

## CADMIUM SORPTION BY DRIED PLANT BIOMASS – REVERSIBILITY STUDIES

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**Abstract:** Heavy metals such as cadmium are hazardous to biosystems and present possible human health risk. Thus, the removal of cadmium from liquid wastes is of great importance from an environmental and industrial point of view. There is a tendency to use agricultural wastes for the sorption of toxic metals as an alternative to the existing conventional technologies. The aim of this work was to describe Cd sorption and desorption equilibria by dried leaf biomass of tobacco (*Nicotiana tabacum* L.), hop (*Humulus lupulus* L.), pumpkin (*Cucurbita pepo* L.), sunflower (*Helianthus annuus* L.), cucumber (*Cucumis sativus* L.), pepper (*Capsidum annuum* L.), tomato (*Solanum lycopersicum* L.) and vine-grape (*Vitis vinifera* L.) using radiotracer technique with  $^{109}\text{CdCl}_2$ . Cadmium sorption  $Q$  values (mg/g, d.w.) of all of plant biomass studied increased proportionally with the initial  $\text{CdCl}_2$  concentration within the range 0.01 – 10 mmol/L  $\text{CdCl}_2$ . Mean sorption capacity of dried leaf biomasses of eight plants for Cd from the solution with the initial concentration  $C_0 = 10$  mmol/L  $\text{CdCl}_2$  in deionized water was  $Q = 213$   $\mu\text{mol/g}$  (d.w.). By single step desorption of Cd from leaf biomass for 30 min at 20 °C with deionized water, 0.1 mmol/L EDTA or 0.1 mmol/L HCl, up to 30 %, 85 % and 98 % of sorbed Cd, respectively, was removed. Obtained data can serve as a model for the prediction of sorption-desorption equilibria of biomass used for removing of Cd from polluted waters and Cd releasing back into waters containing other inorganic solutes. Formation of  $\text{Cd}^{2+}$ ,  $\text{CdCl}^+$ ,  $\text{CdCl}_2^0$ ,  $\text{CdSO}_4^0$ ,  $\text{CdOH}^+$ ,  $\text{Cd}_2\text{OH}_3^+$ ,  $\text{Cd}(\text{OH})_2^0$  and  $\text{Cd}(\text{OH})_3^-$  species in dependence on pH values and the presence of  $\text{Cl}^-$  anions is also discussed.

**Key words:** cadmium,  $^{109}\text{CdCl}_2$ , sorption, desorption, plant biomass

### 1. Introduction

Cadmium is one of the most toxic metals found in effluents discharged from industries involved in metal plating, metallurgical alloying, mining, ceramics and other industrial activities. Also, there is growing environmental concern about Cd as being one of the most ecotoxic metals that exhibit highly adverse effects on soil biological activity, plant metabolism and the health of humans. USEPA has also classified cadmium as group B1 carcinogen (USEPA, 1999). The behaviour of Cd in the environment and related health aspects has been reviewed by KABATA-PENDIAS and PENDIAS (2001).

Broad spectrum of sorbents has received increased attention for heavy metal removal. Data were published in numerous original papers and patents. For reviews see e.g. SINGH and TRIPATHI (2007), SUD *et al.* (2008). Several physical and chemical methods have been used for removal of heavy metals from industrial liquid wastes, such as ion-exchange, chemical precipitation, chemical reduction and

adsorption. There are still problems associated with these methods mainly these are cost-expensive and can themselves produce other wastes, which has limited their industrial applications. Among the available treatment processes, the application of biological sorbents is the most promising due to the following reasons: requirement of chemicals for the treatment process is reduced, lower operating costs, eco-friendly, higher efficiency at low levels of contaminations and cost-effective alternative of conventional techniques.

In our previous papers we described sorption characteristics of Co, Zn and Cd binding by dry biomass of lichen *E. prunastri* (PIPIŠKA et al., 2008) and moss *R. squarrosus* (PIPIŠKA et al., 2010) and by biomass of activated sludge of waste water treatment plant (MAREŠOVÁ et al., 2010). The objective of this study was to obtain quantitative data of cadmium sorption by dried leaf biomass of common agricultural plants and reversibility of the sorption-desorption processes.

