SPECIATION ANALYSIS OF AS(III) AND AS(V) IN SOIL SAMPLES FROM THE AREA OF THE CHEMICAL PLANT IN LUBOŃ NEAR POZNAŃ

LIDIA KOZAK, PRZEMYSŁAW NIEDZIELSKI

Adam Mickiewicz University, Department of Water and Soil Analysis, Faculty of Chemistry
ul. Drzymały 24, 60-613 Poznań, Poland

Abstract: Arsenic content was determined in the soil profiles collected from the former dumping ground of post-crystallization lye (presently under recultivation) in the area of the chemical plant in Luboń, near Poznań. Of particular concern was the content of the two most toxic species of As(III) and As(V) in the environmentally available exchange fraction. Extraction was performed with a phosphate buffer of pH = 6.0 ± 0.2, and the analytical method applied was HPLC-HG-AAS. As(V) species were found in all samples, whereas As(III) species in a few samples collected at different depths. The concentration of As(V) varied from 91 to 1228 ng/g, while that of As(III) – from 17 to 48 ng/g. As there are no watertight rock formations underneath the dumping site, the polluting substances can be easily washed out by ground waters and carried into the Warta River, which is a main source of water for the city of Poznań.

INTRODUCTION

Arsenic is one of the most toxic elements whose excessive presence in the environment is hazardous for all living organisms. Not all arsenic compounds are equally toxic; the most toxic are the inorganic species containing As(III) and As(V), that is derivatives of arsenic(III) acid H_3AsO_3 and arsenic (V) acid H_3AsO_4 [5, 9]. The organic arsenic species such as monomethylarsenic acid (MMAA), dimethylarsenic acid (DMAA) or trimethylarsenic acid (TMAO) are less toxic, while arsenobetaine (AsB), arsenocholine (AsC) arsenolipids (AsL) and arsenosugars (AsS) do not reveal toxic behavior.

In living organisms the toxic species of As(III) and As(V) undergo oxidation and reduction, respectively, followed by methylation so lose their toxicity [12, 16], however, the presence of high concentration of these substances in the environment may provoke serious disturbances in the functioning of organisms or their death [14]. In view of the above, monitoring of the level of arsenic should include determination of its species.

The main source of arsenic in living organisms is the hydrosphere, in which the concentration of arsenic depends on its presence in the soil and sediments from where it can be washed out. The natural concentration of arsenic in soil varies from 0.2 to 16 μg/g [1, 4]. All arsenic compounds, including those incorporated in minerals, are easily washable in particular in the reducing conditions (acid soils) [7]. Particular risk is posed by the inorganic species of As(III), which is the most mobile and the easiest released from the bioavailable fraction of soil and sediments [3].

The main difficulty in determination of arsenic species in soil is related to the choice of the proper extracting agent. As the stability of As(III) species strongly depends on the pH of the extracting agent, care must be taken to choose such an agent that would not disturb the speciation balance by oxidizing As(III) to As(V) or by reducing As(V) to As(III) [2, 8, 10]. The choice of the extracting agent also depends on the type of information to be elicited from a given sample. This study is aimed at isolation of the exchange fraction of soil from which potential pollutants can be easily released into the water environment.

