

Cd²⁺ Ions Removal from Aqueous Solutions Using Alginite

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Abstract—Alginite has been evaluated as an efficient pollution control material. In this paper, alginite from maar Pinciná (SR) for removal of Cd²⁺ ions from aqueous solution was studied. The potential sorbent was characterized by X-ray fluorescence analysis (RFA) analysis, Fourier transform infrared spectral analysis (FT-IR) and specific surface area (SSA) was also determined. The sorption process was optimized from the point of initial cadmium concentration effect and effect of pH value. The Freundlich and Langmuir models were used to interpret the sorption behavior of Cd²⁺ ions, and the results showed that experimental data were well fitted by the Langmuir equation. Alginite maximal sorption capacity (Q_{\max}) for Cd²⁺ ions calculated from Langmuir isotherm was 34 mg/g. Sorption process was significantly affected by initial pH value in the range from 4.0-7.0. Alginite is a comparable sorbent with other materials for toxic metals removal.

Keywords—Alginites, Cd²⁺, sorption, Q_{\max} .

I. INTRODUCTION

THE increasing industrial activities and development of social agglomerations brings many negative impacts on the environment. The liquid and solid wastes become the main problem of recent years. Storage and manipulation with this heterogeneous matter entail many complications focused on entry of wide range of contaminants into soil or water recipient. Organic pollutants can be decomposed but inorganic like heavy metals will be subsequently redistributed in different parts of environment [1]. The solubility and availability are the crucial factors that determine their potential environmental risk. Elevated environmental levels of cadmium ions come from a variety of sources. Cadmium finds its way through wastewater from metal plating industries, batteries, fertilizers, mining, pigments, stabilizers and alloys [2].

For decreasing concentrations of toxic metals in soils are usable remediation and restoration techniques. The application of biological systems for metal removal was described by many authors [3]-[5]. On the other hand there are also other possibilities for altering metal mobility in soil. Application of natural [6], [7] or synthetic [8] soil amendments can cause metal immobilization with high efficiency and without changes in total metal concentration in soil. Equally, the

amendment of organic or inorganic materials to soil is considered as a way to improve physico-chemical properties of soil. However, metal forms begin mobile and thus available only in soil solution. Solubility of metal complexes in liquid phase and subsequently adsorption or redox processes has a crucial role in metal behavior in soil matrix. Removal of toxic metals from liquid phase using different biological materials, that have high sorption capacity and cheaper regeneration cost, can be compared to synthetic sorbents and ion-exchange resins.

Kerogens are wide groups of natural raw materials that can be used as remediation tools [9]. Alginite is a sedimentary laminated rock- an oil shale. Dark laminae are rich in amorphous matter and well preserved cells of green alga *Botryococcus braunii* [10]. This kerogen material contains valuable concentrations of macro and micronutrients. Significant high specific surface area of alginates is important factor for their application in adsorption process.

In the present work we investigate the sorption properties of alginite from the maar Pinciná in Slovak Republic for cadmium as a model of toxic metal. The principal objective of the study was confirmation of alginite utilization for heavy metal removal and their stabilization in aqueous and soil solution, respectively.

II. MATERIALS AND METHODS

A. Sampling and Sample Preparation

Alginite from maar Pinciná (Slovak Republic) was used for sorption experiments. Obtained alginite samples were oven dried at 25°C, ground and sieved. Alginite fraction <450µm was used in sorption experiments.

B. Alginite Characterization

The main physico-chemical properties of the alginite were characterized as follows. Alginite pH was determined in a 1/5 suspension of sediment to deionised water or 0.01 mol/dm³ CaCl₂. To determine the cation exchange capacity (CEC) of the alginite modified method with BaCl₂ was used [1]. Alginite was suspended in 0.1 mol/dm³ BaCl₂ (83.3 g/dm³) and mixed on a laboratory shaker for 1 h at 22°C at 150 rpm. Phases were separated by centrifugation (5min, 5000rpm). For next step of CEC determination, alginite sediment was resuspended in 3 ml of 0.025mol/dm³ BaCl₂ and agitated for 19h at 22°C. After separation of phases 3ml of 0.02 mol/dm³ MgSO₄ was added to alginite sediment. After subsequent agitation (19 h at 22°C) and phases separation CEC value was determined by chelatometric determination of Mg²⁺ ions in