## 2. Materials and methods

### 2.1 Plant biomass

Leaves of sunflower (*Helianthus annuus* L.), pumpkin (*Cucurbita pepo* L.), cucumber (*Cucumis sativus* L.), pepper (*Capsidum annum* L.), tomato (*Solanum lycopersicum* L.) collected from plants growing in garden (Trnava region) and leaves of vine-grape (*Vitis vinifera* L.) from vineyard (Malé Karpaty region) in the middle of summer period.

Tobacco (*Nicotiana tabacum* L.) and hop (*Humulus lupulus* L.) leaves were obtained from plants cultivated in laboratory at 22 °C at light/dark period 12/12 h (2 000 lx). Seeds of tobacco were germinated and grown in pots filled with granulated perlite watered with diluted Hoagland medium pH 7.0 (HOAGLAND, 1920). Hop plants (variety Oswald clone 72, genotype K-72/6/13) were obtained from the Research Institute of Plant Production in Piešťany (SK).

Detached leaves were dried for 3 days at 60 °C, pulverized by rotatory knife blender and sieved by normalized sieves. Fractions < 0.45 mm were used for experiments.

### 2.2 Sorption experiments

A batch equilibrium method was used to determine sorption of Cd by dried leaf biomass of 8 plants. In plastic test tubes (10 mL) 0.05 g of dried biomass was mixed with 2 mL CdCl<sub>2</sub> solution in deionized water (0.01 – 10 mmol/L), spiked with <sup>109</sup>CdCl<sub>2</sub> and placed on reciprocal shaker (200 min<sup>-1</sup>) at 20 °C. Preliminary experiments showed that 10 min reaction time is sufficient for reaching of sorption equilibrium. For sorption experiments the initial pH value of solutions was adjusted to pH 5.0 with 1.0 M NaOH. Biomass was separated by centrifugation for 20 min at 2 800 × g and both sediments and liquid phase were analysed by gamma spectrometry. The experiments were conducted in triplicate. The amount of sorbed Cd (μmol Cd/g d.w.) was calculated according to the following equation:

$$Q = \frac{V * (C_0 - C_{eq})}{m} \quad (1)$$

where  $Q$  is the specific Cd uptake ( $\mu\text{mol Cd/g biomass d.w.}$ );  $V$  is the volume of Cd solution (L);  $C_0$  is the initial concentration of Cd in the solution (mmol/L);  $C_{eq}$  is the concentration of Cd in the solution in equilibrium (mmol/L) and  $m$  is mass of the dried biosorbent (g).

### 2.3 Desorption experiments

Biomass (0.05 g, d.w.) after sorption experiments was separated by centrifugation for 20 min at  $2\ 800 \times g$  and resuspended by vortexing for 30 min in 5.0 mL deionized water, 1.0 mL 0.1 M EDTA or 1.0 mL 0.1 M HCl. Cd concentrations in biomass and in extracts were estimated by similar way as in the sorption experiments.

### 2.4 Radiometric and speciation analysis

A gamma spectrometric assembly using the well type scintillation detector 54BP54/2-X, NaI(Tl) (Scionix, NL) and data processing software ScintiVision-32 (ORTEC, USA) were used for Cd determination in biomass and supernatants. A library of radionuclides was built by selecting characteristic  $\gamma$ -ray peaks (88.04 keV for  $^{109}\text{Cd}$ , 661.66 keV for  $^{137}\text{Cs}$ , 834.81 keV for  $^{54}\text{Mn}$  and 1115.52 keV for  $^{65}\text{Zn}$ ) for energy and efficiency calibration. Counting time 600 s allowed obtaining data with measurement error  $< 2\%$ , which do not reflect other source of errors. Standardized solution of  $^{109}\text{CdCl}_2$  (3.94 MBq/mL, 50 mg/L  $\text{CdCl}_2$  in 3 g/L HCl) was obtained from The Czech Institute of Metrology (Prague, CR). Cd speciation in the solution as a function of pH and concentration of  $\text{Cl}^-$  anions was performed using the Visual MINTEQ (ver. 3.0) modelling software.

