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Sorption separation of cadmium from aqueous solutions by alginite material: kinetic and equilibrium study

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ABSTRACT

Alginite, as a component of some types of kerogen alongside amorphous organic matter, was used for adsorptive separation and removal of Cd^{2+} ions from aqueous solutions. Alginite material was characterized by X-ray diffraction, ATR-FTIR, cation exchange-capacity and specific surface area analyses. Evaluation of alginite sorption properties showed the effect of solution pH value in the range from 2 to 6 on sorption capacity of alginite. At a slightly acidic conditions (pH 6.0–6.5), the alginite samples exhibited a sufficient sorption capacity and stability. The pseudo-second-order kinetic model described the sorption data better than the pseudo-first-order kinetic model. The equilibrium of cadmium sorption by alginite was reached within 120 min. Maximal sorption capacity (Q_{max}) calculated from experimental equilibrium data (Langmuir adsorption isotherm) was 23.62 mg/g. Sorption energy of Cd^{2+} ions calculated from Dubinin–Kaganer–Radushkevich model confirmed the ion-exchange mechanism of cadmium removal for alginite sorbent. The alginite from central European geological maar (Pula, Hungary) can be utilized for production of new non-conventional sorbents or mineral filters for removal of toxic metals.

Keywords: Alginite; Cadmium removal; Sorption isotherms; ATR-FTIR

1. Introduction

The accrual of social agglomerations, and thus upgrading of industrial activities represent the main reasons of safe levels breaching in wastewaters and the environment. There has been a wide range of literature describing heterogeneous materials used for the removal of toxic heavy metal ions from liquid wastes and aqueous solutions [1–4]. Penetration of toxic metals into soil and soil solution can bring tremendous complications in plant production and metal entry into food chain, respectively. The solubility and mobility of toxic heavy metals in soil and soil solution are important factors triggering the above-mentioned hazards. Elevated environmental levels of cadmium ions in soils and waters come from a variety of sources. Plating industry emits a broad range of cadmium containing liquids that require tool to clean and decontaminate. Cadmium ions removal technologies based on precipitation, ion exchange, electrochemical pretreatment, membrane approaches or adsorption on activated carbon have several limitations such as an

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inefficient removal of toxic heavy metals from liquid wastes and high demands for processes realization [5]. Sorption on inexpensive materials is a potential alternative to classical removal of cadmium ions from aqueous solutions. Process of cadmium sorption also has several restrictions that were discussed and clearly explained [6]. The cheap regeneration of sorbents and also efficient sorption capacity represent advantages of this separation process. Bivalent metals ions, such as Cd^{2+}, Zn^{2+} and Co^{2+}, can be removed from waste solutions by microbial-based [7,8], but also inorganic, sorbents [9,10].

Ubiquitous kerogen materials, composed predominantly from amorphous organic matter of marine origin, represent the base of recent year research. The wide group of kerogen materials due to their surface characteristics and sorption capacities represent the valuable tool in remediation or stabilization of toxic metal-polluted soils. The content of clay predetermines the high effect of these “mineral riches” to the inorganic and also organic xenobiotics partitioning between liquid and solid phase in the geosphere, affecting their mobility in soil solutions [11]. Their main physico-chemical properties are variable in dependence on the locality of geological maar and feedstock characteristics. This study evaluated two origins of alginite as a sedimentary laminated rock—oil shales that are rich in amorphous matter and well preserved cells of green alga *Botryococcus braunii* [12]. This alga is a major component of cannel coals and oil shales. The chemical structure of *Botryococcus* is crucial for origin of the alginites themselves, as well as to the clarification of the role of this organic matter type in hydrocarbon generation [13]. In the last decades, there were numerous studies focused on determination and characterization of properties of *Botryococcus*-derived alginite in coals and in source rocks. Chmielewská et al. [14] and Fazekas et al. [15] discussed about the sorption characteristics of alginite materials as a low-cost sorbents and soil amendments. Adsorption, ion exchange, complexation and precipitation on surface of sorbent should be crucial and dominant processes in the metal removal by alginite materials (Fig. 1). But information about sorption properties and also utilization of this material for heavy metals removal is deficient.

