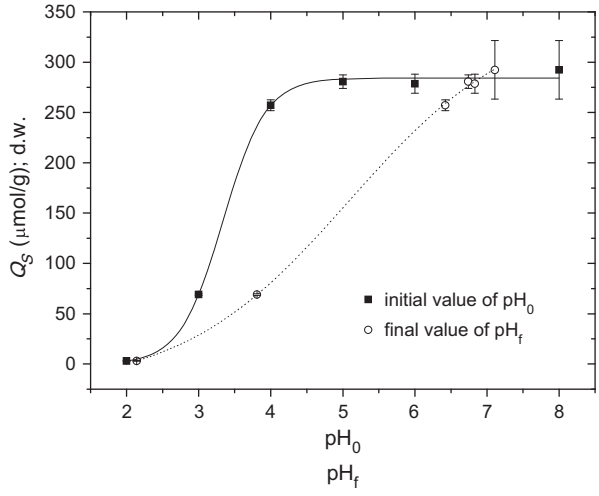

Fig. 3. Effect of pH on Cd adsorption by dried biomass of the freshwater moss *V. dubyana* (0.5 g/l; d.w.) after 2 h of exposure in a solution containing 320 μM $CdCl_2$.

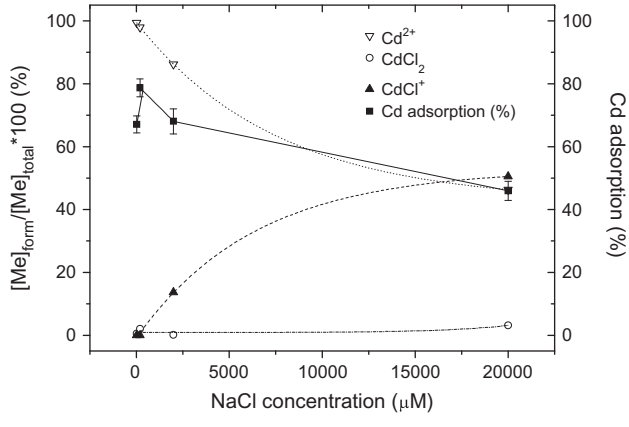

Fig. 4. Effect of NaCl concentration on Cd speciation in solution and Cd adsorption by dried biomass of the freshwater moss *V. dubyana* (0.5 g/l; d.w.) after 2 h of exposure in a solution containing 20 μM $CdCl_2$ at initial pH 4.0 and 25˚C.

processes and the removal of metals by biosorbents from wastewaters or contaminated liquids as well. In our previous paper [46], we found that changes in Cd and Co speciation after adding the chelating agents EDTA (ethylenediaminetetraacetic acid) or NTA (nitrilotriacetic acid) on account of $[Me\text{-}EDTA]^{2-}$ or $[Me\text{-}NTA]^{-}$ complexes formation in cultivation media for hydroponics caused a decrease in the toxic effects of these metals on the growth of tobacco plants (*Nicotiana tabacum*).

3.3. Continuous column mode

The successful design and characterization of adsorption processes in packed bed column systems require modelling the dependence between the ratio of outlet to inlet metal concentration (C_0/C_i) and time (t) or effluent volume (V_{eff}). Cd adsorption by dried *V. dubyana* moss biomass (0.05 g; d.w.) under conditions of continuous column system was carried out in a down-flow packed bed column with an inner diameter of 0.8 cm and bed height of 21 cm containing dried moss biomass. A solution of 36 mg/l $CdCl_2$ spiked with $^{109}CdCl_2$ was passed through the column at a flow rate of 0.8 ml/min. The mentioned experimental conditions taking into consideration the amount of dried biomass of the freshwater moss *V. dubyana*, the initial concentration of $CdCl_2$ in solution or the flow rate of solution passed through the column were chosen according to preliminary experiments (data not shown).

