doi: 10.17221/3/2015-SWR

Biosorption of Cr(VI) from Natural Groundwater and the Effect of DOC-rich Treated Water on Cr Dissolving from Contaminated Soil

Hana ŠILLEROVÁ[1], *Aleš VANĚK*[2], *Vladislav CHRASTNÝ*[1] *and Michael KOMÁREK*[1]

[1]*Department of Environmental Geosciences, Faculty of Environmental Sciences and*
[2]*Department of Soil Science and Soil Protection, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences Prague, Prague, Czech Republic*

Abstract

Šillerová H., Vaněk A., Chrastný V., Komárek M. (2015): Biosorption of Cr(VI) from natural groundwater and the effect of DOC-rich treated water on Cr dissolving from contaminated soil. Soil & Water Res., 10: 236–243.

Brewers draff and grape waste were used as efficient biosorbents for removing Cr(VI) from contaminated groundwater. Additionally, the interactions between the dissolved organic carbon-rich (DOC-rich) treated water and a soil contaminated with Cr(III) was further studied. The breakthrough curves obtained from column (dynamic) adsorption experiments showed higher adsorption efficiency of grape waste compared to brewers draff. The adsorption efficiency was 36.8–40.4% for brewers draff and 56.6–68.3% for grape waste, depending on the initial pH. The detected saturation time was approximately three times higher than in our previous study, where a model solution of Cr(VI) was used. The natural groundwater showed to be rich in dissolved organic matter after the treatment. The consequent interaction of the treated water with the soil led to a partial dissolution of Cr from the contaminated soil (corresponding to < 1% of total soil Cr) in the case of brewers draff, but also to adsorption of the residual Cr from the treated water to the soil in the case of grape waste. The obtained data demonstrated that Cr(III), when abundant in soils, could be potentially mobilized by the DOC-rich solution. On the other hand, the risk associated with this secondary Cr mobilization and its subsequent migration in soils (or sediments) seems to be very low or even negligible.

Keywords: adsorption; biosorbents; chromium; dissolved organic carbon; soil

The main reason why Cr is considered to be a priority pollutant in natural waters (US EPA 2014) is the high toxicity and carcinogenicity of its hexavalent form (Cr(VI)). Cr(III) and Cr(VI) are the predominant species in the environment (Losi *et al.* 1994). Cationic Cr(III) is the most stable and is usually strongly retained by the soil sorption complex. On the other hand, the anionic Cr(VI) is usually weakly adsorbed and can be readily leached to groundwater. Transport within the terrestrial and water system is significantly affected by its chemical form, chemical and photochemical redox transformations, precipitation or dissolution, and adsorption and desorption processes (Kotaś & Stasicka 2000). Chromium can migrate from terrestrial to water systems by surface run-off and transport through the soil to the groundwater. Hexavalent Cr in the environment originates mainly from anthropogenic sources such as mining, metallurgical and steel industry, electroplating, production of paint pigments and dyes, wood preservation etc.

In the last few decades biosorption proved to be a suitable alternative for Cr removal from aqueous solutions (Fiol *et al.* 2003; Miretzky & Cirelli 2010) and the adsorption experiments are usually performed using a Cr(VI) model solution. The adsorption potential of a biosorbent (wood, peat, husk and hulls, shells, stalks, lignin, wool waste etc.) is then evaluated (Gupta *et al.* 2009; Miretzky & Cirelli 2010). However, for real implementation of the studied biosorbent within a conventional Cr(VI) remediation processes, treatment of a "natural" contaminated water should be also studied. Moreover, it is important to point out that during the biosorption processes a significant amount of water-soluble compounds can be leached into the treated water. Dissolved organic carbon (DOC) in such treated waters may reach hundreds of ppm. The DOC concentration varies according to the type of biosorbent, biosorbent particle size, pH of the treated water etc. (Yang & Chen 2008; Vassilev *et al.* 2012; Pujol *et al.* 2013). The DOC originating from the biosorbent is an efficient reductive agent, which could contribute to Cr(VI) reduction in the contaminated water. Additionally, the organic substances in water can affect the uptake, bioavailability, transport, fixation, and toxicity of risk elements in soil and water (Leita *et al.* 2009; Choppala *et al.* 2013).