This paper presents an original study on the characterization of sorption process for cadmium separation and removal from aqueous solutions based on evaluation of physico-chemical properties of alginite material. Application of FTIR analyses and determination of specific surface area (SSA) by adsorption of N_2 represent the effective tools in study of cadmium removal. Alginite material was characterized also by determination of sorption capacity using three adsorption models for fitting obtained data. This study presents the ability for utilization of alginite materials, not only for agricultural approaches but also in remediation, stabilization and water treatment technologies.

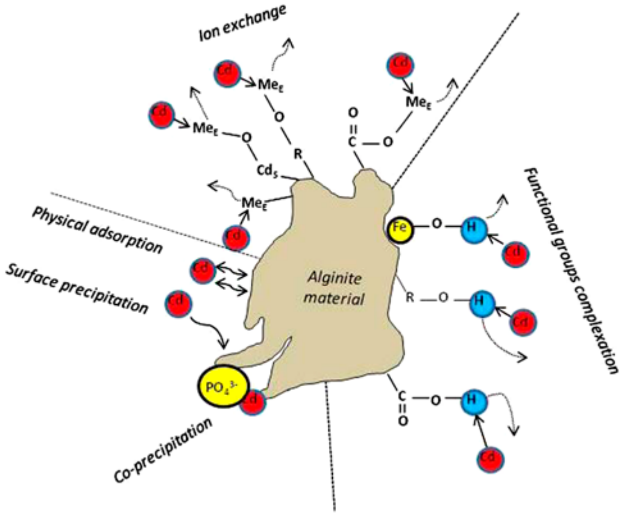

Fig. 1. Postulated mechanisms of alginite material interactions with cadmium. Areas on alginite particle show: cadmium ion exchange with Ca^{2+} and Mg^{2+} ions, attributing with complexation with humic substances and mineral oxides; coprecipitation, physical adsorption and passive diffusion; complexation with free functional (carboxyl, hydroxyl, phenolic, sulfhydryl) groups.

2. Material and methods

2.1. Sampling and sample preparation

Alginite samples were obtained from central European geological maar in Pula (Hungary). Collected alginite samples were oven dried at 25˚C, ground and sieved. Alginite fraction <450 μm was used in characterization and sorption experiments.

2.2. Alginite sample characterization

The main physico-chemical characteristics of alginite sample were determined as follows. The active and potential pH were measured after stirring of alginite with deionized water and 1.0 mol/L KCl (ratio 1: 2.5) for 1 h and stabilization for 1 h (inoLab 330i WTW), Germany. The cation exchange capacity (CEC) of sample was determined according to the STN ISO 11260 modified by Frišták et al. [4]. Sample was analysed for total organic matter (TOC) by modified Walkley–Black titrations. The SSA, volume of micro and mesopores were determined using technique of nitrogen adsorption and desorption by SORPTOMATIC 1990 (Italy) and obtained data were evaluated by Brunauer–Emmett–Tellers (BET) adsorption model. The alginite total metal concentrations were measured by X-ray fluorescence analysis. For determination of total concentrations of As, Ba, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, La, Mg, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Sr, Th, U, V, W, Y, Zn and Zr, the high-performance X-ray fluorescence spectrometer X-LAB 2000 (Spectro, Germany) was used.

The surface functional groups of alginite sample were detected by infrared spectroscope with Fourier transformation (ATR-FTIR) (Nicolet NEXUS 470, Thermo Scientific, USA). The spectra were recorded from 4,000 to 400/cm.