## 3. Results and discussions

### 3.1 Cadmium sorption

Sorption experiments showed that dried leaf biomass is able to bind remarkable amounts of cadmium.  $Q$  values ( $\mu\text{mol/g, d.w.}$ ) at biomass concentration 25 g/L (d.w.) are proportional to the initial  $\text{CdCl}_2$  concentration within the range studied 0.01 – 10 mmol/L  $\text{CdCl}_2$ . However as can be seen from the data in Fig. 1 even at initial concentration  $C_0 = 10$  mmol/L  $\text{CdCl}_2$  plant sorbents were not saturated under given conditions and higher  $Q_{max}$  values at saturation of sorbent can be expected.

Sorption capacity  $Q$  of the dried leaf biomass of studied plants differs within the same order, ranging from 145 to 289  $\mu\text{mol/g}$  (d.w.), despite of different taxonomic classification (Tab. 1).

In Table 2, the value sorption capacities  $Q$  (mg/g Cd, d.w.) for naturally occurring sorbents are presented. We can conclude that studied plant biomasses showed similar results in comparison with others inorganic, organic and biological sorbents origin.

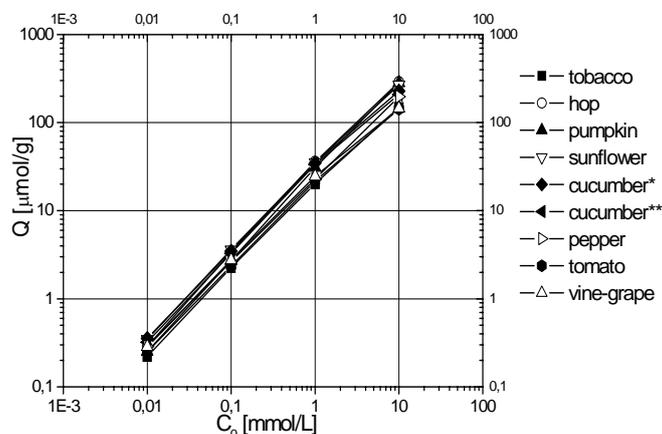


Fig. 1. Cadmium sorption  $Q$  ( $\mu\text{mol/g}$ ; d.w.) by dried leaf biomass of different plants (25 g/L, d.w.) in dependence on initial  $\text{CdCl}_2$  concentration. Data after 10 min reaction at 20 °C, pH 5.0 are the mean of three replicates. \**C. sativus* L. convar. *longus*, \*\**C. sativus* L. convar. *viridis*

Table 1. Cadmium sorption  $Q$  ( $\mu\text{mol/g}$ ; d.w.) by dried leaf biomass (25 g/L, d.w.) of different plants after 10 min reaction in 10 mmol/L  $\text{CdCl}_2$  in deionized water at 20 °C, pH 5.0. Data are the mean of three replicates.

Plant	Family	$Q$ [ $\mu\text{mol/g}$ ]
<i>Humulus lupulus</i> L.	<i>Cannabaceae</i>	288.8 ± 3.8
<i>Cucurbita pepo</i> L.	<i>Cucurbitaceae</i>	283.1 ± 8.7
<i>Helianthus annuus</i> L.	<i>Asteraceae</i>	268.4 ± 5.6
<i>Cucumis sativus</i> L. convar. <i>Longus</i>	<i>Cucurbitaceae</i>	228.4 ± 7.6
<i>Cucumis sativus</i> L. convar. <i>viridis</i>	<i>Cucurbitaceae</i>	209.7 ± 6.1
<i>Capsicum annuum</i> L.	<i>Solanaceae</i>	196.9 ± 4.3
<i>Nicotiana tabacum</i> L.	<i>Solanaceae</i>	148.8 ± 4.0
<i>Solanum lycopersicum</i> L.	<i>Solanaceae</i>	147.2 ± 4.0
<i>Vitis vinifera</i> L.	<i>Vitaceae</i>	145.0 ± 2.0

Table 2. Sorption capacities  $Q$  (mg/g Cd; d.w.) of naturally occurring sorbents.