This work enhances previous research on brewers draff and grape waste as biosorbents for Cr(VI) removal from aqueous solutions (Šillerová *et al.* 2013, 2014). In this study, natural ground water contaminated by Cr(VI) is used for the treatment instead of Cr(VI) model solution. Consequently, the DOC concentration in the treated water and its effect on Cr-contaminated soil is studied. The objective is to evaluate the efficiency of the biosorbents for Cr(VI) removal from natural groundwater and to test whether the dissolved organics in the treated water (extracted from the biosorbents during the biosorption process) can cause any dissolution of Cr from a contaminated soil, simulating thus a scenario of accidental leaching during *in situ* treatment.

MATERIAL AND METHODS

Material. The brewers draff, a typical by-product of fermentation in beer production, was provided by the research and teaching brewery of the Czech University of Life Sciences Prague. The brewers draff is a residue of grain husks used in brewing, nowadays mainly used as a food supplement for domestic animals. Grape waste (mixed stalks and husks) was supplied by a wine producer from Most, Czech Republic. According to Fourier Transform Infrared Rays analysis (FTIR), both materials contain carboxylic groups (-COOH), hydroxyl groups (-OH), and to a lesser extent, amino groups (-NH_2). The specific surface area S_{BET} is 1.99 and 1.77 m^2/g, pH at point of zero charge (pH_{PZC}) is 5.6 and 4.7 for brewers draff and grape waste, respectively (Šillerová *et al.* 2013). Dried (80°C overnight) and sieved (particle size < 0.2 mm) materials were used for the experiments. All chemicals used in this study were of analytical grade (Sigma Aldrich, St. Louis, USA).

Cr-contaminated groundwater and soil. The groundwater samples originate from the vicinity of an electroplating industry manufacturing bicycle parts and components near Zlaté Hory in the northeastern part of the Czech Republic. The predominant contaminants in the area include Cr(VI), Ni, oil products, and chlorinated hydrocarbons. During the years 2011 and 2012, the extent of groundwater contamination (by Cr and Ni) was investigated. The average concentration of Cr(VI) in the groundwater reaches 7 mg/l (total Cr reaches 7.8 mg/l) with a Cr(VI) peak value reaching 26 mg/l (limit for Cr(VI) in drinking water is set to 0.1 mg/l by the US EPA 1996). The groundwater sample was collected from one well in the centre of the contamination plume using a low flow submersible pump. The well was first purged until the stabilization of conductivity

Table 1. General characteristics of the groundwater used for the biosorption experiments

Variables	Method	Measured values
pH (–)	ISO 10523	6.91
Electrical conductivity (EC, mS/m)	ISO 7888	129
Acidity (mmol/l)	CSN 757372	0.55
Alkalinity (mmol/l)	ISO 9963-1	0.66
Ammonium (NH_4, mg/l)	ISO 11732	1.68
Bi-carbonate (HCO_3^-, mg/l)	ISO 9963-1	42.4
Carbonate (CO_3^{2-}, mg/l)	ISO 9963-1	0.0
Total chromium (Cr, mg/l)	ISO 11885	19.6
Chromium(VI) (Cr(VI), mg/l)	EPA 7199	18.8
Dissolved organic carbon (DOC, mg/l)	ISO 8245	2.34
Iron(II) (Fe(II), mg/l)	ISO 6332	< 0.01
Iron(III) (Fe(III), mg/l)	ISO 6332	< 0.50
Nickel (Ni, mg/l)	ISO 11885	18.2
Nitrite (NO_2^-, mg/l)	ISO 13395	0.18
Nitrate (NO_3^-, mg/l)	ISO 13395	16.7
Sulphate (SO_4^{2-}, mg/l)	ISO 10304-1	121
Sulphide (S^{2-}, mg/l)	ISO 10530	< 0.01
Total dissolved solids (TDS, mg/l)	CSN 757346	852

and the water was sampled (0.05 l/s) into plastic bottles, filtered immediately (0.45 µm) and kept in a freezer until their use. The chemical composition of the collected sample is summarized in Table 1.

The organo-mineral soil (contaminated with Cr) used in all experiments originated from the area of a historical electroplating plant Buzuluk (Komárov, Central Bohemia, Czech Republic). The soil was air-dried, homogenized, and sieved through a 2-mm stainless-steel sieve before use; according to Food and Agriculture Organisation of the United Nations (FAO) the soil was classified as an Arenic Fluvisol. Basic physico-chemical properties of the soil are summarized in Table 2 and were determined using the methods described in Vaněk *et al.* (2010). The mineralogy of the bulk soil (determination by the X-ray diffraction (XRD) analysis) was dominated by quartz (SiO_2), albite ($NaAlSi_3O_8$), muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$), and illite ($(K,H_3O)Al_2(SiAl)_4O_{10}(OH)_2$) with traces of hematite (Fe_2O_3), goethite (FeOOH), calcite ($CaCO_3$) and kaolinite ($Al_2Si_2O_5(OH)_4$). It should be noted that there were no Cr phases identified in the soil matrix using XRD, probably due to the unidentifiable amounts of Cr species (below the detection limit of the method) and/or their amorphous/poorly crystalline nature.