2.3. Batch sorption experiments

Sorption experiments were carried out by suspending alginite (2.5 g/L) in reaction solution with initial concentration of $CdCl_2$ in the range from 1 to 50 mg/L. The sorption was carried out at pH 6.0 and temperature at 22°C. After agitation on a rotary shaker (4 h, 150 rpm), alginite sediments were separated from liquid phase by centrifugation (4,000 rpm, 15 min, 22°C). Concentration of cadmium in liquid phase was measured by electrochemical analyser. Sorption of cadmium ions was calculated according to Eq. (1):

$$Q_{\mathrm{eq}} = \frac{(C_0 - C_{\mathrm{eq}}) \times V}{m} \tag{1}$$

where Q_{eq} is the cadmium uptake (mg/g), C_0 is the initial liquid-phase concentrations of cadmium (mg/L), C_{eq} is the equilibrium liquid-phase concentrations of cadmium (mg/L), V is the volume (L) and m is the amount of alginite (g).

Effect of pH on sorption process of cadmium by alginite (2.5 g/L) was studied in 8 mL of 10 mg/L $CdCl_2$ solution with pH in the range from 2.0 to 8.0. Polypropylene tubes were shaken on a rotary shaker (150 rpm, 22°C, 4 h). After agitation and centrifugation, concentrations of cadmium in liquid phases were determined electrochemically. The sorption of cadmium ions was calculated according to Eq. (1). Calculation of the cadmium speciation in aqueous solution as a function of total salt concentrations, stability constants and solution pH was performed using the Visual MINTEQ software (version 2.52). Visual Minteq [16] works with extensive thermodynamic database for the calculation of metal speciation, solubility and equilibrium. Data were calculated considering the carbonate system naturally in equilibrium with atmospheric CO_2 ($p(CO_2) = 38.5$ Pa).

Kinetics study was performed by batch sorption experiments of cadmium ions by alginite (2.5 g/L) at reaction time in the range from 5 to 1,440 min. The initial concentration 10 mg/L $CdCl_2$ of reaction solution was used. The sorption system was shaken on a rotary shaker (150 rpm, 22°C) at pH 6.0. The concentrations of non-sorbed cadmium in liquid phase were measured electrochemically. Consequently, the sorption of cadmium ions was calculated according to Eq. (1).

All the chemicals used were of analytical reagent grade. Deionized water (< 0.05 µS/cm), prepared by Simplicity 185 (Millipore, France), was used for the preparation of all solutions. The pH values of reaction solutions were adjusted with 0.1 mol/L HCl or 0.1 mol/L NaOH solutions.

For fitting of experimental data obtained from kinetics sorption experiments, the models of pseudo-first order and pseudo-second order were used. The pseudo-first-order equation (Lagergren equation) can be defined as:

$$\frac{\mathrm{dQ_t}}{\mathrm{d}t} = k_1(Q_{\mathrm{eq}} - Q_t) \tag{2}$$

in which Q_t is the amount of Cd^{2+} ions sorbed at time t (mg/g), Q_{eq} is its value at equilibrium (mg/g) and k_1 is the rate constant of pseudo-first-order process (min^{-1}).

The pseudo-second-order model can be defined as:

$$\frac{\mathrm{dQ_t}}{\mathrm{d}t} = k_2(Q_{\mathrm{eq}} - Q_t)^2 \tag{3}$$

in which k_2 is the rate constant of the pseudo-second-order process (mg/g/min) and Q_t and Q_{eq} have the same meaning as in the pseudo-first-order equation.

2.4. Adsorption isotherms

The obtained equilibrium sorption data were analysed by mathematical equations of adsorption models under terms of Langmuir, Freundlich and Dubinin–Kaganer–Radushkevich (DKR). Parameters of adsorption isotherms were calculated by non-linear regression analysis using the Micro Cal Origin 8.0 Professional program (Origin Lab Corporation, Northampton, USA).

Langmuir model is given by equation:

$$Q_{\mathrm{eq}} = \frac{bQ_{\max}C_{\mathrm{eq}}}{1 + bC_{\mathrm{eq}}} \tag{4}$$

where Q_{eq} is the amount of sorbed cadmium at equilibrium (mg/g), b is the isotherm coefficient characterizing alginite affinity to cadmium ions in solution (L/mg), $Q_{\max}$ is the maximum cadmium sorption capacity at saturated alginite binding sites (mg/g) and C_{eq} represents the cadmium equilibrium concentration in solution (mg/L).