To describe the obtained data and find a suitable mathematical kinetic model characterizing Cd adsorption by dried moss biomass in the packed bed column, equations according to Clark, Thomas, Yoon–Nelson or Bohart–Adams, and MDR (modified dose–response) were used. The mentioned mathematical equations represent widely applied kinetic models for fundamental understanding of packed bed column dynamics and were adopted from studies focused on metal adsorption in column systems [47–51]. However, their practical applications are rather limited, mainly due to the complicated solution methods. On the other hand, these simplified models can be used as a tool for quantitative study of the effects of packed bed column design, experimental conditions or sorbent characteristics on metal adsorption performance as well as of mutual competitive relationships between sorbates. The breakthrough curves of Cd adsorption by dried moss biomass in the form of C_0/C_i vs. t or C_0/C_i vs. V_{eff} dependences were analysed using the nonlinear equations of all five kinetic models (Fig. 5).

In most adsorption column system studies, the nonlinear solution of the kinetic models gives a better fit than the linear solution with lower values of root mean square errors (*RMSE*) and equal or greater values of correlation coefficients (R^2) [48,52]. The calculated parameters of the kinetic models and values of R^2, *RMSE* or residual sum of squares (*RSS*) are presented in Table 1. The higher value of the correlation coefficient ($R^2 = 0.981$) and smaller value of *RMSE* (0.033) or *RSS* (0.048) demonstrate that the Clark model represented the most suitable mathematical equation among the used kinetic models. Application of the Thomas and Yoon–Nelson models showed very similar results with regard to the obtained values of R^2 and *RSME* or *RSS*. A slightly poorer result was found in the case of data fitting by the MDR kinetic

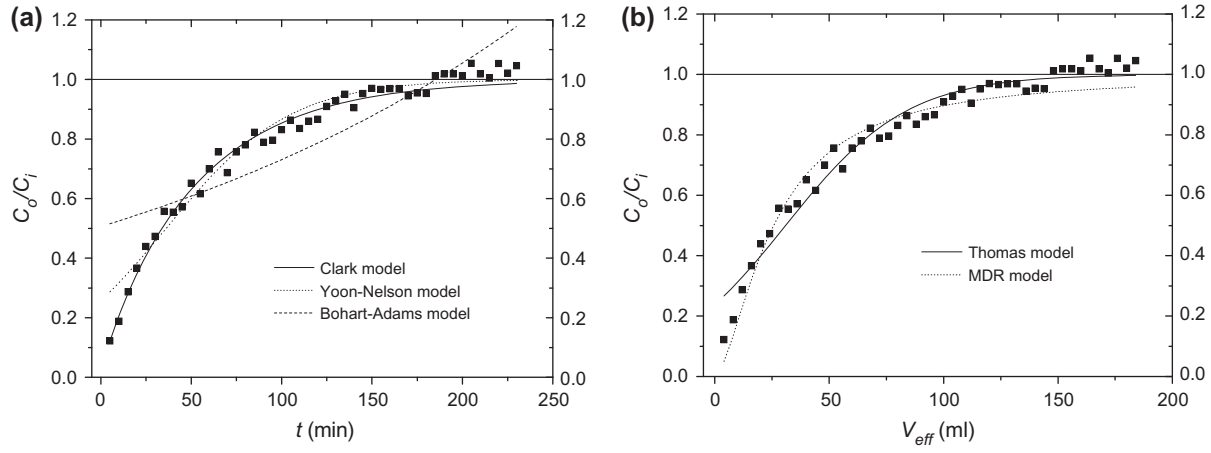

Fig. 5. Kinetics of Cd adsorption by dried biomass of the freshwater moss *V. dubyana* (0.05 g; d.w.) in a packed bed column system described as C_0/C_i vs. t (a) or C_0/C_i vs. V_{eff} dependence (b) at a flow rate of 0.80 ml/min and 25°C. The initial conditions were 36 mg/l $CdCl_2$ and pH 6.0.