Biosorption of Cr(VI) from contaminated groundwater. Packed bed column experiments were performed using glass columns (2.5 cm internal diameter, 10 cm column length; Bio-Rad, Hercules, USA). The effect of flow rate as well as the bed depth was previously tested on different types of biosorbents (Calero *et al.* 2009; Vinodhini & Das 2010). The adsorption efficiencies were higher at lower flow rates (Q, ml/min) and the most often used flow rates ranged between 1 and 10 ml/min. Metal uptake capacities also increase with increasing bed height (Z, cm). Parameters Q (1 ml/min) and Z (approximately 10 cm) were optimized using literature data (Calero *et al.* 2009; Vinodhini & Das 2010) and kept constant during the experiment. The pH values were set to 3, 4.5 and 7 for the experiment (with pH ~7 being the original pH of the treated water). The Cr(VI)-contaminated water was fed to the top of the column using a peristaltic pump with a flow adapter (Bio-Rad). The samples were collected at periodic time intervals until the outlet Cr concentration reached 85% of the inlet Cr concentration. The breakthrough curves were constructed and the following parameters were calculated:

Total volume of effluent V_{ef} (l)

$$V_{ef} = Q \times t_s \tag{1}$$

Total amount of metal sent to the column m_{tot} (mg)

$$m_{tot}(Cr) = \frac{C_{in} \times Q \times t_s}{1000} \tag{2}$$

Total amount of sorbed metal m_{sorbed} (mg)

$$m_{sorbed}(Cr) = \frac{Q}{1000} \int_{t=0}^{t=t_s} C_R(t)dt \tag{3}$$

Total metal removal (%) R

$$R = \frac{m_{sorbed}(Cr)}{m_{tot}(Cr)} \times 100 \tag{4}$$

Sorption capacity q (mg/g)

$$q = \frac{m_{sorbed}(Cr)}{m_{fixed\ bed}} \tag{5}$$

where:

Q – flow rate (ml/min)
t_s – saturation time (min)
C_{in} – initial concentration of Cr in the solution (mg/l)
C_R – concentration of Cr removed from the solution (mg/l)
$m_{fixed\ bed}$ – mass of the biosorbent (g)

Table 2. Basic physico-chemical characteristics of the Cr-bearing soil

Parameter	Value
Particle size distribution	
Clay (%)	4.00
Silt (%)	19.0
Sand (%)	77.0
pH_{H_20}	6.7
pH_{KCl}	6.2
pH_{PZC}	6.5
CEC (cmol/kg)	13.1
C_{org} (%)	4.30
Oxalate extractable	
Fe (g/kg)	9.03
Al (g/kg)	1.92
Mn (g/kg)	1.27
Total Cr (g/kg)	5.89

CEC – cation exchange capacity; PZC – point of zero charge

Effect of DOC in treated water on Cr dissolving from Cr-contaminated soil. Batch (kinetic) leaching experiments with DOC-rich treated water and

Cr-contaminated soil were performed in order to evaluate the effect of DOC on Cr mobilization in the soil. Besides that, the effect of DOC on Cr dissolving was evaluated. Two types of DOC-rich samples were used for this experiment: (*i*) a treated natural groundwater; and (*ii*) a leachate prepared by leaching the brewers draff and grape waste in deionized water. The DOC-rich samples were prepared by agitating (250 rpm) 200 g of brewers draff or grape waste with 2000 ml of natural groundwater or deionized water for 24 h in a plastic flask. The concentration of DOC in filtered (0.45 μm) samples was determined by a TOC-L analyzer (Schimadzu, Columbia, USA). Consequently, the samples were diluted by deionized water to four different DOC concentrations (2, 1, 0.5, and 0.1 g/l). A volume of 20 ml of each sample was mixed with 2 g of the Cr-contaminated soil (i.e. at L/S = 10) and agitated (250 rpm) for 0.5, 1, 2, 5, and 24 h. Each sample was prepared in triplicate. A control with deionized water was included. The final concentration of Cr was determined by ICP-OES (Agilent Technologies, Santa Clara, USA). All results were plotted against time and the risk of Cr dissolving was evaluated.

