



# Biosorption of Lead and Cadmium Ions on the Green Parts of *Daucus Carota*

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## Abstract

*This study deals with utilization of milled stems and leaves of carrot (*Daucus carota*) for the adsorptive removal of Pb(II) and Cd(II) from the aqueous solution. Carrot was bought in the local grocery, it was dried at the laboratory temperature and milled. Prepared material was analysed by the infrared spectrometry which confirms good structural homogeneity of the sample. Kinetic measurements were performed for estimation of adsorption equilibrium time. Equilibrium of Pb(II) adsorption was established after 6 hours of contact time, equilibrium of Cd(II) adsorption was established after 24 hours of contact time. The isotherms' measurements were realized with the contact time 24 hours for the estimation of adsorption capacities of the studied sorbent. Adsorption capacities were around 47 mg/g for Cd(II) and 154 mg/g for Pb(II). Changes of pH values of the sorption solutions were negligible but some amount of Ca(II), Mg(II), K(I) and Na(I) ions was released to the solution during adsorption process. *Daucus carota* stems and leaves exhibit good sorption capacities and they could be utilized for adsorptive removal of Pb(II) and Cd(II) ions from the aqueous solutions.*

**Keywords:** biosorption, carrot, lead, cadmium

## Introduction

Heavy metals represent potentially dangerous species for the plants, animals and human health. They negatively affect many biochemical processes (Chen et al., 2017). Heavy metals ions can be released to the environment through some types of pesticides, by the combustion of fossil fuels or they can get to the environment from the industrial wastes (Kafka and Punčochářová, 2002). Processing of industrial wastes containing heavy metals is currently widely studied (Al-Enezi et al., 2004; Sreesai and Sthiannopkao, 2009). Industrial wastewater containing heavy metals can be decontaminated by various techniques such as precipitation (Wu, 2019), electrodeposition (Vivas et al., 2019), or adsorption (Mohan et al., 2007). Adsorption represents the most utilized technique for heavy metals removal. Clays (mainly bentonites) (Yang et al., 2010) and activated carbons (Mohan et al., 2007) belong to the most common adsorbents used in the praxis. Sorption capacities of these materials vary for various metals ions. They can be up to tens of mg/g of sorbent (Mohan et al. 2007; Yang et al., 2010). Unfortunately, clays belong to the exhaustible resources and production of activated carbons is relatively energy-intensive. Research in the field of heavy metals adsorption is currently targeted to the utilization of various waste materials (Bláhová et al., 2018; Wang et al., 2015). Slags as a by-product from the metallurgical industry exhibit promising sorption properties. Sorption capacity of blast furnace slag for Pb(II) can be around 20 mg/g but sorption capacity of steelmaking slag for Pb(II) can reach 70 mg/g of material (Bláhová et al., 2018). Unfortunately slags interact with water, they cause increase of the solution's pH value as well as they release some ions to the solution. Therefore they are potentially dangerous, which limit their utilization for the wastewater treatment (Mucha, 2018). Biosorption represents other approach to the research of the new sorption materials. Plants or their parts (Dubey

and Mishra, 2017, Mucha and Mucha, 2015) or fungi (Zhao et al., 2016) can be utilized as sorption materials. These materials are of natural origin and compounds which can be released from these materials would not be dangerous for environment in the comparison to waste materials. Biosorbents can reach or even exceed the sorption capacities of above mentioned materials (Mucha and Mucha, 2015).

Presented work deals with utilization of carrot (*Daucus carota*) dried and milled stems and leaves for adsorption of Pb(II) and Cd(II) ions from the aqueous environment. Material was characterized by infrared spectroscopy and kinetics and adsorption isotherms were measured.