The Freundlich adsorption model is given by equation:

$$Q_{\text{eq}} = KC_{\text{eq}}^{(1/n)} \tag{5}$$

where Q_{eq} is the amount of sorbed cadmium at equilibrium (mg/g), K (mg/g) and n are the Freundlich empirical constants related to the sorption capacity and sorption affinity of sorbent and C_{eq} is the cadmium equilibrium concentration in solution.

The DKR model has the linear form:

$$\ln Q_{\text{eq}} = \ln Q_m - \beta\varepsilon^2 \tag{6}$$

where Q_m is the monolayer maximum sorption capacity, β is the activity coefficient related to mean sorption energy and ε is the Polanyi potential, which is equal to

$$\varepsilon = \text{RT}\,\ln\left(1 + \frac{1}{C_{\text{eq}}}\right) \tag{7}$$

where R is the gas constant (J/mol K) and T is the temperature (K).

2.5. Electrochemical and ETAAS analyses

Experimental measurements were carried out on electrochemical analyser EcaFlow model GLP 150 (Istran, Ltd, Bratislava, Slovak Republic) equipped with electrochemical cell of type 104 with auxiliary, Ag/AgCl reference and E-104L graphite porous working electrodes. Obtained data were compared with data from ETAAS (Shimadzu AA-7,000, USA). The bulk standard solution and calibration solution of cadmium were prepared in the background electrolyte from Certified Reference Material (999 mg/L $Cd(NO_3)_2$ and Sigma-Aldrich, Germany).

3. Results and discussion

3.1. Physico-chemical characterization of alginite samples

Utilization of alginite as sorbent for heavy metals separation and removal depends greatly on physico-chemical properties of the material. Total concentrations of As, Ba, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, La, Mg, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Sr, Th, U, V, W, Y, Zn and Zr in alginite material measured by X-ray fluorescence analysis are taken in Table 1. The cadmium concentration was lower than the detection limit of equipment used for detection (<2 mg/kg). The determination of pH value confirmed the slightly alkaline character of sample (Table 2). The alginite surface contains a large number of binding sites [17]. Assuming that surface sites (≡XOH) are amphoteric, i.e. they may be positively charged at low pH due to the protonation reaction on surfaces and can also be negatively charged due to the deprotonation reaction at high pH values [18].

The CEC was determined as 23 meq/100 g. This characteristic showed the better ability of alginite material to provide the active sites for exchange

Table 1
Elemental characterization of studied alginite

Element	Unit	Value
As	mg/kg	7
Ba	mg/kg	325
Bi	mg/kg	<2
Br	mg/kg	4
Ca	%	16.2
Cd	mg/kg	<2
Ce	mg/kg	41
Co	µg/kg	16
Cr	mg/kg	119
Cs	mg/kg	<3
Cu	mg/kg	28
Fe	%	3.6
Ga	mg/kg	11
Ge	mg/kg	<2
La	mg/kg	22
Mg	%	2.2
Mn	%	0.08
Mo	mg/kg	7
Nb	mg/kg	29
Ni	mg/kg	77
Pb	mg/kg	< 5
Rb	mg/kg	62
Sb	mg/kg	<2
Se	mg/kg	2
Sn	mg/kg	2
Sr	mg/kg	461
Th	mg/kg	6
U	mg/kg	11
V	mg/kg	127
W	mg/kg	<10
Y	mg/kg	13
Zn	mg/kg	88
Zr	mg/kg	136

Table 2
Physico-chemical properties of alginite

Characteristic	Value
pH_{H2O}	7.8
pH_{KCl}	7.6
Density [g/mL]	1.2
SSA [m^2/g]	40.98
Micropores volume [mL/g]	0.013
Mesopores volume [mL/g]	0.089
TOC [%]	7.5
CEC [meq/100 g]	23

mechanism of bivalent cations in aqueous solution. According to the IUPAC, the nitrogen adsorption isotherm of alginite sample (Fig. 2) was evaluated as type H4, but with relatively wide hysteresis loop as a H2 type. The difficulty of pore shape determination, pore size distribution and consequently, interpretation of obtained values for this type of material was described by Sing et al. [19].