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0.02 mol/dm³ Na₂EDTA standardized liquid phase. The CEC was calculated according equation:

$$CEC = \frac{(M_0 V_0 - M V_v) \varepsilon}{10^{-3}} \quad (1)$$

where *CEC* is cation exchange capacity (meq/100g), *M₀* is molar concentration of magnesium added to the sample (mol/dm³), *V₀* is volume of solution of magnesium added to the sample (dm³), *M* is molar concentration of the magnesium in the leachate (mol/dm³), *V_v* is volume of obtained extract (dm³) and *ε* is the conversion factor that has for the bivalent ions and amount 0.25g of sorbent value 800 meq (100g/mol).

Alginite sample was analyzed for organic matter (OM) by modified Walkley-Black titrations. The specific surface area (SSA) was determined using technique of nitrogen adsorption and desorption by SORPTOMATIC 1990 (Italy) and obtained data were evaluated by Brunauer–Emmett–Tellers (BET) adsorption model. This technique was used also for determination of micro and mezopores volumes. The total concentrations of metals namely 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, Zr were determined by X-ray fluorescence analysis using the high performance X-ray fluorescence spectrometer X-LAB 2000, Spectro (Germany). The concentrations of soluble inorganic salts in aqueous solution of alginite (1/20) were measured by IC (Dionex ICS-5000 RFIC, Reagent-Free™ Ion Chromatography, Dionex - Thermo Fisher Scientific, USA).

C. Sorption Experiments

Sorption experiments were carried out by suspending 0.02g of alginite in 8ml of reaction solution with initial concentration of CdCl₂ in the range from 1 to 50mg/dm³. The sorption was realized at pH 6.0 and temperature 22°C. After agitation on a rotary shaker (4h, 150rpm, 22°C), alginite sediment was separated from liquid phase by centrifugation (4000rpm). Concentration of cadmium in liquid phase was measured by electrochemical analyser. Sorption of cadmium ions was calculated according to (2):

$$Q_{eq} = \frac{(C_0 - C_{eq}) \times V}{m} \quad (2)$$

where: *Q_{eq}*: the cadmium uptake (mg/g), *C₀*: the initial liquid-phase concentrations of cadmium (mg/dm³), *C_{eq}*: the equilibrium liquid-phase concentrations of cadmium (mg/dm³), *V*: the volume (dm³), *m*: the amount of alginite (g).

Effect of pH on sorption process of cadmium by alginite was studied. Experiments were carried out by resuspension of alginite (2.5g/dm³) in 8ml of 10mg/dm³ CdCl₂ solution. Flasks were shaken on a rotary shaker (150min⁻¹, 22°C, 4h) at pH in the range from 4.0 to 8.0. After agitation and centrifugation, concentration on cadmium in liquid phase was determined electrochemically. The sorption of cadmium ions was calculated according to (2). Calculation of the cadmium

speciation in aqueous solution as a function of total salt concentration and solution pH was performed using the Visual Minteq program (version 2.52) [11]. Visual Minteq works with extensive thermodynamic database for the calculation of metal speciation, solubility and equilibrium. Data were calculated at atmospheric CO₂ (p(CO₂) = 38.5 Pa).

D. Sorption Isotherms

The obtained data from sorption experiments were evaluated by mathematical models of adsorption isotherms according to Langmuir and Freundlich. Maximum sorption capacity of alginite was calculated by non-linear regression analysis using the program MicroCal Origin 8.0 Professional (OriginLab Corporation, Northampton, USA). The Langmuir isotherm equation is given as:

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

where: *Q_{eq}*: the amount of sorbed cadmium at equilibrium (mg/g), *b*: the isotherm coefficient characterizing alginite affinity to cadmium ion in solution (dm³/mg), *Q_{max}*: the maximum cadmium sorption capacity at saturated alginite binding sites (mg/g), *C_{eq}*: the cadmium equilibrium concentration in solution (mg/dm³).