EXPERIMENTAL

Instruments and reagents

Determination of the inorganic species of As(III) and As(V) was performed with the help of a system coupling the high-performance liquid chromatography (HPLC) to separate the species, the hydride generation system as a coupling one and the absorption atomic spectrometry as a detection method [6]. The system HPLC-HG-AAS was composed of a liquid chromatograph LC-10A (Shimadzu) equipped with a pump LC-10AT, a degassing device GT-104 and an ion-exchange column LC-SAX1 (Supelco, 250 × 4.6 mm, 5 μm). The wires in contact with the sample and the eluent were made of PEEK. The next element was the hydride generating system VGA 77 (Varian) with an electrothermally heated quartz cell ETC-60 (900°C) employed as an atomizer and the last element was a SpectrAA 220FS spectrometer (Varian). Arsenic was detected at the wavelength of 193.7 nm. The carrier gas was argon (BOC GAZY Poland); the mobile phase in LC was phosphate buffer. The flow rate of the mobile phase was 3 cm^3/min, while the volume of the injected sample was $200 \cdot 10^{-6}$ dm^3 [6]. All the reagents used were analytically pure, while the water used was redistilled and additionally purified in a Milli-Q (Millipore, USA). The standard solutions of the two arsenic species of the concentration of 1 mg/cm^3 were prepared of the weighted portions of sodium arsenate(III) NaAsO$_2$ and sodium hydroarsenate(V) Na$_2$AsO$_4$*7H$_2$O (Sigma Aldrich, USA). Lower concentration standard solutions were obtained by diluting the standard solution of 1 mg/cm^3. All vessels used for standard storing were made of polyethylene.

A solution of hydrochloric acid of the concentration 1 mol/dm^3 was obtained by diluting the acid of $\rho = 1.19$ g/cm^3. A solution of sodium borohydride was obtained by dissolving NaBH$_4$ in a 1% sodium hydrochloride (Merck, Germany). The flow rate of the acid and the reducing agent was 1 cm^3/min. The phosphate buffer 50 mM K, 5 mM Na of pH 6.0 ± 0.2 was made by mixing a solution of Na$_2$HPO$_4$ and KH$_2$PO$_4$, made by Merck.

The analytical method is characterized in Table 2.

Table 1. Characteristic of analytical method

	Retention time	Linearity [ng/g]	Slope	Correlation coefficient	Determination limit [ng/g]	RSD (at 20 ng/cm^3)
As (III)	127.2	2000	0.0562	0.9900	5	6.8
As (V)	224.9	2000	0.0338	0.9929	5	4.3

The study area

Samples to be studied were collected from four soil profiles (sites 1, 2, 3, 4 in Fig. 1) in the area of the former dumping ground of post-crystallization lye, presently under recul-

tivation, within the area of the chemical plant in Luboń near Poznań. The chemical plant founded in 1914, produced mainly dust superphosphate and sulphuric acid. The plant presently produces also other agricultural fertilizers, wood and fabric impregnates and hydrofluoric acid. The plant belongs to the most hazardous for the natural environment because of the toxicity of the substrates, products and technological wastes [13]. The plant is localized on the left bank of the Warta River above the city of Poznań. Because of such localization the surface and ground waters from the waterbearing horizon flow to the river and with the river to the city. The Warta River valley near this chemical plant is built of the Quaternary sediments of 4 to 20 m thick [11]. The Holocene sediments – mainly fine-grained sands – occur at the depth of 4–8 m (sometimes to 10 m below the ground level). Under the Holocene sediments there are middle- and coarse-grained sands and gavels. At about 13–15 m below the ground level there are Tertiary clay formations [13]. The study area is localized between the Warta River and its former bed, the ground water table is at about 4 m below the ground level. In view of the lack of watertight geological formations the waterbearing horizon in the area is at a high risk of pollution which can easily migrate into greater depths and to the river.
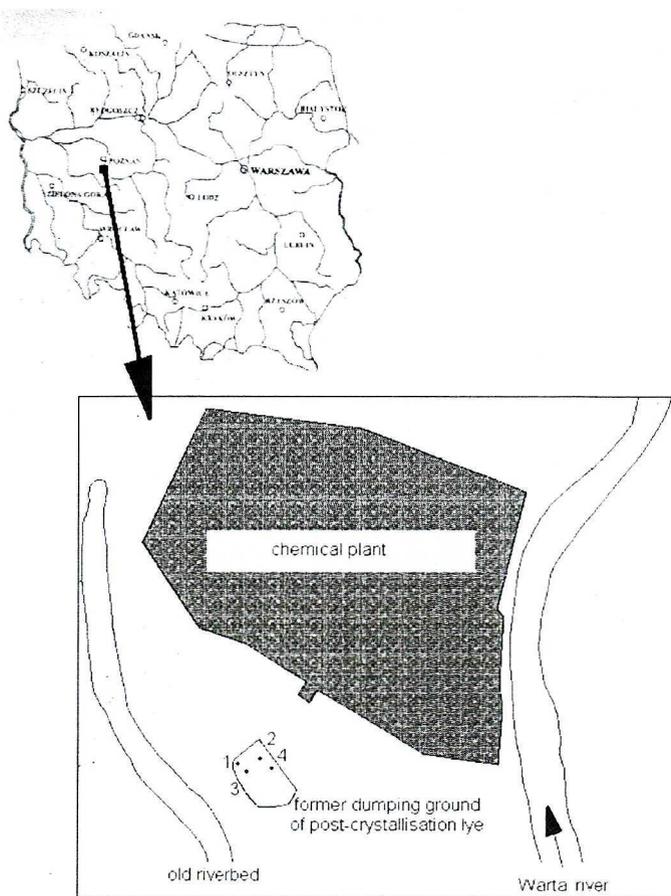
Fig. 1. The study area; 1, 2, 3, 4 – sampling sites, follow [13]