Sorbent	$Q$ [mg/g]	Ref.	Sorbent	$Q$ [mg/g]	Ref.
Bark	32	3	Activated sludge	121	2
Chitosan	558	3	Hop leaves	32.5	4
Clay	16.5	3	Pumpkin leaves	31.8	4
Microbial biomass	28	3	Sunflower leaves	30.2	4
Modified wool	87	3	Cucumber leaves*	25.7	4
Peat	5.1	3	Cucumber leaves**	23.6	4
Seaweed	215	3	Pepper leaves	22.1	4
Xanthate	33.3	3	Tobacco leaves	16.7	4
Zeolite	84.3	3	Tomato leaves	16.5	4
Moss biomass	19.4	1	Vine leaves	16.3	4

(1) PIPÍŠKA et al., 2010; (2) MAREŠOVÁ et al., 2010; (3) BAILEY et al., 1999; (4) This paper.

\**C. sativus* L. convar. *longus*, \*\**C. sativus* L. convar. *viridis*

### 3.2 The influence of pH

It is generally accepted that the pH optimum of biosorption for bivalent metal cations is within pH 4 – 6. In strong acid media the efficiency of cation sorption is minimal due to competitive effect of  $H^+$  ions. In alkaline region the situation is more complicated due to the existence of multiple Cd species. Data obtained by speciation program Visual MINTEQ shows that eight Cd species can exist in alkaline solutions. Molar fractions of cationic, anionic and nonionic forms of Cd expressed in molar fraction  $X$  in dependence on pH value are shown in Fig. 2.

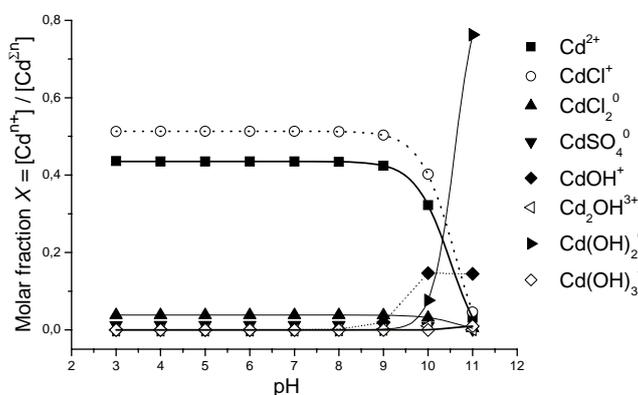


Fig. 2. Molar fraction  $X$  of cadmium species in dependence on solution pH at concentration 10 mmol/L  $CdCl_2^0$  and 20 °C. Solution of inorganic salts corresponding to synthetic waste water according to IAQUINTA *et al.* (2006) (ppm):  $Cl^-$  - 455;  $SO_4^{2-}$  - 87;  $Na^+$  - 418;  $K^+$  - 78;  $Mg^{2+}$  - 45;  $Ca^{2+}$  - 138. Calculated by Visual MINTEQ ver. 3.0.

As can be seen from the data in Fig. 2, prevailing part of Cd is present in  $Cd^{2+}$  form (42 %) and  $CdCl^+$  form (51 %) and this proportion stay the same within pH range from pH 3.0 to pH 8.5. Concentration of  $Cd(OH)_2^0$  increases above pH 9. During the sorption of metals by sorbents from alkaline liquid wastes besides sorption of  $Cd^{2+}$  cations also the existence of other than ionic metal forms with different solubility in water have to be taken into consideration. Similar data was obtained also by GUIBAUD *et al.* (2009), where sigmoidal pH dependence of  $Cd^{2+}$  sorption by polysaccharides of activated sludge with inflection point at pH 8.6 was observed.

### 3.3 The influence of $Cl^-$ ions

As can be seen from the data in Fig. 3, molar fraction  $X$  of  $Cd^{2+}$  significantly decreases in the presence of  $Cl^-$  ions up to  $10^{-1}$  mol/L NaCl, as a result of the increase of  $CdCl^+$  molar fraction. At 1.0 mol/L NaCl (5.8 %, w/v) concentration of  $Cd^{2+}$  is minimal and prevailing Cd species are non dissociated  $CdCl_2^0$  or  $CdCl^+$ .