The Freundlich isotherm is given by equation:

$$Q_{eq} = KC_{eq}^{(1/n)} \quad (4)$$

where: *Q_{eq}*: the amount of sorbed cadmium at equilibrium (mg/g), *K, n*: the Freundlich empirical constants characterizing parameters and intensity of sorption process (dm³/g), *C_{eq}*: the cadmium equilibrium concentration in solution (mg/dm³).

E. Analytical Methods

Experimental measurements of cadmium concentration were carried out on electrochemical analyser EcaFlow model GLP 150 (Istran, Ltd., Bratislava, Slovakia) equipped with electrochemical cell of type 104 with auxiliary, Ag/AgCl reference and E-104L graphite porous working electrodes. Measured data were compared with data from GFAAS (Shimadzu AA-7000, USA). All 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 bulk standard solution and calibration solutions were prepared in the background electrolyte from Certified Reference Material (999 mg/dm³ Cd(NO₃)₂, Sigma-Aldrich, Germany). Spectral analysis of alginite in infrared region was used to determine functional groups of kerogen. The surface functional groups were detected by infrared spectroscopy with Fourier transformation (FT-IR) (Nicolet NEXUS 470, Thermo Scientific, USA). The spectra were recorded from 4000 to 400 cm⁻¹.

III. RESULTS AND DISCUSSION

A. Physico-Chemical Properties of Alginite

For utilization of kerogens materials as sorbents of toxic metals or their application to the heavy metal polluted soil as amendments for metal stabilization is important the initial or natural concentration of these elements in raw matter.

TABLE I
ELEMENTAL CHARACTERIZATION OF ALGINITE

Element	Unit	Value
As	mg/kg	7
Ba	mg/kg	581
Bi	mg/kg	< 2
Br	mg/kg	6
Ca	%	0,5
Cd	mg/kg	< 2
Ce	mg/kg	85
Co	µg/kg	18
Cr	mg/kg	169
Cs	mg/kg	5
Cu	mg/kg	32
Fe	%	3.4
Ga	mg/kg	23
Ge	mg/kg	< 2
La	mg/kg	48
Mg	%	0,6
Mn	%	0,02
Mo	mg/kg	< 3
Nb	mg/kg	25
Ni	mg/kg	133
Pb	mg/kg	15
Rb	mg/kg	86
Sb	mg/kg	2
Se	mg/kg	1
Sn	mg/kg	3
Sr	mg/kg	81
Th	mg/kg	12
U	mg/kg	< 3
V	mg/kg	144
W	mg/kg	< 10
Y	mg/kg	29
Zn	mg/kg	100
Zr	mg/kg	243

In our study, concentration of 33 metals were determined using X-ray fluorescence analysis focused on the cadmium, which concentration was lower than detection limit of equipment used for analyses (Table I).

TABLE II
PHYSICO-CHEMICAL PROPERTIES OF ALGINITE

Characteristic	Value
pH _{H2O}	5.1
pH _{KCl}	5.0
Density [g/ml]	1.2
SSA [m ² /g]	64.82
Micropores volume [ml/g]	0.021
Mesopores volume [ml/g]	0.086
TOC [%]	5.4
CEC [meq/100g]	32
Soluble nitrites [mg/L]	58.74
Soluble chlorides [mg/L]	0.47

It suggests the ability of free functional groups for binding of cadmium ions. The efficiency of sorption process is related to physico-chemical characteristics which are presented in Table II.