The proportion of the total amount of cadmium ions adsorbed that were adsorbed during the full adsorption phase was 72% with the solution containing only cadmium sulfate ions, 63.5% with the solution containing cadmium sulfate and zinc sulfate, and 76% with the solution containing cadmium sulfate and copper sulfate.

The pH of the eluate leaving the column fell from 6.43 to 4.60 with the solution containing only cadmium sulfate ions, from 6.51 to 4.40 with the solution containing cadmium sulfate and zinc sulfate, and from 6.32 to 4.03 with the solution containing cadmium sulfate and copper sulfate (Fig. 3A).

With the solution containing cadmium sulfate and copper sulfate, the concentration of cadmium ions in the eluate leaving the column was higher than in the solution entering the column when the pH fell below 4.25 (Fig. 3B). This was due to displacement of the cadmium ions already adsorbed on the column by copper ions.

The same general patterns were observed in solutions prepared using chloride salts (Fig. 4A, B).
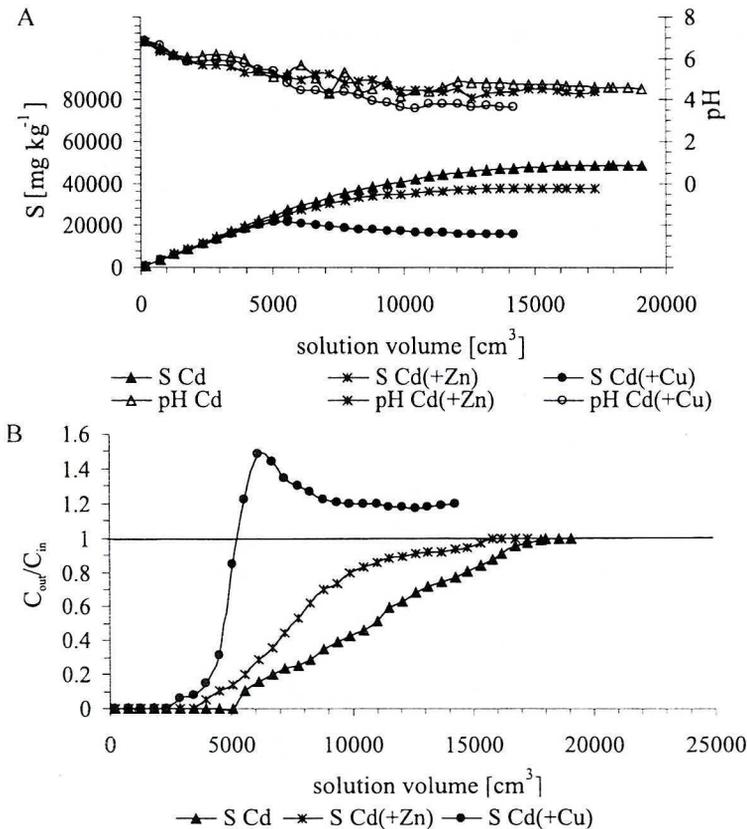
Fig. 4. Effect of zinc(II) and copper(II) ions on cadmium adsorption capacity in Alder Peat with solutions prepared using chloride salts under dynamic flow conditions: A – total amount of cadmium ions adsorbed, B – dimensionless liquid phase concentration

The total amount of cadmium adsorbed was 47300 mg·kg^{-1} with the solution containing only cadmium chloride ions, 37520 mg·kg^{-1} with the solution containing cadmium

chloride and zinc chloride, and 15680 mg·kg⁻¹ with the solution containing cadmium chloride and copper chloride.