In interactions of biosorbents with Cd(II) in the presence of  $Cl^-$  anions, what is typical for many kinds of liquid wastes, the existence of complex mixture of different Cd species can be expected. Mechanism of Cd biosorption will then depend both on the pH values of liquid phase, as well as on the concentration of other solutes, mainly

Cl<sup>-</sup> salts, but also on the presence of other solutes able to form complexes with high values of stability constants  $\log K$ .

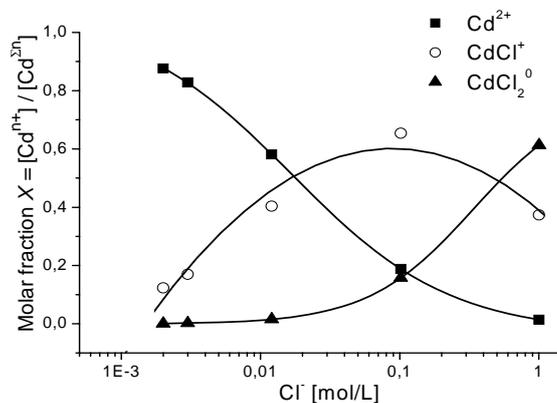


Fig. 3. Molar fraction  $X$  of  $\text{Cd}^{2+}$ ,  $\text{CdCl}^+$  and  $\text{CdCl}_2^0$  species in dependence on NaCl concentration in 1.0 mol/L  $\text{CdCl}_2$  in deionized water and 20 °C. Calculated by Visual MINTEQ ver. 3.0.

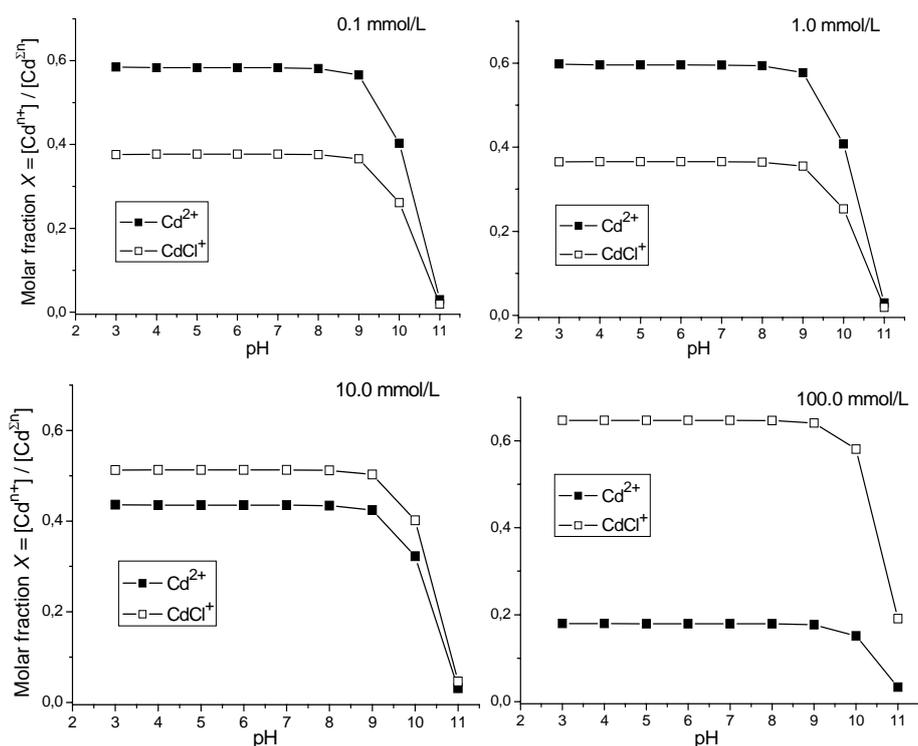


Fig. 4. pH dependence of molar fraction  $X$  of  $\text{Cd}^{2+}$  and  $\text{CdCl}^+$  ions at different  $\text{CdCl}_2$  concentration and 20 °C in solution of inorganic salts simulating waste water according to IAQUINTA *et al.* (2006) (ppm): Cl<sup>-</sup> - 455; SO<sub>4</sub><sup>2-</sup> - 87; Na<sup>+</sup> - 418; K<sup>+</sup> - 78; Mg<sup>2+</sup> - 45; Ca<sup>2+</sup> - 138. Calculated by Visual MINTEQ ver. 3.0.