However, the volume of micropores was determined as 0.086 mL/g. The volume of mesopores was 0.089 mL/g. SSA calculated by BET adsorption model was estimated at 40.98 m^2/g. The correlation between SSA and porosity of alginite sample is evident. The stepwise N_2 adsorption–desorption isotherms are suggestive of 3D intersection of porous materials [20].

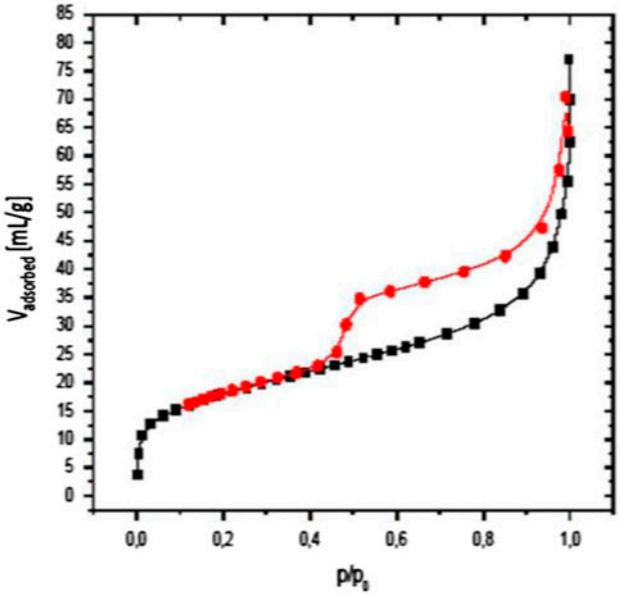

Fig. 2. Adsorption (-■-) and desorption (-●-) of N_2 by alginite for the determination of SSA. Experimental conditions: 39˚C, total stroke volume 17.06 mL, run time 8 h.

The spectral analysis in infrared area belongs to the most important structural qualitative and semi-qualitative analyses. The ATR-FTIR spectra (Fig. 3) of alginite showed that the peaks at 3,205 and 1,688/cm correspond to the stretching vibration of O–H groups of adsorbed water or zeolitic water. This physisorbed water is indicating the hydrophilic character of alginite sample. From spectra, the strong and broad peak area at λ 1,039–1,261/cm can be recognized. These peaks are mainly due to siloxane (Si–O–Si) stretching. The peaks at 760–800/cm correspond to the stretching vibration of Al–O–Si. Also the peak at 922/cm mainly due to stretching vibration of Si–O groups was detected.

3.2. Sorption characteristics

Alginite, as a natural material locally available in central area of Europe, can be utilized as a low-cost sorbent for heavy metals. For its application, the sorption properties and optimization of removal process are decisive. The cadmium removal at initial concentration 10 mg/L and pH 6.0 is relatively fast process and occurs in two steps (Fig. 4). For the first step, the rapid Cd^{2+} ions sorption within 60 min of contact time was monitored.

This step was subsequently followed by the uptake of Cd^{2+} ions until reaching the sorption equilibrium in 120 min of sorption. Sag and Kutsal [21] also described this two-steps type of heavy metal kinetic for heavy metal removal. Sorption process of Cd^{2+} by natural sorbents is performed by first, rapid and quantitatively predominant step. The second step is slower and quantitatively not so significant. The rate of the first step is due to the abundant availability of active sorption sites [22]. These results and also our previous study [4] showed that the contact time 240 min is suitable for equilibrium experiments. Obtained kinetics