## Materials and methods

Carrot (*Daucus carota*) was purchased in the local grocery. Green parts (stems and leaves) were separated from the root and they were dried at laboratory temperature. Green parts were milled after the drying and they were characterized by infrared spectrometry (FTIR) on the Nicolet 6700 FTIR spectrometer (Thermo scientific, USA). Spectra were measured by ATR technique with single bounce diamond crystal at 256 scans and with resolution 4 cm<sup>-1</sup>. The bulk density, loss by drying at 105°C (using the Memmert UNB 300 dryer, Memmert GmbH, Germany) and loss of ignition (amount of ash) at 1100°C (using the muffle furnace, LAC Ltd. Czech Republic) were determined. Material was decomposed by 1:1 HNO<sub>3</sub> (p.a., Mach chemicals Ltd., Czech Republic) and contents of Ca(II), Mg(II), K(I), Na(I), Pb(II) and Cd(II) were determined by atomic absorption spectrometry (AAS) at Varian AA240FS spectrometer (Varian, USA). Standards of particular cations were supplied by Sigma-Aldrich GmbH (Germany), wavelengths 422,7 nm (Ca), 202,6 nm (Mg), 404,4 nm (K), 330,3 nm (Na), 205,3 nm (Pb) and 326,1 nm (Cd) were utilized for analysis. Adsorption experiments were carried out by batch

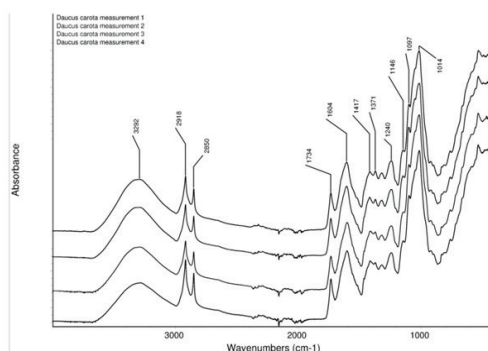


Fig. 1. Infrared spectra of various portions of the studied material  
Rys. 1. Widma w podczerwieni różnych części badanego materiału

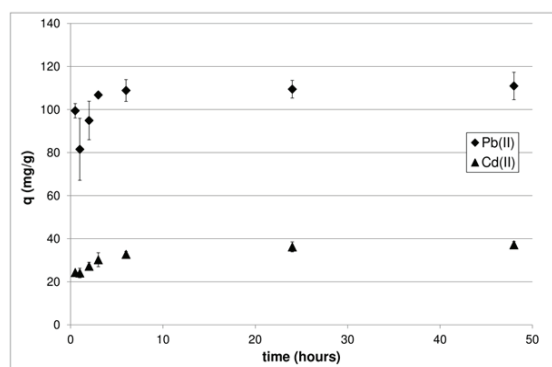


Fig. 2. Kinetics of Cd(II) and Pb(II) adsorption on the carrot biomass  
Rys. 2. Kinetyka adsorpcji Cd (II) i Pb (II) na biomacie z marchwi

method. Kinetic experiments were realized at times 0.5, 1, 2, 3, 6, 24 and 48 hours. Concentrations of studied cations in the sorption solutions were 5 mmol/L. Sorption solutions were prepared from  $\text{Pb}(\text{NO}_3)_2$  (p.a., LachNer Ltd., Czech Republic) and  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (p.a., Sigma-Aldrich GmbH, Germany). The mass 0.25 g of carrot biomass was weighted to the centrifugation tube and 50 mL of sorption solution was added. Samples were occasionally stirred and filtered after given time period. The pH values of the solutions were measured by WTW InoLab 735 equipped by WTW SenTix 41 electrode (WTW GmbH, Germany). Concentrations of Pb(II), Cd(II), Ca(II), Mg(II), K(I) and Na(I) were determined by above mentioned AAS methods. Equilibrium measurements of isotherms were carried out in the centrifugation tubes with 0.25 g of carrot biomass and 50 mL of sorption solution. Concentrations of the Pb(II) and Cd(II) cations in the sorption solutions were 0.1, 0.5, 1, 2.5, 5, 10 and 20 mmol/L. Contact time was 24 hours and it was selected according to kinetic measurements. Samples were filtered after 24 hours and contents of Pb(II), Cd(II), Ca(II), Mg(II), K(I) and Na(I) were determined by AAS method. All sorption experiments were carried out in 3 parallel assessments at temperature  $22 \pm 1^\circ\text{C}$ .

