Adsorption of copper and cadmium from aqueous solution by various types of sediments under static and dynamic conditions

Hana Müllerová [1,2] – Ondřej Kruml [1] – Karel Vybíhal [1] – Josef Zeman [1] – Pavel Müller [2]

[1] Masaryk University in Brno, Faculty of Science, Institute of Geological Sciences, Kotlářská 2, 611 37 Brno, Czech Republic.
E-mail: hana.muller@volny.cz, o.kruml@post.cz, kerberos-@post.cz, jzeman@sci.muni.cz
[2] Czech Geological Survey, Leitnerova 22, 658 69 Brno, Czech Republic. E-mail: hana.muller@volny.cz, muller@cgu.cz

Abstract. The mobility of heavy metals in sediments and soils depends strongly on physical properties and chemical and mineralogical composition of such environments. Five types of samples with different amounts of carbonates, organic matter, chemical composition and various grain sizes were chosen. Experimental sorption data from batch tests were evaluated by Langmuir and Freundlich type isotherms, which provided main sorption characteristics of sediment samples for heavy metals (Cu, Cd). In order to simulate natural conditions more realistically, several leaching column tests were also performed. The sample sorption capacities under static and dynamic conditions were evaluated. All chosen samples bonded Cu more efficiently and firmly than Cd. Distilled water washed out about 6 % of Cu and 44 % of Cd from HBS 2 (quartz-dominated sample with 74 wt% of sand-sized fraction) and 6 % of Cu and 9 % of Cd from HBS 6 (finer-grained sample with some amount of organic matter and carbonates). Carbonates proved to be crucial for the mobility of heavy metals in natural samples. Free metals were washed out of pores at the very beginning of the desorption experiments. Then, weakly adsorbed metals (electric double layer) were washed out and finally, a low stationary metal concentration was established. Such behaviour should result in a slow release of small amounts of a heavy metal, which should therefore not represent significant danger to the environment.

Key words: Cu, Cd, adsorption, isotherm, soil, leaching column, sequential extraction analysis

Introduction

Heavy metals produced and released by human activity represent a serious environmental problem. Interest in the fate of heavy metals has increased because of their potential toxicity to biota and human. Soils, groundwater, plants and animals can be considered as potential secondary sources of contamination. In this study, the solubility and mobility of Cu and Cd were investigated in five sediment (soil) types. The strength of their bonding onto mineral surfaces was evaluated using sequential extraction analysis.

In general, significant factors determining the ability of samples to retain heavy metals are soil pH, amount of carbonates, organic matter and clay minerals.

Ions of toxic metals can bind to the mineral surface in a number of ways, including absorption, adsorption, precipitation and cation exchange (Steele et al. 2000). Trivedi et al. (2001) investigated adsorption of metals onto goethite surface and found a connection between metal affinities for goethite and order Cu > Pb > Zn > Cd > Co > Ni > Mn > Ca > Mg, which tends to follow the decrease in electronegativity and radii of the hydrated cations, with a slight variation.

Morera et al. (2001) evaluated the mobility and distribution of Cd, Cu, Ni, Pb and Zn in four different types of soils. They concluded that soils have a higher affinity with Pb and Cu than with Cd, Ni or Zn. Sequential extraction analyses showed that in the case of soils with a higher content of carbonates, metals were extracted predominantly from the carbonate fraction. The authors also confirmed the high affinity of Cu with organic matter.

Materials and methods

Sediments

Five samples of sediments were chosen to cover the range of grain sizes, abundance of carbonates, organic matter and clay minerals, typical for natural conditions. Their characteristics are shown in Tab. 1.

Samples HBS 2, HBS 6 and HBV 4 are recent bottom deposits from a drained reservoir at Horní Bečva in the Beskydy Mountains. Microscopic observation revealed quartz, microcline, orthoclase, plagioclase, glauconite, muscovite and chlorite in HBS 2, quartz, microcline, glauconite, plagioclase, chlorite, muscovite (rare) and Fe-oxyhydroxides in HBS 6 and the same minerals but of smaller grain sizes in HBV 4.