RESULTS AND DISCUSSION

Biosorption of Cr(VI) from contaminated groundwater. The dynamic behaviour of the biosorbents is described in terms of effluent "concentration-time" profile, i.e. breakthrough curve. The breakthrough curves (Figure 1) of brewers draff and grape waste for three different pH values (3, 4.5, and 7) were compared in terms of breakthrough time (t_b, the time at which metal concentration in the effluent reached 5% of the influent value) and bed saturation time (t_s, the time at which metal concentration in the effluent exceeded 85% of the influent value). The breakthrough time for biosorbents is usually very short (minutes) depending mainly on the flow rate, Cr concentration, and bed height. In most of the cases, it is impossible to determine t_b because the limit is already achieved at time close to zero (López-García *et al.* 2010; Sreenivas *et al.* 2014). In this study, Cr concentration higher than 5% of the influent value was observed after the first 10 min and afterwards increased slightly throughout the whole time interval. The saturation point of the column was reached more rapidly in the case of brewers draff (approximately 31 h), while in the case of grape waste it was significantly longer (52 h). The detected saturation time is approximately three times longer than in our previous study, where a model solution of Cr(VI) was used (Šillerová *et al.* 2013). The Cr concentration in the effluent did not reach 100% of the initial Cr concentration, but slightly increased after the saturation point. This is most probably a consequence of the complex nature of the biosorption and other processes, such as precipitation (Šillerová *et al.* 2013, 2014). The experimental conditions and calculated parameters are summarized in Table 3. The adsorption efficiency was between 36.8 and 40.4% for brewers draff and 56.6 and 68.3% for grape waste, depending on the initial pH. It is surprising that the biosorption process is not much affected by the pH value. It is well known that the biosorption of Cr(VI) is most effective at strongly acidic conditions (pH ≤ 3) (Kotaś & Stasicka 2000; Mohan

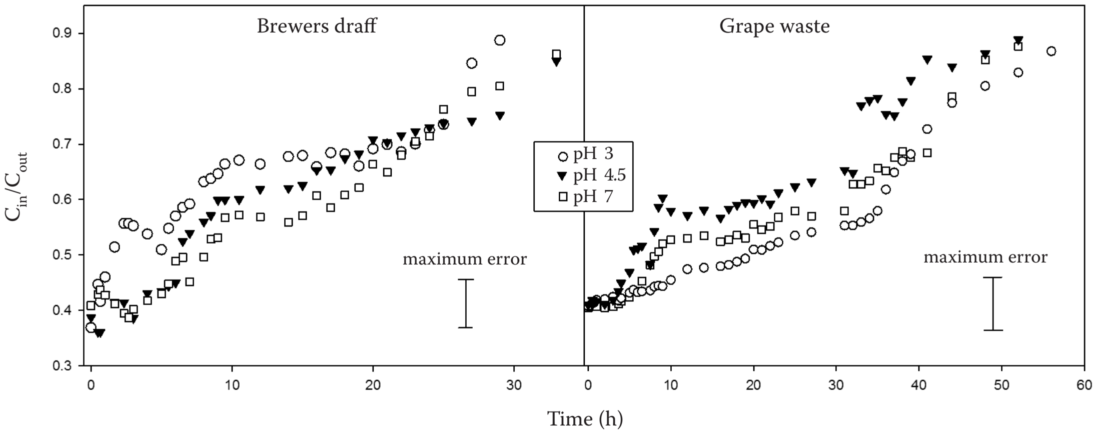

Figure 1. Cr biosorption by brewers draff and grape waste – breakthrough curves at a constant flow rate (1 ml/min) and various pH values

doi: 10.17221/3/2015-SWR

& Pittman 2006; Li *et al.* 2011); however, in our study, lowering the pH did not improve the adsorption efficiency of the biomaterials. This fact could simplify practical implementation of this method, as no pre-treatment of the water would be necessary.