## Results and discussion

Dried and milled sorption material (carrot biomass) was characterized at first. It was found out that material contains  $9.4 \pm 1.7\%$  of free water (moisture) and  $6.9 \pm 0.8\%$  of ash. Bulk density of the used carrot biomass was  $172.4 \pm 6.8 \text{ kg/m}^3$ . Contents of selected ions in the used material were  $17.98$

$\pm 3.25 \text{ mg/g}$  (Ca),  $5.45 \pm 0.26 \text{ mg/g}$  (Mg),  $33.59 \pm 4.38 \text{ mg/g}$  (K),  $14.21 \pm 0.87$  (Na),  $< 3.14 \pm 0.07 \text{ mg/g}$  (Pb) and  $< 5.84 \pm 0.14 \text{ mg/g}$  (Cd). It can be stated that contents of Pb(II) and Cd(II) in the studied material were negligible for purposes of this study.

Infrared spectra were measured for the verification of homogeneity of the sample as well as for the description of material's chemical composition. Measured spectra are depicted on the Fig. 1. It can be seen that spectra of various portions of biomass are almost identical, only negligible changes occur in the region of  $-\text{CH}_2-$  and  $-\text{CH}_3$  groups deformation vibrations ( $1417$  and  $1371 \text{ cm}^{-1}$ ). It can be stated that material is homogeneous enough for the utilization in sorption experiments in this study. Chemical composition of the carrot biomass is mainly organic. The broad band at  $3292 \text{ cm}^{-1}$  can be assigned to the stretch vibration of O–H or N–H bonds. Bands at  $2918$  and  $2850 \text{ cm}^{-1}$  belong to the stretch vibrations of C–H bond in the saturated hydrocarbons. Presence of carbonyl group (C=O, aldehydes, ketones or carboxylic acids) is confirmed by the band at  $1734 \text{ cm}^{-1}$ . Broad band around  $1604 \text{ cm}^{-1}$  can be assigned to the stretch vibration of C=C in aromates and it can contain the band of C=O stretch vibration in carboxylates as well. Bands of deformation vibrations of  $-\text{CH}_2-$  and  $-\text{CH}_3$  groups occur at  $1417$  and  $1371 \text{ cm}^{-1}$ . Content of C–O or C–N bonds in various functional groups can be assumed from the presence of bands at  $1240$ ,  $1146$ ,  $1097$  and  $1014 \text{ cm}^{-1}$ . Studied material contains aliphatic as well as aromatic hydrocarbon parts and mainly hydroxyl, amine and carboxyl functional groups (Socrates, 2007). Heavy metals cations could bond

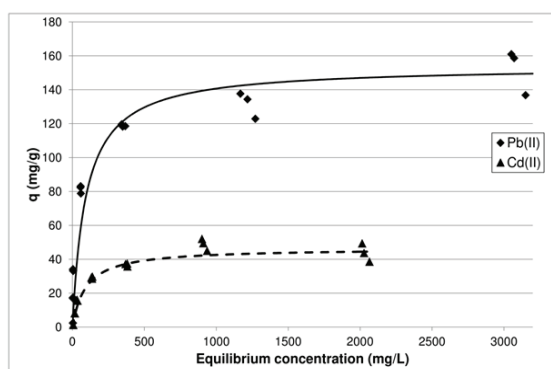


Fig. 3. Adsorption isotherms of Cd(II) and Pb(II) on the carrot biomass  
Rys. 3. Izotermy adsorpcji Cd (II) i Pb (II) na biomacie z marchwi

Tab. 1. Parameters of Langmuir isotherm for studied cations ( $q_{\max}$  – maximal adsorbed amount)  
Tab. 1. Parametry izotermy Langmuira dla badanych kationów ( $q_{\max}$  - maksymalna zaadsorbowana ilość)

Metal cation	$q_{\max}$ [mg/g]	$b$ [L/mg]
Pb(II)	$154,50 \pm 13,70$	$0,011 \pm 0,005$
Cd(II)	$47,26 \pm 6,97$	$0,011 \pm 0,004$

on the surface of carrot biomass probably on the carboxylic groups via chemisorption or on the hydroxyl or amine functional groups or on the  $\pi$ -electron systems by the electrostatic interactions.