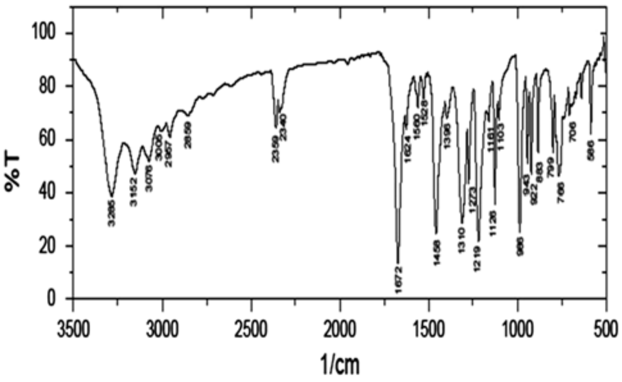

Fig. 3. ATR-FTIR spectrum of alginite.

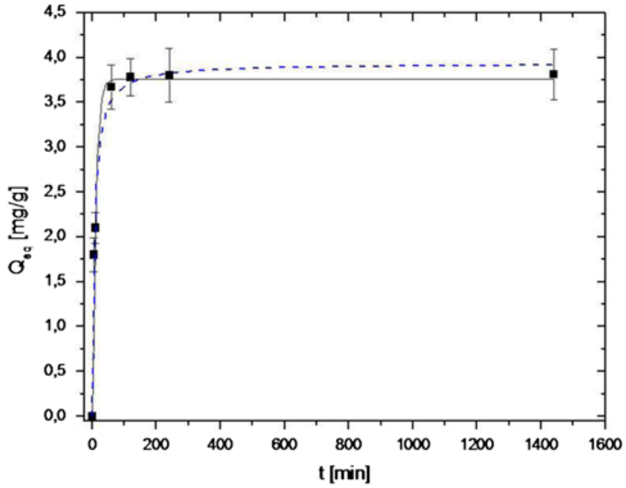

Fig. 4. Effect of contact time on sorption capacity of alginite (-■-) (2.5 g/L) for Cd^{2+} ions in a single-metal sorption system: $C_0 = 10$ mg/L $CdCl_2$, pH 6.0, 22˚C, contact time period from 5 to 1,440 min. All experiments were performed in triplicates. Applied model of pseudo-first (—) and pseudo-second (------) order.

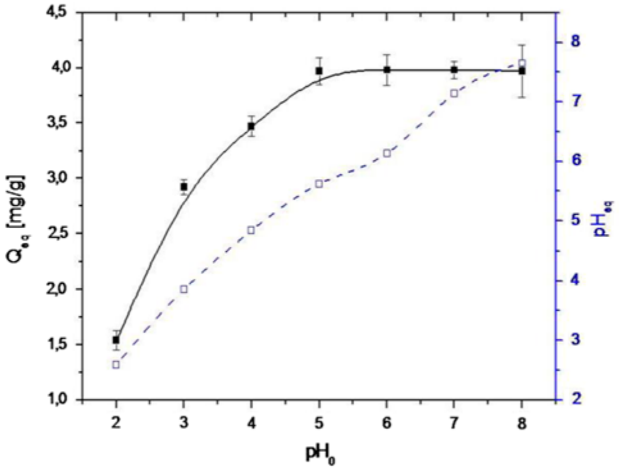

Fig. 5. Effect of initial pH on cadmium sorption capacity of alginite (-■-). Comparison of initial pH and pH in equilibrium for alginite (-□-).

data were analysed by models of pseudo-first and pseudo-second order proposed by Lagergren and Svenska [23] and Ho [24]. The equilibrium cadmium sorption (Q_e), the rate constants (k) and the coefficient of determination (R^2) for alginite sample were obtained by nonlinear regression analysis using Eqs. (2) and (3) (Table 3).

Comparison of R^2 of pseudo-first and pseudo-second order suggests that the removal of Cd^{2+} ions by alginite followed a pseudo-second-order type of reaction kinetics. Ünlü and Ersoz [25] discussed about the role of diffusion and particle diffusion as a control point in exchange process of metals. We confirmed that the process rate of Cd^{2+} ions removal by alginite is significantly controlled by chemisorption as a general controlling point of pseudo-second-order kinetic processes.