Table 1
Obtained values of parameters of mathematical models characterizing the Cd adsorption in a packed bed column system and values of R^2, *RMSE* and *RSS* calculated for the applied models

Model	Parameter A	Parameter B	R^2	*RMSE*	*RSS*
Clark (Eq. (9))	n 0.092 ± 0.129	r (mg/l min) 0.018 ± 0.001	0.981	0.033	0.048
Thomas (Eq. (6))	k_{TH} (ml/mg min) 0.835 ± 0.045	Q_{max} (mg/g; d.w.) 22.3 ± 1.0	0.964	0.046	0.094
Yoon–Nelson (Eq. (7))	k_{YN} (l/min) 0.029 ± 0.002	τ (min) 36.1	0.962	0.047	0.098
MDR (Eq. (8))	a_{mdr} 25.7±1.1	b_{mdr} 1.59 ± 0.08	0.954	0.052	0.118
Bohart–Adams (Eq. (5))	k_{BA} (ml/mg min) 0.102 ± 0.010	N_0 (mg/ml) 0.506 ± 0.019	0.754	0.120	0.632

model. The data description by the Bohart–Adams kinetic model showed that the given mathematical equation is inappropriate for this type of packed bed column system and adsorption process. The Bohart–Adams kinetic model was developed for fitting the initial part of the breakthrough curve. Researchers have used this model either for the entire breakthrough curve or for 10–50% of the initial sorbate concentration in the outlet solution [50].

Muhamad et al. [49] found that, of the applied mathematical kinetic models (Thomas, Bohart–Adams and Yoon–Nelson model) to describe Cd and Cu adsorption by wheat straw (*Triticum sativum*) in a continuous up-flow fixed-bed column, the Thomas model was most appropriate, with calculated values of the correlation coefficient R^2 in the range 0.96–0.99. The Thomas kinetic model offers the Q_{max} parameter defining the maximum adsorption capacity of a biosorbent. However, this parameter can be used to evaluate or characterize not only a given biosorbent but also adsorption column systems and their optimal configuration or operation. We found that the calculated value Q_{max} = 22.3 ± 1.0 mg/g (d.w.) obtained from the Thomas kinetic model for dried biomass of the freshwater moss *V. dubyana* was slightly lower than the real measured value of specific adsorption for Cd Q_{SA} = 26.5 mg/g (d.w.).

In many cases, the suitability of kinetic models to describe experimental data of metal adsorption in continuous column systems has been evaluated only on the basis of the differences between the calculated values of the correlation coefficient (R^2). However, some papers dealing with adsorption processes description have reported the possibility of better determining the suitability of mathematical models regarding the selection criteria. In this context, the suitability of the used mathematical models characterizing the dependence of C_0/C_i vs. t (Clark and Yoon–Nelson model) or C_0/C_i vs. V_{eff} (Thomas and MDR model) for Cd adsorption by dried moss biomass in a packed bed column system was evaluated using the corrected Akaike's information criterion (AIC_c) (Table 2). We found that the Clark and Thomas models showed lower AIC_c values and higher Akaike's weight (AW) values than the Yoon–Nelson or MDR models, which reflects the fact that the Clark and Thomas models were more likely to be correct.

Table 2
Comparison of the values of corrected AIC_c and AW for the applied mathematical kinetic models describing the dependence of C_0/C_i vs. t or C_0/C_i vs. V_{eff}

Dependence	Model	AIC_c	AW
C_0/C_i vs. t	Clark (Eq. (9))	−309	1
	Yoon–Nelson (Eq. (7))	−279	2.09×10^{-7}
C_0/C_i vs. V_{eff}	Thomas (Eq. (6))	−279	0.995
	MDR (Eq. (8))	−268	0.005

From the obtained results, it can be concluded that adsorption processes of metal removal by biomass of freshwater plants or mosses in continuous column systems can be described by the mentioned mathematical kinetic models, which provide predictions of breakthrough curves and determine the characteristic parameters of column systems. However, it should be noted that the behaviour of these processes will be strongly dependent on the initial concentration of metals, the flow rate of the solution passed through the column, the bed height and the biomass concentration [53]. Muhamad et al. [49] found that the Thomas rate constant k_{TH} characterizing Cd and Cu adsorption by wheat straw increased significantly with an increasing flow rate of the solution passed through the column. On the other hand, this constant as well as specific adsorption Q_{SA} (mg/g; d.w.) decreased with increasing bed height or with the amount of wheat straw in the column, respectively. Bunluesin et al. [24] observed that the saturation phase $C_0/C_i = 1$ of Cd adsorption by 0.5 g of *H. verticillata* freshwater plant biomass was achieved faster in comparison with a twofold higher quantity of biomass in the column at an initial concentration of 10 mg/l $Cd(NO_3)_2$ and flow rate of 11 ml/min. Also, they found that in the presence of Zn as a physicochemical analogue of Cd in equimolar concentration of $Zn(NO_3)_2$ to $Cd(NO_3)_2$

(10 mg/l), the concentration ratio $C_0/C_i = 1$ was reached earlier than in the case of the column without addition of Zn.