The results of kinetic measurements are shown on the Fig. 2. It can be stated that equilibrium of the sorption on carrot biomass is established after 6 hours of contact time in the case of Pb(II) ions and after 24 hours of contact time in the case of Cd(II) ions. The adsorbed amount of Cd(II) increases continuously with increasing contact time. The adsorbed amount of Pb(II) ions increases significantly in the first 0.5 hour, then small decrease in the adsorbed amount occurs after 1 hour and then further increase of adsorbed amount occurs. The decrease can be probably caused by changes in the composition of the Pb(II) complex particles on the biomass surface or by reorganization of adsorbed Pb(II) cations on the surface due to chemical reactions with surface functional groups (chemisorption), which can lead to the release of small amount of Pb(II) ions back to the solution. The changes of the pH values during sorption were negligible (maximal 0.5 pH units after 48 hours). These changes can be caused by changes of the solution composition during sorption as Pb(II) or Cd(II) were removed from the solution and other cations were released from the material. Each cation forms various aqua- and hydroxo- complexes in the aqueous environment and therefore changes in the cationic composition of solution can cause small changes of the pH values. Carrot biomass contains higher amounts of Ca(II), Mg(II), K(I) and Na(I) which are released to the solution during sorption. The amount of released K(I) was up to  $33.14 \pm 1.22$  mg/g, released amount of Na(I) was  $14.87 \pm 1.34$  mg/g, released amount of Mg(II) reach  $3.52 \pm 0.21$  mg/g and released amount of Ca(II) was up to  $15.12 \pm 0.83$  mg/g. It can be stated that almost all of cations present in the material were released to the solution during the sorption. Chemisorption can be other factor that influences the solution pH value. If the chemisorption on the carboxylic functional groups occurs during contact of biomass with solution, small amount of H(I) ions or other cations can be released to the solution due to formation of carboxylates

containing Pb(II) or Cd(II) ions. Release of H(I) ions as well as the formation of hydroxocomplexes of cations present in the solution can cause the pH values decrease. Adsorption of Cd(II) and Pb(II) on the carrot biomass take probably place by combination of physisorption and chemisorption, which can be concluded from the fast first stage of adsorption but the longer time to reach equilibrium as well as from the release of cations from the material.

Adsorption isotherms were measured for contact time 24 hours and they are depicted on the Fig. 3. The model of Langmuir isotherm is more suitable in the case of both studied cations. Model isotherms were calculated using linear forms of isotherms' equations. The coefficients of determination of the linear forms of isotherms were 0.98 (Pb(II) isotherm) and 0.97 (Cd(II) isotherm) in the case of Langmuir model in the comparison to 0.68 (Pb(II) isotherm) and 0.79 (Cd(II) isotherm) in the case of Freundlich model. Parameters of Langmuir isotherms calculated from measured data are shown in the Table 1. The maximal adsorption capacities ( $q_{\max}$ ) of the carrot biomass were  $154.5 \pm 13.7$  mg/g for Pb(II) and  $47.3 \pm 7.0$  mg/g for Cd(II) ions. The sorption capacities recalculated to molar expression were 0.75 mmol/g for Pb(II) and 0.42 mmol/g for Cd(II), so it can be stated that carrot biomass has higher affinity to Pb(II) ions in the comparison to Cd(II) ions. Changes of the pH values during sorption were negligible as in the case of kinetic measurements. Cations (Ca(II), Mg(II), K(I) and Na(I)) were released to the solution as well. The amount of released cations is practically independent at the initial concentration of Pb(II) or Cd(II) in the case of Mg(II) and Na(I) and it increases with increasing initial concentration of Pb(II) or Cd(II) in the case of Ca(II) and K(I). Studied heavy metals cations probably interact with various parts of biomass surface because Ca(II) release is more affected compared to K(I) release in the case of Pb(II) sorption but release of cations exhibits opposite trend (more affected K(I) release than Ca(II) release) in the case of Cd(II) sorption. Estimated adsorption capacities are comparable or higher than adsorption capacities of other materials studied for the removal of heavy metals cations from the aqueous solutions. Other stud-