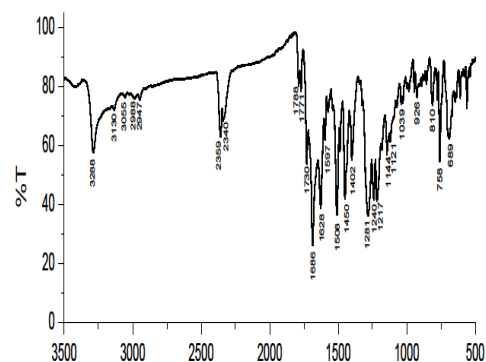


Fig. 1 FT-IR spectrum of alginite

Values of pH, CEC, organic matter (OM) are responsible for regulation the fate of metals [12]. Determination of pH noted low acid character of sample.

We found out that organic matter of alginite was 5.40%. Gupta and Sinha [13] showed the possibility of metal ion complexation with functional groups of solid and also dissolved organic matter. Formation of stable metal complexes can alter the releasing of the toxic element. The CEC value of alginite $32.00 \pm 1.10 \text{ meq/100g}$ is comparable to CEC of soil samples from our previous work [14]. SSA of alginite was more than $64 \text{ m}^2/\text{g}$. We found, that after one step extraction by deionized water at 22°C , alginite had well sedimentation properties. However, significant amount of water-soluble nitrites (58.74 mg/dm^3) and chlorides (0.47 mg/dm^3) were released, what was confirmed by ion chromatography.

For more detailed characterization of alginite spectral analysis in infrared area (FT-IR) was performed. It is clear that spectrum on Fig. 1 reflect the complex nature of the alginate structure particularly in terms of the complexity of the absorption bands pertaining to the vibration of functional groups. On the base of the most intense absorption bands, we specified the main symmetric, asymmetric, valence and deformation vibrations of typical functional groups (Table III).

These groups (carboxyl, hydroxyl, amino) can be involved into cadmium sorption process.

TABLE III
BAND ASSIGNMENTS FOR FT-IR SPECTRA OF ALGINITE

Assignment	Characteristic compounds	ν / cm^{-1}
O—H stretching vibration	alcohols and phenols	3450-3250
=C—H vibration	aromatic and unsaturated hydrocarbons	3100-3000
C—H stretching (asymmetric) vibration	aliphatic hydrocarbons	3000-2800
C—H stretching (symmetric) vibration	aliphatic hydrocarbons	2864-2843
C=O stretching vibration	aliphatic esters	1772-1729
NH ₂ bending vibration	Amides	1690-1680
NH ₂ bending vibration	Amides	1600-1585
NH ₃ bending vibration	Amides	1600-1520
C=C vibration	aromatic hydrocarbons	1618-1498
=C—O—C stretching vibration (symetric)	aromatic ethers	1240-1218
=C—O—C stretching vibration (asymmetric)	aliphatic ethers	1040-980
=C—H bending vibration	aromatic hydrocarbons	900-700

B. Sorption of Cd^{2+} Ions

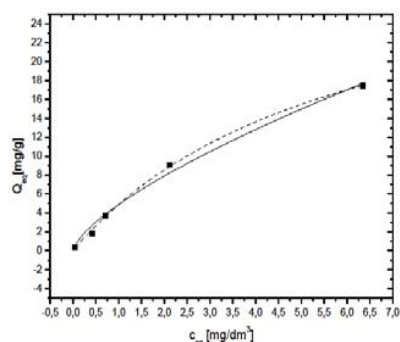


Fig. 2 Experimental data of Cd sorption by alginite described by adsorption isotherms models: Langmuir (dashed line), Freundlich (solid line). The adsorption isotherms were studied at pH 6.0 for concentration range from 1 to 50 mg/dm^3

For a description of sorption data mathematical models are often used [15]. The sorption isotherm of cadmium by alginite showed a typical shape (Fig. 2) with a maximum sorption capacity of approximately 34 mg/g which is lower than that of most inorganic materials [16]. On the other hand sorption capacity of alginite for cadmium is higher than that of dried algae or other organic sorbents (Table IV).