Sample Le 4 comes from a soil profile from Lelekovice near Brno in southern Moravia. This soil contains about 2 wt% of organic matter and more than 7 wt% of

Tab. 1. Main fractions of unconsolidated sediments used for experiments

	Clay- and silt-sized fraction	Sand-sized fraction	Gravel-sized fraction	$C_{org.}$	$CaCO_3$
Sample	wt%	wt%	wt%	wt%	wt%
HBS 2	3	74	23	0.31	0
HBS 6	50	50	0	0.77	0.31
HBV 4	98	2	0	4.81	0.39
Le 4	78	14	8	2.05	7.38
Žd	33	67	0	0	12.97

Tab. 2. Results of silicate analyses recalculated to the amount of normative minerals (Koubová 2002)

	HBS 2	HBS 6	HBV 4	Le 4	Žd
Mineral	mol%	mol%	mol%	mol%	mol%
apatite	0.02	0.04	0.12	0.07	0.02
rutile	0.36	0.56	1.03	1.17	0.31
goethite	1.58	2.81	5.47	6.90	0.84
dolomite	–	–	–	2.33	7.93
calcite	0.28	0.29	0.41	4.62	6.11
albite	0.88	1.30	2.19	4.97	4.30
pyrolusite	0.04	0.07	0.13	0.20	0.06
pyrite	0.06	0.17	0.32	0.00	0.00
Mg-chlorite	0.25	0.44	0.66	0.03	0.05
Fe-chlorite	0.22	0.37	0.52	0.04	0.18
anorthite	0.56	1.38	0.64	2.72	1.24
feldspar	1.64	1.44	1.31	1.80	3.08
omontmorillonite	0.04	0.48	0.84	2.20	0.68
muscovite	0.77	1.91	2.49	1.42	0.11
paragonite	0.61	1.24	–	–	–
illite	0.08	0.74	1.44	1.23	0.33
diaspore	4.81	3.82	13.36	–	–
kaolinite	0.12	1.17	2.83	2.93	0.50
amorphous quartz	1.23	3.97	12.19	5.69	0.00
quartz	86.44	77.80	54.04	59.60	74.26
actinolite	–	–	–	2.07	–
Total	100.00	100.00	100.00	100.00	100.00

Fig. 1. Experimental column arrangement.

carbonates. Quartz, calcite, muscovite, plagioclase, weathered amphibolite, epidote and sericitized feldspar were again identified by microscopic observation.

Sample Žd is partly consolidated sandstone from the Ždánice Unit of the West Carpathians. This sediment consists of quartz, calcite, feldspar, plagioclase, muscovite and glauconite.

All samples were analysed using X-ray diffraction and IR spectroscopy in order to identify clay minerals. Tab. 2 contains recalculation of silicate analyses, which provided the contents of normative minerals.

All samples were dried at ambient temperature, put into glass columns and fit into experimental dynamic arrangements (Fig. 1). Concentrations of main cations (Ca^{2+}, K^+, Na^+, Mg^{2+}) and SiO_2 were measured using atomic absorption spectrometry (AAS), both in the outflow from the column and in the overflow, for almost a year. Temperature, pH and Eh were registered, too. The acidimetric titration (solution of 0.05 M HCl) of carbonate forms was carried out twice throughout monitoring. A pycnometric method was used for the definition of bulk density and porosity. Batch tests were carried out on all samples, sorption under dynamic conditions and sequential extraction procedure only on HBS 2 and HBS 6, due to their favourable flow rates.

Sorption of copper and cadmium

Solutions of $CuSO_4$ and $CdSO_4$ were prepared for the simulation of a contamination by Cu and Cd. Batch tests were applied on 1 ml (or 10 ml for calcareous samples – Le 4, Žd) of waterlogged subsamples of chosen sediments, which were then covered by 10 ml (35 ml for calcareous samples) of Cu and Cd solutions. Initial concentrations were 0.001; 0.0025; 0.005; 0.0075; 0.01 and 0.015 mol/l (Kruml 2002, Vybíhal 2002), 0.001; 0.0025; 0.005; 0.01; 0.025 and 0.05 mol/l for calcareous samples. The experiment lasted one week and was carried out at ambient temperature (intermittent agitation).

The results from the batch experiment were interpolated with Langmuir and Freundlich curves (Plate I).

Langmuir equation: $\Gamma = \Gamma_{max} \cdot \dfrac{K_L \cdot c_{aq}}{1 + K_L \cdot c_{aq}}$,

where G stands for an experimentally acquired number of sorption sites (meq/100 g), c_{aq} is a balanced concentration of metal in solution after sorption (mmol/l), G_{max} represents the maximal sorption capacity (asymptote of the Langmuir function) and K_L stands for an equilibrium constant of adsorption or for a linear distribution coefficient (l/100 g).