The total sorption capacity for cations occurring in solution was 84.5 cmol(+)·kg⁻¹ with the solution containing only cadmium chloride ions, 202.0 cmol(+)·kg⁻¹ with the solution containing cadmium chloride and zinc chloride, and 149.0 cmol(+)·kg⁻¹ with the solution containing cadmium chloride and copper chloride.

The pH of the eluate leaving the column fell from 6.45 to 4.26 with the solution containing only cadmium chloride ions, from 6.39 to 4.20 with the solution containing cadmium chloride and zinc chloride, and from 6.12 to 4.11 with the solution containing cadmium chloride and copper chloride (Fig. 4A).

With the solution containing cadmium chloride and copper chloride, the concentration of cadmium ions in the eluate leaving the column was higher than in the solution entering the column when the pH fell below 4.27.

With the highly acidic wastewater from the galvanizing plant, the total amount of cadmium ions adsorbed by the adsorbent was only 2080 mg·kg⁻¹, which represents only 3% of the total cation exchange capacity of the peat. As the pH of the eluate leaving the column fell, the cadmium ions were displaced from the adsorbent by oxonium ions (Fig. 5).
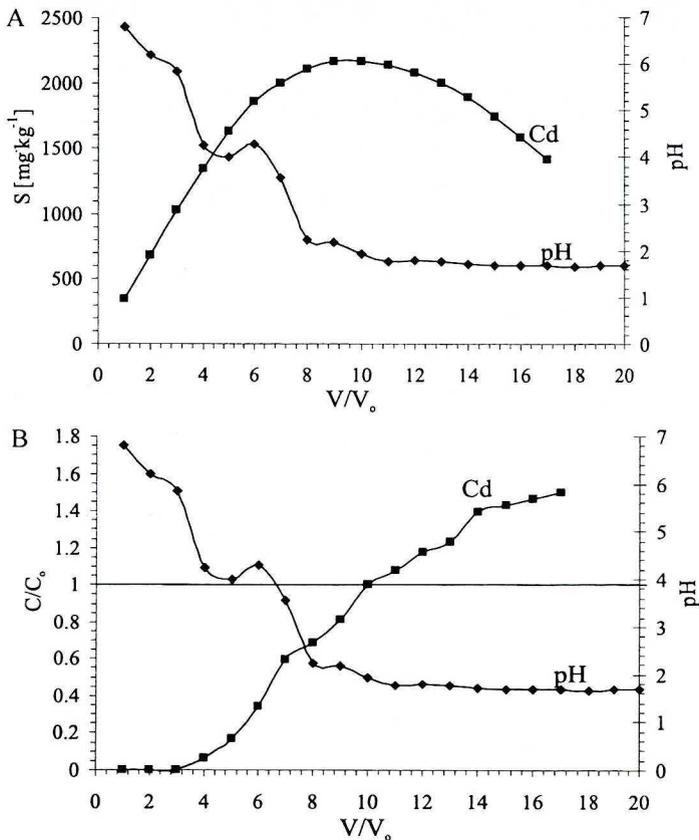
Fig. 5. Cadmium adsorption capacity in Alder Peat with highly acidic wastewater from a galvanizing plant:
A – total amount of cadmium ions adsorbed, B – dimensionless liquid phase concentration
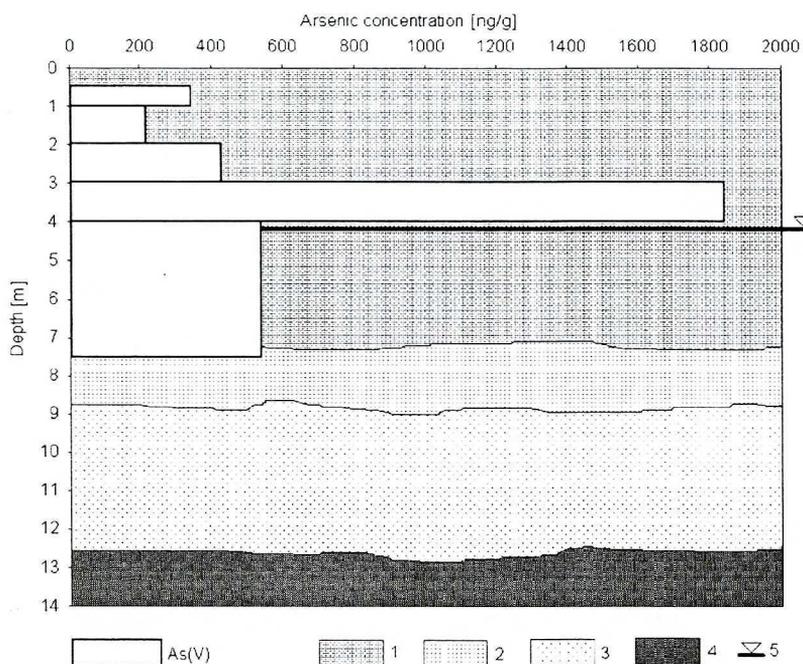
Fig. 3. Occurrence of As(III) and As(V) in profile no. 2 [ng/g]; 1 – fine-grained sands, 2 – middle-grained sands, 3 – coarse-grained sands, 4 – clay, 5 – ground water table
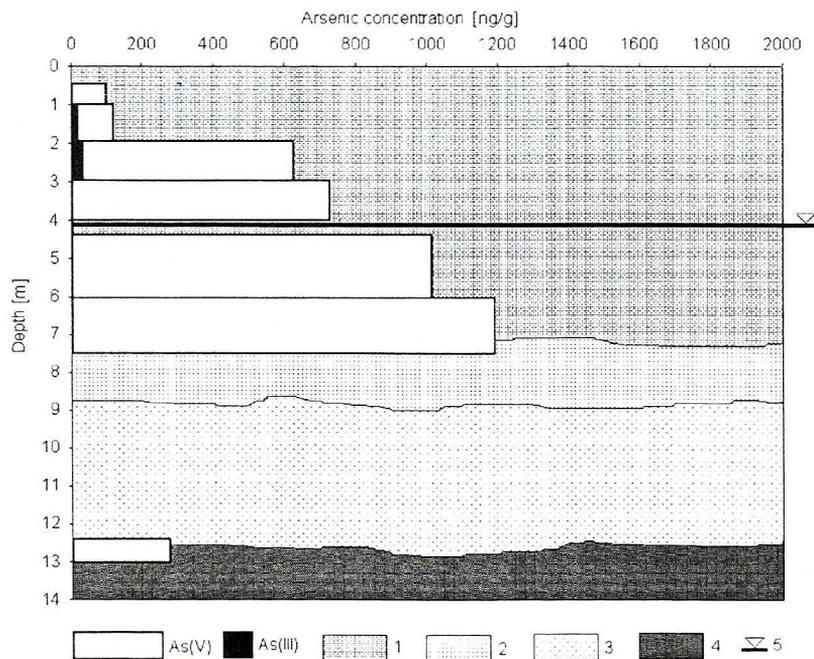
Fig. 4. Occurrence of As(III) and As(V) in profile no. 3 [ng/g]; 1 – fine-grained sands, 2 – middle-grained sands, 3 – coarse-grained sands, 4 – clay, 5 – ground water table
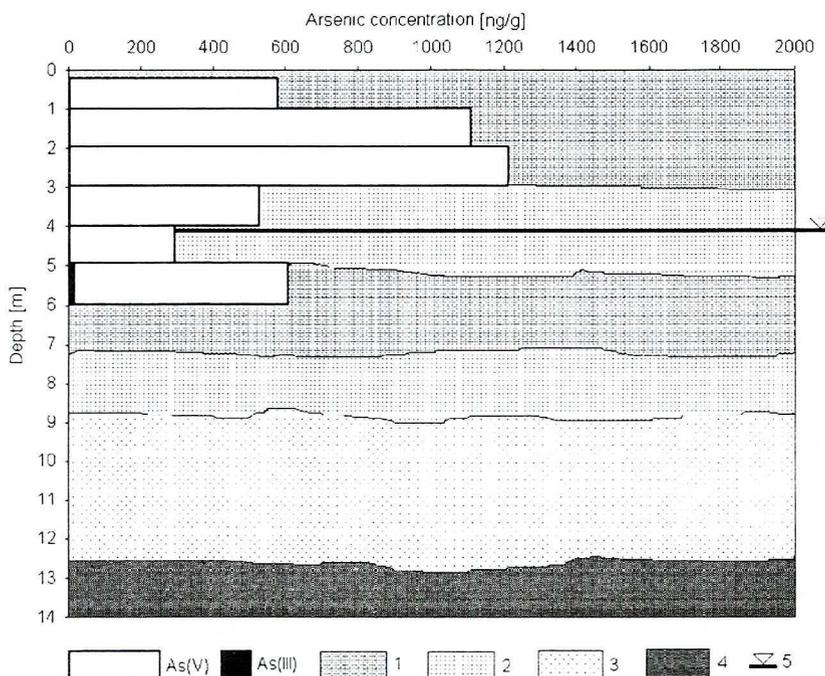
Fig. 5. Occurrence of As(III) and As(V) in profile no. 4 [ng/g]; 1 – fine-grained sands, 2 – middle-grained sands, 3 – coarse-grained sands, 4 – clay, 5 – ground water table