TABLE IV
THE COMPARISON OF SORBENTS FOR CADMIUM REMOVAL

Sorbent	Q_{max} [mg/g]	Ref.
Alginite	34 ± 2.0	Present work
Dried activated sludge	54 ± 2.0	[15]
GMZ bentonite	110 ± 5.0	[17]
Kaoline	2 ± 0.1	[18]
<i>Rhytidadelphus squarrosus</i>	19 ± 1	[19]

Both Langmuir and Freundlich adsorption models reproduced the isotherm data fairly well with coefficient of determination larger than 0.99 (Table V).

TABLE V
PARAMETERS OF APPLIED ADSORPTION MODELS

Model	Q_{max} [mg/g]	B [dm^3/mg]	K [dm^3/g]	$1/n$	R^2
Langmuir	33.78 ± 2.23	0.17 ± 0.02	-	-	0.9986
Freundlich	-	-	4.85 ± 0.44	0.69 ± 0.06	0.9919

It is well known that the sorption of transition metals is primarily influenced by coordination with the surface functional groups, which often follows a Langmuir process of uniform and single layer adsorption [20]. In contrast, the Freundlich adsorption model is valid for heterogeneous surfaces and predicts an increase in the concentration of the ionic species sorbed onto the surface of the solid [21]. Melichová and Hromada [22] also showed an application and higher efficiency of Langmuir model for description of sorption process of bivalent ions by natural bentonites.

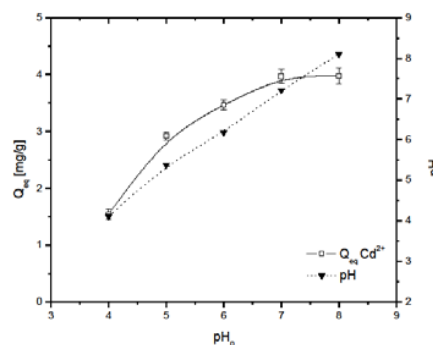


Fig. 3 Effect of pH on sorption capacity of alginite for cadmium ions ($-\square-$) at 22 °C, c_0 10 mg/dm^3 CdCl_2 , 33.3 g/dm^3 biomass (d.w.); pH in equilibrium ($-\blacktriangle-$)

The values of experimental pH were gently altered by alginite mass (Fig. 3). The sorption capacity of alginite increased with increasing value of initial reaction pH in the range from 4.0 to 7.0. At $\text{pH} > 7$ the sorption capacity was stabilized by formation another cadmium forms. Speciation of cadmium (Fig. 4) confirmed that at selected $\text{pH}=6$ and concentration of cadmium more than 95% of cadmium was in form Cd^{2+} ions. At $\text{pH} > 7$ in reaction solution new hydroxide forms of cadmium as CdOH^+ , and $\text{Cd}(\text{OH})_2$

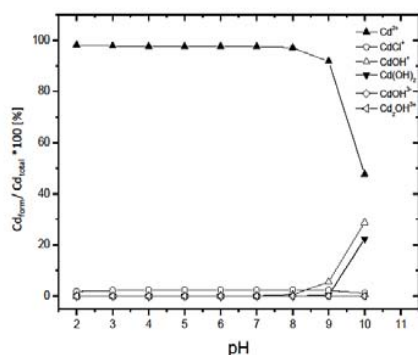


Fig. 4 Cadmium speciation forms depending on the pH: used speciation program Visual MINTEQ ver. 2.53 under conditions: 10 mg/dm³ Cd in form CdCl₂, 22°C, deionized water, p(CO₂) 38.5 Pa

IV. CONCLUSIONS

Alginite was demonstrated as effective sorbent for Cd²⁺ ions removal from aqueous solutions. FT-IR analysis showed the wide range of surface functional groups for heavy metal binding. Specific surface area of alginite was more than 64 m²/g. The sorption experiment showed that sorption process is affected by value of cadmium initial concentration and pH of reaction solution. The Langmuir model of adsorption isotherm gave the best fit for the sorption data. Maximal sorption capacity (Q_{\max}) of alginite was determined as a 33.78 ± 2.23 mg/g. Alginite as a member of kerogen material group can be used as a low cost and usable material to control toxic metals in soil or liquid solutions.

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