### 3.4 Desorption

In dependence on the [biomass]: [extractant] ratio, different percentage of cadmium can be removed. By extracting with deionized water at the [biomass]: [extractant] = 1: 100 (w/v) ratio and in dependence on plant species up to 30 % of Cd was removed by single step extraction at 20 °C. By extraction with 0.1 mol/L EDTA at [biomass]: [extractant] = 1: 20 (w/v) ratio, up to 85 % and with 0.1 M HCl up to 98 % was removed under identical conditions.

By desorption with water, new concentration equilibrium expressed as  $P = [\text{Cd}]_{\text{sorbent}} / [\text{Cd}]_{\text{solution}}$  is formed. Cadmium is released with higher efficiency from the binding sites of lower stability constants  $\log K$ . Stability constant of the metal complex can be described by the equation (2):

$$\log K = [\text{ML}] / [\text{M}] * [\text{L}] \quad (2)$$

where  $K$  is the stability constant,  $[\text{M}]$  is the concentration of  $\text{Cd}^{2+}$  ions and  $[\text{L}]$  is the concentration of a ligand such as carboxylic or amino acids.

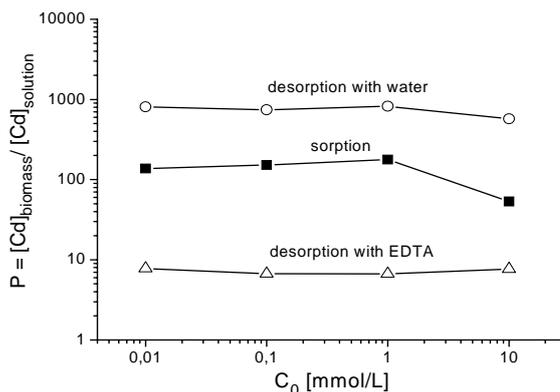


Fig. 5. Sorbent to solution concentration ratio (mmol/kg)/(mmol/L) for cadmium in dependence on initial concentration of  $\text{CdCl}_2$ . Sorption process (—■—); desorption with deionized water (—○—) and desorption with 0.1 mol/L EDTA (—△—). Experimental points are the mean values obtained from sorption experiments of 8 plants shown in Fig. 1 (—■—); and of data obtained by desorption of biomass with deionized water (—○—) and 0.1 mol/L EDTA as described in Materials and methods.

Metal ions can form more or less stable complexes with many biomolecules differing in stability constants  $\log K$ . Cd complexes with organic compounds can be divided into four groups. A:  $\log K \sim 1 - 2$  (carboxylic acids); B:  $\log K \sim 5 - 6$  (amino acids and citric acid); C:  $\log K \sim 9 - 10$  (cysteine, glutathione and other —SH compounds); D:  $\log K \sim 16 - 18$  (complexing ligands such as EDTA). Classification is based on published data of Cd and other bivalent metal complexes (MARTELL and SMITH, 1964; SRIVASTAVA *et al.*, 1993; GUNTHER and KASTENHOLZ, 2005).

We can suppose that by extracting with deionized water only Cd atoms bind into complexes of low  $\log K$  values are released. Characterization of the mode of cadmium

binding not extractable with the strongest ligands such as EDTA will require more detailed study. However differences in the efficiency of Cd desorption with water and EDTA reflects the fact that broad spectrum of reactive groups differing in stability constants is taking place.

#### 4. Conclusions

Dried leaf biomass of eight vascular plants shows the sorption capacity for cadmium binding from CdCl<sub>2</sub> water solution depending on the initial concentration of the solute, and is comparable with the sorption capacity of other sorbents of plant origin. Sorbed cadmium is partially leachable with deionized water and with high efficiency by EDTA solution and diluted mineral acids. This supports the idea that in sorption processes Cd complexes with different stability constants *log K* are formed. Calculation by speciation program Visual MINTEQ showed, that both alkaline pH values and concentration of chloride anions determines the existence at least seven Cd species with cationic, anionic and neutral charge. Obtained data can serve for the prediction of cadmium transport in biosphere and at penetration into food chain from contaminated vegetable crops.

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