We assume that the Cr adsorption process depends strongly on the nature of the groundwater (pH, O_2 concentration, ionic strength, chemical composition, presence of natural reductants and complexing agents etc.), and the biosorbents (functional organic groups, structure, surface properties etc.). The observed behaviour may be a result of a combination of all the factors. The presence of different anions may affect the removal of Cr(VI) and/or Cr(III). The reduced form, Cr(III), is a hard acid, which exhibits a strong tendency to form hexacoordinate octahedral complexes with a variety of ligands such as water molecules, sulfates, ammonia, organic matter etc. (Kotaś & Stasicka 2000). The stability constant of metal-anion complexes can be greater than that of metal-biosorption sites and the biosorption could thus be reduced considerably (Kapoor & Viraraghavan 1995). However, it was reported that presence of sulfate in the treated water can enhance the biosorption of Cr(VI) (Gao *et al.* 2008; Han *et al.* 2008). Han *et al.* (2008) observed that in the presence of sulfate, a new species $CrO_3SO_4^{2-}$ was formed and could be more easily adsorbed on biomass surface than $HCrO_4^-$. Albadarin *et al.* (2011) studied the effect of various salts on the biosorption of Cr(VI) onto a lignin biosorbent and found a positive effect of SO_4^{2-} and NH_4^+ on the adsorption efficiency (NH_4^+ may attribute to the reduction of the repulsion between the Cr(VI) and the surface), but a negative effect in the presence of CO_3^{2-} and $P_2O_7^{2-}$ (which can be due to the competition of these anions with Cr(VI) for the binding sites of the biosorbents). Moreover, presence of DOC in water positively affects the Cr(VI) reduction to Cr(III) (Saputro *et al.* 2014). If we respect the Cr(VI) sorption mechanism described in Šillerová *et al.* (2014), which considers primarily reduced Cr(III) to be the form adsorbed on the biosorbent surface, then the presence of reductive species in the natural water and their interaction with Cr(VI) and the biosorbent can have a significant effect on the biosorption process. The treated water (Table 1) contains some species that may have a positive effect on the Cr(VI) reduction/biosorption, mainly high concentration of SO_4^{2-}, and to a lesser content NH_4^+ and DOC.

The DOC concentration in the effluent was monitored in order to compare leaching of water soluble fraction of the studied biosorbents (Figure 2). The first effluent contained DOC at concentrations 37 g/l (pH 3), 15 g/l (pH 4.5), and 18 g/l (pH 7) in the case of brewers draff and 14 g/l (pH 3), 7 g/l (pH 4.5), and 11 g/l (pH 7) in the case of grape waste. The concentration decreased rapidly within the first 30 min indicating a very fast dissolution of water extractable components from the biosorbent. The concentration decreased below 0.5 g/l after 2.5 h and then continued to decrease slowly to values close to zero. The studied biosorbents can be characterized as a mixture of, almost entirely, organic compounds based on polysaccharides, proteins, and carboxylic acids with aromatic structures. The most frequented functional groups on the surface are carboxylic groups (-COO), hydroxyl groups (-OH), amino groups ($-NH_2$)

Table 3. Parameters of breakthrough curves of the fixed-bed column experiments for Cr biosorption by brewers draff and grape waste

Initial pH	Q (ml/min)	m (g)	t_s (h)	V_{ef} (l)	m_{tot} (mg)	m_{sorb} (mg)	R (%)	q (mg/g)
Brewers draff								
3	1	10	27.5	1.65	23.6	8.71	36.8	0.87
4.5	1	10	33.0	1.98	35.8	13.5	37.7	3.57
7	1	10	32.0	1.92	43.3	17.5	40.4	4.33
Grape waste								
3	1	10	56.0	3.36	48.1	31.9	66.3	4.81
4.5	1	10	48.5	2.91	52.5	29.7	56.6	5.25
7	1	10	50.5	3.03	68.3	45.2	66.1	6.83

Q – flow rate; m – mass of the sorbent; t_s – saturation time of the fixed bed; V_{ef} – total volume of effluent, m_{tot} – total amount of metal (Cr) sent to the column; m_{sorb} – total amount of sorbed metal (Cr); R – metal removal; q – sorption capacity