3.4. Desorption

In practice, where inorganic sorbents are used for the removal of metals from wastewaters, the regeneration of the sorbent represents an important step in such decontamination technologies. In this step, the application of chelating agents or acids as desorption solutions is generally accepted. In this regard, Cd desorption from dried *V. dubyana* moss biomass originating from the sorption experiments was carried out with deionized water or 0.1 M solutions of $ZnCl_2$, EDTA-Na_2 and HCl under batch conditions. This type of desorption experiment can also evaluate the strength of the bond between Cd ions and binding sites on the surface of the moss biomass as well as the stability of the biosorbent during the regeneration step. We found that more than 90% of adsorbed Cd was removed from the moss biomass by 0.1 M HCl or 0.1 M EDTA-Na_2 and the desorption efficiency D_{eff} decreased in the order: 0.1 M HCl (93%) ≈ 0.1 M EDTA-Na_2 (92%) > 0.1 M $ZnCl_2$ (85%) > deionized water (20%) (Fig. 6).

Gupta and Rastogi [54] studied Cd desorption from *Oedogonium* sp. algal biomass using eight desorption solutions. They found that the maximum desorption efficiency was achieved in the case of 0.1 M HCl (85%), whereas the efficiency of Cd desorption decreased in the order: HCl > EDTA > H_2SO_4 > HNO_3 > NaOH > $CaCl_2 \cdot 2H_2O$ > Na_2CO_3 > deionized water. These facts

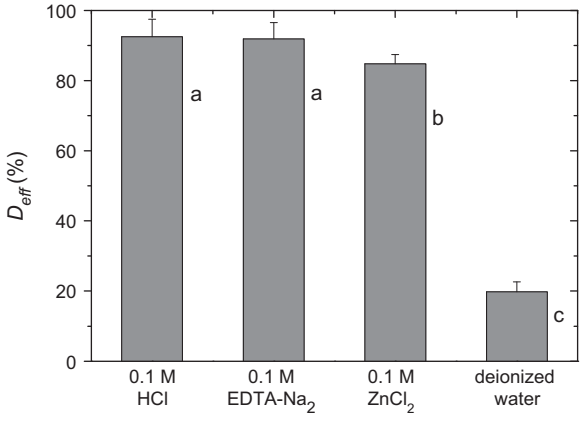

Fig. 6. Efficiency of Cd desorption from dried biomass of the freshwater moss *V. dubyana* (0.5 g/l; d.w.) after 2 h batch desorption. Adsorption experiment: 2 h in a 320 μM $CdCl_2$ solution at initial pH 4.0 and 25°C. Means with the same letter in columns are not significantly different at the $p = 0.05$ level based on the multiple range test.

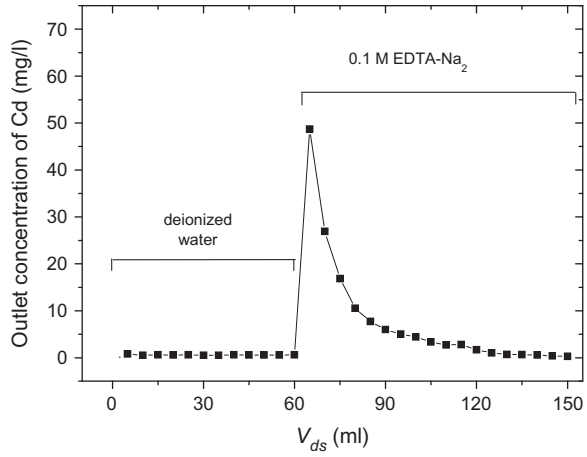

Fig. 7. Desorption of Cd from dried biomass of the freshwater moss *V. dubyana* (0.05 g; d.w.) by a two-step desorption with deionized water and 0.1 M EDTA-Na_2 in a packed bed column system.

indicate that the application of bases or inorganic salt solutions shows low efficiency at metal desorption.