Generally, the removal of bivalent heavy metal ions from aqueous solution depends on pH value caused by adsorption and complexation of cations on sorbent surface. The effect of pH in the range from 2.0 to 8.0 was also examined in sorption process of Cd^{2+} ions by alginite. In Fig. 5, the sorption capacity of alginite (Q_{eq}) versus initial solution pH (pH_0) and equally, the equilibrium solution pH (pH_{eq}) versus pH_0 were plotted. Cadmium removal increases with increase in solution pH in the range from 2.0 to 5.0 or 6.0, respectively. At strongly acidic conditions ($pH < 2.0$) the sorption process can be considered inactive due to high concentration of competitive protons. On the other hand, at $pH > 8.0$, stronger hydroxide forms of cadmium are present that can change the species equilibrium and prevail the precipitation on alginite surfaces or in pores.

This fact was confirmed also by speciation analyses using Visual MINTEQ speciation program (Fig. 6). Calculation showed that cadmium, at concentration, 10 mg/L in aqueous solution occurs predominantly as Cd^{2+} ions (> 98.5%) within the pH 2.0–8.0. At higher pH values, other forms of cadmium, such as $CdOH^+$, $Cd(OH)_2$ and $CdOH^{3-}$, are created.

Cadmium removal processes by alginite can be affected by initial concentration of ions in reaction solution. For description and regression simulation of experimental data, Langmuir, Freundlich and DKR models were used. The relative values calculated from the three models are listed in Table 4. From values of coefficients of determination, R^2, it can be assumed

Table 3
Pseudo-first- and pseudo-second-rate constants for sorption process of Cd^{2+} ions by alginite

Pseudo-first order rate constants			Pseudo-second order rate constants		
Q_{eq} [mg/g]	k_1 [1/min]	R^2	Q_{eq} [mg/g]	k_2 [1/min]	R^2
3.87 ± 0.15	0.016 ± 0.001	0.9826	3.93 ± 0.04	0.036 ± 0.001	0.9916

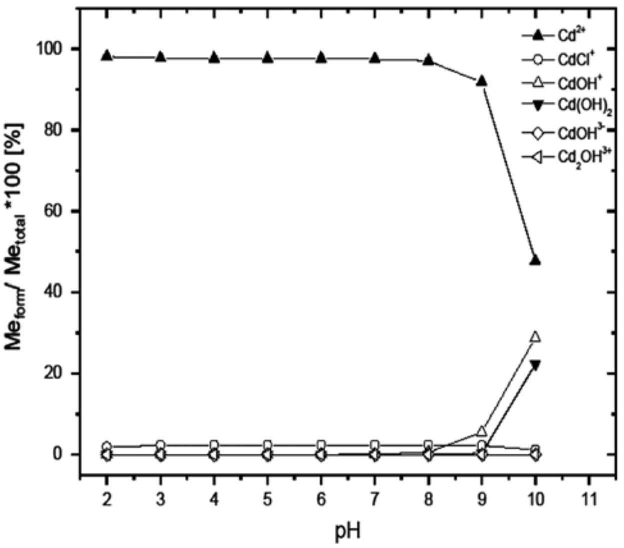

Fig. 6. Cadmium speciation as a function of pH calculated by Visual MINTEQ version 2.52. Initial conditions: 10 mg/L $CdCl_2$, 22°C, p(CO_2) 38.5 Pa.

that the Langmuir model (Eq. (4)) simulates the sorption data better compared with Freundlich model (Eq. (5)) and DKR model (Eq. (6)). R^2 values of all three models were > 0.90 but Langmuir model fitted the data with R^2 closer to 1.0. The fact that the sorption data of Cd^{2+} ions can be described with highest significance by Langmuir isotherm indicates that the binding energy on the surface alginite is uniform. However, the sorption surfaces of alginite have identical sorption activity and therefore the bound Cd^{2+} ions do not compete with each other. This fact also demonstrates that chemisorption is the principal uptake mechanism in sorption process [26].