doi: 10.17221/3/2015-SWR

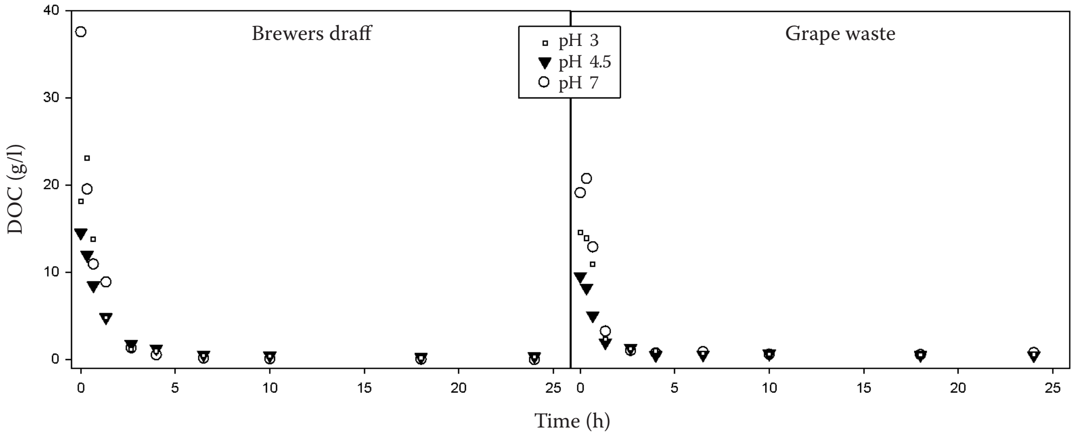

Figure 2. Cr biosorption by brewers draff and grape waste – time-dependent release of dissolved organic carbon (DOC) in the effluent water

(Šillerová *et al.* 2013). A significant effect of pH on DOC concentration was observed, because these compounds can be removed easily from the biomass under acidic conditions (Dupont *et al.* 2005).

Effect of aqueous DOC on Cr mobilization from a contaminated soil. Figure 3 shows Cr concentration mobilized from the contaminated soil after its contact with the DOC-rich leachate originating from the biosorbents. In the case of the grape waste leachate (Figure 3a), approximately 0.1% of total Cr present in the soil (Table 2) was determined in the leachate after 24 h of leaching. The initial effect of pH (4.4–4.8; $t = 0$) of the leachate and the complexation reactions of soluble/unidentified organic species with Cr probably led to an enhanced Cr release. In the case of brewers draff (Figure 3b) an opposite behaviour, with an apparent decrease of soluble Cr with increasing leaching time and the portion of DOC, was observed, indicating Cr (re)adsorption onto the soil surface.

Figure 4 shows Cr concentrations dissolved from the contaminated soil after its contact with DOC-

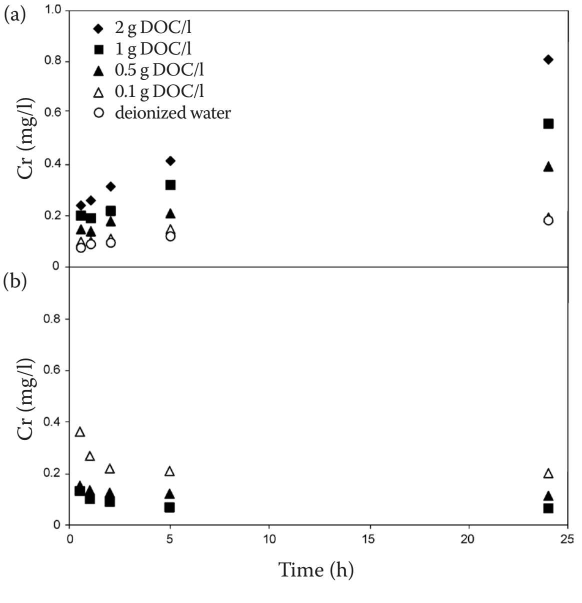

Figure 3. Time-dependent concentration of Cr determined in the leachate of (a) grape waste and (b) brewers draff in deionized water after its contact with Cr-contaminated soil; depicted values are means of 3 replicates with relative standard deviation (RSD) lower than 10% (not shown)

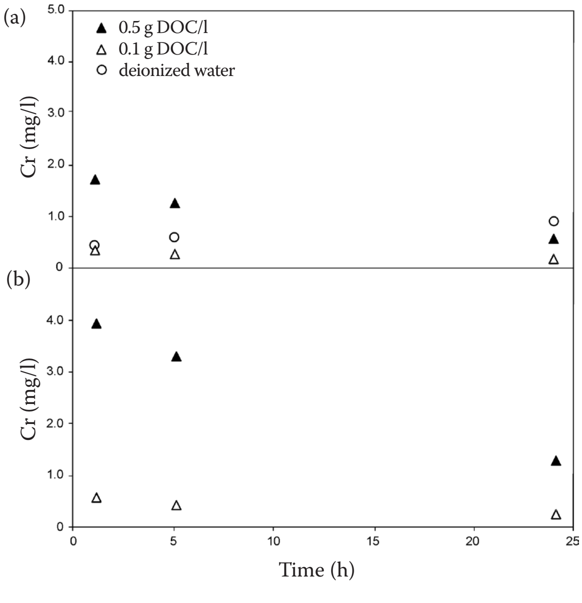

Figure 4. Time-dependent concentration of Cr determined in the natural groundwater treated by (a) grape waste and (b) brewers draff after interaction with Cr-contaminated soil; depicted values are means of 3 replicates with relative standard deviation (RSD) lower than 10% (not shown)