Biosorbent stability as well as reusability and adsorbate desorption also represent significant aspects in adsorption column systems. Fig. 7 depicts Cd desorption from moss biomass in a packed bed column system carried out by a two-step desorption with deionized water and 0.1 M EDTA-Na_2 solution passed through the column under the same conditions as in the case of the adsorption experiment described in Fig. 5. The Cd desorption efficiency was evaluated on the basis of the volume of desorption solution (V_{ds}) that ran through the continuous column system. Only 3.8% of the adsorbed Cd was removed from the moss biomass by the application of deionized water, $V_{ds} = 60$ ml. In the case of 0.1 M EDTA-Na_2, even small volume of this desorption solution ($V_{ds} = 5$ ml) caused 34.7% of the total Cd adsorbed on the moss biomass to be desorbed, while 92.3% of the Cd was removed from the moss biomass at $V_{ds} = 45$ ml and at the end of desorption process represented by $V_{ds} = 90$ ml more than 98.0% of the Cd was desorbed. Similar results were found by Rao et al. [50] for Cd desorption from powdered leaves of *Syzygium cumini* L. plants in a fixed bed mini column (bed height 5 cm; 2 g of dried biomass), where 100 ml of 0.05 M HCl was sufficient for 98% removal of the loaded Cd.

4. Conclusions

From the adsorption experiments carried out in batch systems, it can be concluded that Cd adsorption by dried *V. dubyana* moss biomass was a rapid process

that was strongly affected by pH, initial concentration of Cd and changes in Cd speciation induced by the presence of Cl^- anions in the solution. The adsorption of Cd onto moss biomass under the conditions of a continuous column system was described by mathematical kinetic models according to Clark, Thomas and Yoon–Nelson or the MDR model. These models provided fitting of the obtained breakthrough curves and predicted the characteristic parameters of the designed adsorption packed bed column system comprised of dried moss biomass. The suitability of the applied mathematical models was also confirmed on the basis of differences in values of *RMSE*, *RSS* or corrected AIC_c. The applicability of dried *V. dubyana* moss biomass as a metal or radionuclides biosorbent was evaluated in consideration of the stability and reusability of this biosorbent by independent desorption experiments under conditions of batch and continuous column systems.

According to these findings, it can be assumed that dried biomass of the freshwater moss *V. dubyana* can be used as a potential biosorbent for the removal of toxic metals or radionuclides from wastewaters or contaminated liquids. Also, mathematical modelling of the adsorption dynamic under the conditions of a continuous column system can provide important parameters from the point of view of practical application.

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Nomenclature

a_{mdr} — MDR model constant
A_B — ^{109}Cd radioactivity adsorbed on moss biomass
A_C — ^{109}Cd radioactivity in solution that run through the column
A_D — ^{109}Cd radioactivity released from the moss biomass into the supernatant
A_S — initial ^{109}Cd radioactivity in solution
b_{mdr} — MDR model constant
C_0 — initial concentration of $CdCl_2$ in solution
C_{break} — breakthrough concentration
C_i — inlet metal concentration
C_0 — outlet metal concentration
C_t — concentration of $CdCl_2$ at the end of the experiment
C_T — total amount of Cd in solution run through the column
D_{eff} — desorption efficiency
F — flow rate
k_{BA} — Bohart–Adams rate constant
k_{TH} — Thomas rate constant
k_{YN} — Yoon–Nelson rate constant
M — weight of moss biomass in the experiment
n — Freundlich constant
N_0 — bed saturation capacity
Q_{max} — maximum adsorption capacity of the biosorbent
Q_S — amount of Cd adsorbed on moss biomass
Q_{SA} — specific Cd adsorption
$Q_{\%}$ — percentage of Cd adsorption
r — adsorption rate
t — time
t_{break} — breakthrough time
U_0 — superficial velocity
V — volume of solution in the experiment
V_{eff} — volume of the effluent
Z — bed height
τ — time required for 50% adsorbate breakthrough, when $C_0/C_i = 0.5$ min

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