In the area of the same chemical plant in Luboń the hitherto performed works included the monitoring of the water from the underground waterbearing horizon and analyses of rock samples collected from a few drill profiles of which one was in direct neighborhood of the dumping ground of the post-crystallization lye [13] at that time, before recultivation, also a sample of sediments from this damping ground was analyzed. In the samples of the rocks and in those of the sediments the total content of arsenic, antimony and selenium was determined in the fraction extracted with a 2.5 M solution of hydrochloric acid. The content of arsenic was elevated in the sample collected at the surface – at the depth of 0.4 m, (1030 ng/g) and in the sample of the sediments from the area of the post-crystallization lye dumping ground (2867 ng/g). A comparison of the results with those reported [13], shows that a conclusion about As(V) migration in the depth of the profile is fully justified.

CONCLUSION

The above-presented results evidence a significant contamination of the dumping ground area studied. Recultivation of this area will not be simple as the contamination runs deep along the soil profile and the lack of the watertight rock bed (e.g. clays) underneath the area permits continuous washing out of arsenic into the ground waters and then into the Warta River. The results from profiles 1 and 3 can suggest that the layer of Poznań clay at

[9]   Gąszczyk R., P. Muszyński, T. Paszko: *Wpływ metali ciężkich na sorpcje kadmu w glebach mineral-nych*, [w:] Kadm w środowisku – problemy ekologiczne i metodyczne, Zeszyty Naukowe Komitetu PAN „Człowiek i Środowisko", 26, 93–99 (2000).

[10]   Gomez-Serrano V., A. Macias-Gorcia, A. Espinosa-Mansilla, C. Valenzuela-Calahorro: *Adsorption of mercury, cadmium and lead from aqueous solution on heat-treated and sulphurized activated carbon*, Water Research, **32**, 1–4 (1998).

[11]   Heavey M.: *Low-cost treatment of landfill leachate using peat*, Waste Management, **23**, 447–454 (2003).