On the other hand, calculation of maximum sorption capacity (Q_{max}) as a parameter of Langmuir model showed that Q_{max} of alginite was 23.62 mg/g. This value is much larger than Q_m value obtained by the DKR model because Q_m may represent the total specific micropore volume of the alginite sorbent. Equally, DKR equation is applicable in the low C_{eq} region of heavy metal ions [27]. Sorption energies, *E*, calculated from DKR isotherm showed the value 11.06 kJ/mol, which can be the order of an ion-exchange mechanism [28]. The relationship between value of *b* parameter and affinity of sorbent for metal sorption is proportional, based on Arrhenius equation to express energy of sorption process [29]. The value of Freundlich adsorption parameter *n* is from unity, indicating that a nonlinear sorption process of Cd^{2+} ions takes place on surfaces of alginite. Zhao et al. [30] confirmed the same relation for binding Cd^{2+} ions on bentonite sorbent.

Alginite sorbent, as a member of natural material sorbent group, showed the significant sorption efficacy. Clay materials, as an inorganic and mineral sorbents, have high CEC, and thus can be involved into the removal process of toxic metals from waste solution [33]. Sorption capacity of studied alginite sample for cadmium is comparable with other inorganic and organic sorbents (Table 5). Obtained results propose the ability of alginite utilization as a suitable material for cadmium separation, removal and pre-concentration. There is also possibility of alginite application for

Table 4
Parameters of Langmuir, Freundlich and DBK adsorption isotherms for Cd^{2+} ions removal

Sorbent	Model	Q_{max} [mg/g]	*b* [L/mg]	*K* [L/g]	*n*	Q_m [mg/g]	β [mol^2/J^2]	R^2
Alginite	Langmuir	23.62 ± 1.80	0.23 ± 0.01	–	–	–	–	0.9968
	Freundlich	–	–	8.81 ± 0.41	0.33 ± 0.04	–	–	0.9942
	DKR	–	–	–	–	20.92 ± 0.15	-4.07×10^{-9}	0.9168

Table 5
Comparison of sorbents for Cd^{2+} ions focused on Q_{max} and CEC values

Sorbent	CEC [meq/100 g]	Q_{max} [mg/g]	Ref.
Alginite	25	24	Present work
Dried activated sludge	–	57	[7]
Bentonite	–	110	[27]
Kaolinite	11	7	[31]
Montmorillonite	153	31	[31]
Smectite	80	29	[32]

the production of inorganic or mineral filters for continual systems of wastewater treatment as well as in the case of diatomite [34].

4. Conclusions

It was found that alginite from geological locality Pula (HU) can be used as an effective sorbent for the separation and removal of Cd^{2+} ions from aqueous solutions. Sorption capacity of the material can be affected by reaction solution pH value in the range from 2 to 5 or 6. At slightly acidic conditions (pH ca. 6.0–6.5), the alginite sample exhibits a sufficient sorption capacity and stability. At higher pH, the new forms of cadmium are formed. The cadmium sorption process was really rapid process and equilibrium was reached within 120 min. The pseudo-second-order kinetic model described the sorption data better than pseudo-first-order kinetic model. Sorption capacity was affected by initial concentration of cadmium in solution. Maximal sorption capacity ($Q_{\max}$), estimated from equilibrium measurements (Langmuir adsorption isotherm), was 23.62 mg/g. This value is comparable with the capacity of other non-conventional sorbents. Not only adsorption, but also intraparticiple diffusion and intrapore precipitation are responsible for cadmium separation and removal by alginite. ATR-FTIR, CEC and SSA analyses confirmed that sorption behaviour can be affected by composition of feedstock and componential properties. The utilization of alginite for production of new non-conventional sorbents and filters for toxic metals removal should be discussed.

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