rich treated natural groundwater. Chromium was detected in both cases, i.e., groundwater treated by grape waste (Figure 4a) and brewers draff (Figure 4b). However, Cr concentrations in the leachates associated with grape waste were lower, as compared to the residual Cr concentration in the treated water. This finding surprisingly indicates that Cr was partially immobilized during the extraction process; the concentration of Cr accounted for 6.0 and 1.8 mg/l (at 0.5 g/l of DOC) for grape waste and brewers draff waters before leaching, respectively. In contrast, the leachates from brewers draff led to an increased Cr concentration (~4 mg Cr/l) after 1 h of soil extraction followed by a gradual slight decrease, proving thus the active role of DOC in Cr mobilization in the soil.

CONCLUSION

The Cr biosorption from natural groundwater by brewers draff and grape waste is an efficient method of Cr removal. Moreover, the biosorbent saturation time, calculated from breakthrough curves, was approximately three times longer than in previous experiments with model Cr(VI) solutions, highlighting thus the differences between using a model solution containing Cr(VI) and "natural" contaminated groundwater. The treated water was significantly enriched with DOC due to the extraction (oxidation) of various organic compounds from the biosorbents. The possibility of an accidental discharge of the DOC-rich treated water onsite was also evaluated. An obvious correlation between the DOC concentration in the treated water and Cr mobilized from the contaminated soil was observed. The obtained data demonstrated that Cr(III), when abundant in soils, could be potentially dissolved and the rate of Cr dissolving strongly depends on the type of biosorbent used for the water treatment, highlighting thus the possible risks associated with such accidental discharges of the treated water in contaminated areas. On the other hand, when a maximum amount of dissolved Cr (corresponding to < 1% of total soil Cr) in the treated water is taken into account, the risk associated with secondary Cr mobilization and its subsequent migration in soils (or sediments) seems to be very low or negligible.

Acknowledgements. The authors are grateful for the financial support provided by the Technology Agency of the Czech Republic (Project No. TA01021055). H. Šillerová is thankful for the financial support from the Czech University of Life Sciences Prague (Project CIGA No. 42400/1313/3111).

References

Albadarin A.B., Al-Muhtaseb A.H., Al-Laqtah N.A., Walker G.M., Allen S.J., Ahmad M.N.M. (2011): Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts. Chemical Engineering Journal, 169: 20–30.

Calero M., Hernáinz F., Tenorio G., Martín-Lara M.A. (2009): Study of Cr(III) biosorption in a fixed-bed column. Journal of Hazardous Materials, 171: 886–893.

Choppala G., Bolan N., Park J.H. (2013): Chapter two – Chromium contamination and its risk management in complex environmental settings. Advances in Agronomy, 120: 129–172.

Dupont L., Bouanda J., Dumonceau J., Aplincourt M. (2005): Biosorption of Cu(II) and Zn(II) onto a lignocellulosic substrate extracted from wheat bran. Environmental Chemical Letters, 2: 165–168.

Fiol N., Villaescusa I., Martinez M., Miralles N., Poch J., Serarols J. (2003): Biosorption of Cr(VI) using low cost sorbents. Environmental Chemistry Letters, 1: 135–139.

Gao H., Liu Y., Zeng G., Xu W., Li T., Xia W. (2008): Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste – rice straw. Journal of Hazardous Materials, 150: 446–452.

Gupta V.K., Carrott P.J.M., Ribeiro Carrott M.M.L., Suhas (2009): Low-cost adsorbents: Growing approach to wastewater treatment – a review. Critical Reviews in Environmental Science and Technology, 39: 783–842.

Han X., Wong Y.S., Wong M.H., Tam N.F.Y. (2008): Effects of anion species and concentration on the removal of Cr(VI) by a microalgal isolate, *Chlorella miniata*. Journal of Hazardous Materials, 158: 615–620.