ies state sorption capacities for bentonite 47.9 mg/g of Pb(II) (Yang et al. 2010) or 117.6 mg/g of Pb(II) (Mucha and Mucha, 2015). The sorption capacities for activated carbons around 30.1 mg/g of Pb(II) and 8.0 mg/g of Cd(II) were published (Mohan et al. 2007). Slags were studied as sorption material as well with sorption capacities of Pb(II) around 22.8 mg/g for blast furnace slag and 78.7 mg/g for steelmaking slag (Bláhová et al. 2018). It can be stated that carrot biomass could be promising material for sorption purposes.

### Conclusion

Carrot (*Daucus Carota*) biomass obtained by drying and milling of green parts (stems and leaves) of carrot was utilized for removal of Pb(II) and Cd(II) cations from the aqueous solutions. Sorption material was characterized to determine basic parameters (moisture content, ash content, bulk density) and information about chemical composition. It was found out using infrared spectroscopy that material is homo-

geneous enough for utilization as sorbent. Kinetic measurements reveal that sorption equilibrium was reached after 24 hours in the case of Cd(II) ions and it was reached after 6 hours in the case of Pb(II) ions. Only negligible changes of the pH values occur during contact of carrot biomass with solutions containing Pb(II) or Cd(II) ions and various cations (Ca(II), Mg(II), Na(I) and K(I)) were released to the sorption solution during contact with sorbent. Equilibrium measurements show that adsorption of Pb(II) and Cd(II) ions on the carrot biomass takes place according to Langmuir isotherm model and the adsorption capacities of the studied sorbent were  $154.5 \pm 13.7$  mg/g for Pb(II) and  $47.3 \pm 7.0$  mg/g for Cd(II) ions. These sorption capacities are comparable or higher than capacities of other sorption materials (bentonite, activated carbon, slags) published in the literature. Carrot biomass could be utilized as alternative sorbent for the Pb(II) and Cd(II) ions removal from the aqueous solutions.

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### *Biosorpccja jonów ołowiu I kadmu na zielonych częściach marchwi Daucus Carota*

Artykuł dotyczy wykorzystania zmielonych łodyg i liści marchwi (*Daucus carota*) do adsorpcyjnego usuwania Pb (II) i Cd (II) z roztworu wodnego. Marchewkę kupiono w lokalnym sklepie spożywczym, wysuszono w laboratorium i zmielono. Przygotowany materiał analizowano za pomocą spektrometrii w podczerwieni, co potwierdziło dobrą jednorodność strukturalną próbki. Pomiary kinetyczne przeprowadzono w celu oszacowania czasu osiągnięcia równowagi adsorpcji.

Równowagę adsorpcji Pb (II) ustalono po 6 godzinach czasu kontaktu, równowagę adsorpcji Cd (II) ustalono po 24 godzinach czasu kontaktu. Pomiary izoterm wykonano z czasem kontaktu 24 godziny w celu oszacowania zdolności adsorpcji badanego sorbentu. Zdolności adsorpcyjne wynosiły około 47 mg / g dla Cd (II) i 154 mg / g dla Pb (II). Zmiany wartości pH roztworów sorpcyjnych były znikome, ale pewna ilość jonów Ca (II), Mg (II), K (I) i Na (I) została uwolniona do roztworu podczas procesu adsorpcji. Łodygi i liście *Daucus carota* wykazują dobre zdolności sorpcyjne i można je wykorzystać do adsorpcyjnego usuwania jonów Pb (II) i Cd (II) z roztworów wodnych.

**Słowa kluczowe:** biosorpccja, marchew, ołów, kadm