[12]   Huang C.P., M.W. Tsong, Y.S. Hsieh: *The removal of cobalt(II) from water by activated carbon*, [in:] K. Peters, D. Bhattaacharya (eds.), American Institute of Chemical Engineers Symposium Series: Heavy Metal Separation Processes, American Institute of Chemical Engineers, USA 1985.

[13]   Hutton M., M. Chaney, C.R. Krishnamurti, A. Olade, A.L. Page: *Group report: Cadmium*, [in:] T.C. Hutchinson, K.M. Meema (eds.), Lead, Mercury, Cadmium and Arsenic in the Environment, John Wiley and Sons, New York 1987, pp. 35–41.

[14]   Kersten M., U. Forstner: *Assessment of metal mobility in dredged material and mine waste by pore water chemistry and solid speciation*, [in:] W. Salomons, U. Forstner (eds.), Chemistry and Biology of Solid Waste, Dredged Material and Mine Tailings, Springer-Verlag, Berlin 1988, pp. 214–237.

[15]   Kyzioł J.: *Sorption and binding strength of selected ions of heavy metals by organic matter (a case study on peats)*, Wydawnictwa IPIŚ PAN, Zabrze 2002 (in polish).

[16]   McBride M.B.: *Environmental chemistry of soils*, Oxford University Press, Oxford 1994.

[17]   McKay G.: *Use of adsorbents for removal of pollutants from wastewaters*, CRC Press., Florida, 1996.

[18]   Nriagu J.O., J.M. Pacyna: *Quantitative assessment of worldwide contamination of air, water and soils by trace metals*, Nature, **333**, 134–139 (1988).

[19]   Ringqist L., I. Oborn: *Copper and zinc adsorption onto poorly humified Sphagnum and Carex peat*, Water Research, **36**, 2233–2242 (2002).

[20]   Sanchez A.G., E.A. Ayuso, O.J. de Blas: *Sorption of heavy metals from industrial wastewater by low-cost mineral silicates*, Clay Miner., **34**, 469–467 (1999).

[21]   Tessier A., P.G.C. Campbell, M. Bisson: *Sequential extraction procedure for the speciation of particulate trace metals*, Analytical Chemistry, **51**(7), 884 (1979).

[22]   Twardowska I., J. Kyzioł: *Sorption of metals onto natural organic mater as a function of complexation and adsorbent-adsorbate contact mode*, Environment International, **28**, 783–791 (2003).

[23]   Wang W.Z., L. Brusseau, J.F. Artiola: *The use of calcium to facilitate desorption and removal of cadmium and nickel in subsurface soils*, J. Connt. Hydr., **25**, 325–336 (1997).

WIĄZANIE JONÓW Cd(II) ZE ŚCIEKÓW PRZEMYSŁOWYCH PRZEZ TORFY WYSTĘPUJĄCE W NADKŁADZIE ZŁÓŻ WĘGLI BRUNATNYCH

Wyznaczono pojemność sorpcyjną dla torfu olesowego występującego w nadkładach złoża węgla brunatnego w Bełchatowie w stosunku do jonów Cd(II). Badania przeprowadzono w dynamicznych warunkach kontaktu faza stała – roztwór. W badaniach wykorzystano zarówno wzorcowe roztwory chlorków i siarczanów jak i kwaśne ścieki polimetaliczne z zakładu galwanizerskiego. Ponadto określono podatność na ługowanie zasorbowanych jonów Cd(II). Stwierdzono znaczny wpływ pH, rodzaju anionu i kationów współwystępujących na ilość wiązanych jonów Cd(II). Wiązanie jonów Cd(II) na pozycjach wymiennych kompleksu sorpcyjnego wpływa na ich wysoką podatność do uwalniania i pozwala na kilkukrotne użycie sorbentu w cyklu sorpcja – desorpcja. Przeprowadzone badania pokazują, że torfy występujące w nadkładzie złóż węgli brunatnych charakteryzują się wysoką skutecznością usuwania jonów Cd(II) z roztworów, co pozwala na wykorzystanie ich jako efektywnych sorbentów w oczyszczaniu wód i ścieków.