Kapoor A., Viraraghavan T. (1995): Fungal biosorption – an alternative treatment option for heavy metal bearing wastewaters: A review. Bioresource Technology, 53: 195–206.

Kotaś J., Stasicka Z. (2000): Chromium occurrence in the environment and methods of its speciation. Environmental Pollution, 107: 263–283.

Leita L., Margon A., Pastrello A., Arčon I., Contin M., Mosetti D. (2009): Soil humic acid may favour the persistence of hexavalent chromium in soil. Environmental Pollution, 157: 1862–1866.

Li Q., Qian Y., Cui H., Zhang Q., Tang R., Zhai J. (2011): Preparation of poly(aniline-1,8-diaminonaphtalene) and its application as adsorbent for selective removal of Cr(VI) ions. Chemical Engineering Journal, 173: 715–721.

López-García M., Lodeiro P., Barriada J.L., Herrero R., Sastre De Vicente M.E. (2010): Reduction of Cr(VI) levels in solution using bracken fern biomass: Batch and column studies. Chemical Engineering Journal, 165: 517–523.

doi: 10.17221/3/2015-SWR

Losi M.E., Amrhein C., Frankenberger W.T. Jr. (1994): Environmental biochemistry of chromium. Reviews of Environmental Contamination and Toxicology, 136: 91–121.

Miretzky P., Cirelli A.F. (2010): Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review. Journal of Hazardous Materials, 180: 1–19.

Mohan D., Pittman C.U. (2006): Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. Journal of Hazardous Materials, 137(B): 762–811.

Pujol D., Liu C.H., Fiol N., Olivella M.A., Gominho J., Villaescusa I., Pereira H. (2013): Chemical characterization of different granulometric fractions of grape stalks waste. Industrial Crops and Products, 50: 494–500.

Saputro S., Yoshimura K., Matsuoka K., Takehara K., Narsito, Aizawa J., Tennichi Y. (2014): Speciation of dissolved chromium and the mechanism controlling its concentration in natural water. Chemical Geology, 364: 31–44.

Šillerová H., Komárek M., Chrastný V., Novák M., Vaněk A., Drábek O. (2013): Brewers draff as a new low-cost sorbent for chromium (VI): Comparison with other biosorbents. Journal of Colloid and Interface Science, 396: 227–233.

Šillerová H., Chrastný V., Čadková E., Komárek M. (2014): Isotope fractionation and spectroscopic analysis as an evidence of Cr(VI) reduction during biosorption. Chemosphere, 95: 402–407.

Sreenivas K.M., Inarkar M.B., Gokhale S.V., Lee S.S. (2014): Reutilization of ash gourd (*Benincasa hispida*) peel waste for chromium (VI) biosorption: Equilibrium and column studies. Journal of Environmental Chemical Engineering, 2: 455–462.

US EPA (1996): Region III Risk Based Concentration Table. Available at http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/Generic_Tables/docs/indair_sl_table_01run_MAY2013.pdf (accessed Mar 5, 2014).

US EPA (2014): Toxic and Priority Pollutants List Appendix A to Part 423—126. Available at http://water.epa.gov/scitech/methods/cwa/pollutants.cfm (accessed Apr 12, 2014).

Vaněk A., Chrastný V., Komárek M., Galušková I., Drahota P., Grygar T., Tejnecký V., Drábek O. (2010): Thallium dynamics in contrasting light sandy soils – soil vulnerability assessment to anthropogenic contamination. Journal of Hazardous Materials, 173: 717–723.

Vassilev S.V., Baxter D., Andersen L.K., Vassileva C.G., Morgan T.J. (2012): An overview of the organic and inorganic phase composition of biomass. Fuel, 94: 1–33.

Vinodhini V., Das N. (2010): Packed bed column studies on Cr(VI) removal from tannery wastewater by neem sawdust. Desalination, 264: 9–14.

Yang L., Chen J.P. (2008): Biosorption of hexavalent chromium onto raw and chemically modified *Sargassum* sp. Bioresource Technology, 99: 297–307.

Received for publication January 3, 2015
Accepted after corrections April 27, 2015

Corresponding author:

Ing. Hana Šillerová, Ph.D., Česká zemědělská univerzita v Praze, Fakulta životního prostředí, Katedra geoenvironmentálních věd, Kamýcká 129, 165 21 Praha 6-Suchdol, Česká republika; e-mail: sillerovah@fzp.czu.cz