Freundlich equation: $\Gamma = K_F \cdot c_{aq}^n$,

where K_F represents a Freundlich constant and n stands for a degree of non-linearity (Stumm and Morgan 1996).
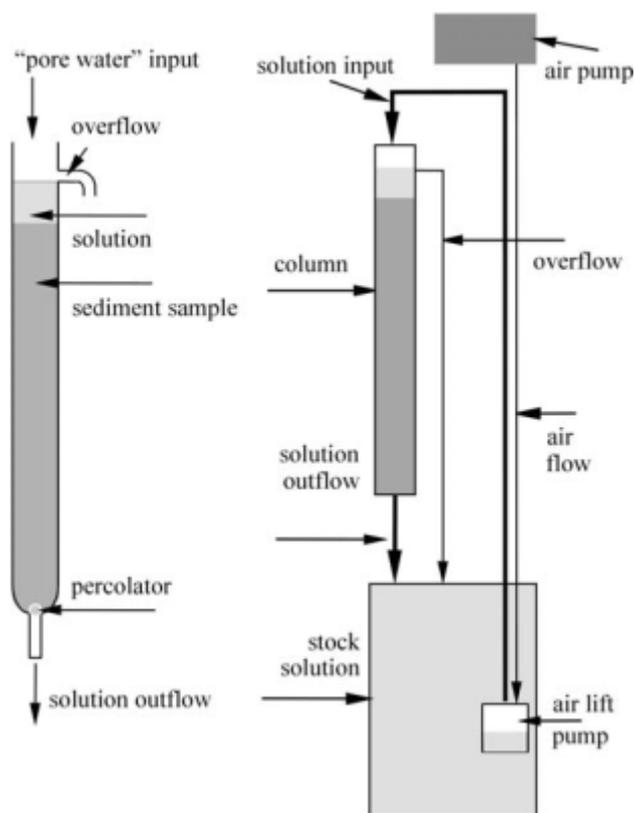
Tab. 3. Concentration of main cations, SiO_2, carbonate forms, pH and Eh in the steady state

Sample	SiO_2	Ca^{2+}	Mg^{2+}	Fe	K^+	Na^+	H_2CO_3	HCO_3^-	CO_3^{2-}	pH	Eh
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm		mV
HBS 2/1	7.00	7.15	1.81	0.00	2.49	0.30	4.10	59.00	0.08	7.4	381
HBS 2/2	8.00	7.15	1.81	0.00	1.66	0.30	3.50	81.96	0.19	7.6	379
HBS 6/1	23.00	3.57	3.62	2.00	3.32	0.59	4.03	68.09	0.11	7.4	397
HBS 6/2	20.00	2.86	2.41	1.00	3.32	0.30	4.03	57.18	0.08	7.4	397
HBV 4/1	40.00	2.14	7.24	7.00	4.98	0.89	9.58	7.05	0.00	7.5	322
HBV 4/2	40.00	2.86	7.24	3.00	4.98	0.74	7.75	11.00	0.00	7.7	297
Le 4/1	15.00	9.29	3.02	0.00	2.49	0.37	3.25	126.18	0.49	7.8	329
Le 4/2	17.00	14.29	4.82	0.00	3.32	0.59	2.61	114.26	0.50	8.2	297
Žd /1	7.00	9.29	6.03	0.00	3.32	0.45	2.94	138.95	0.66	7.8	397
Žd /2	7.00	7.86	4.82	0.00	2.49	0.52	2.45	139.28	0.79	8.0	397

Sorption experiments under dynamic conditions were performed on HBS 2 and HBS 6. The same amounts of contaminants were introduced into columns by two different ways: 1) by contamination of the stock solution; 2) by direct injection on the sediment surface in the column (point contamination). The initial amount was comparable to the double of the maximum sorption capacity acquired from batch tests. Concentrations of Cu and Cd in solutions were determined by the AAS. Experiments were carried out at room temperature and under atmospheric pressure.

Desorption by distilled water

The columns were disconnected from circulation arrangements and the distilled water freely flowed through the column. The outflows from column were collected and analysed by the AAS.

Sequential extraction analysis (SEA)

A slightly modified five-step sequential extraction procedure of Tessier et al. (1979) was used (see Plate V).
1. Two subsamples (2 g) of each soil were mixed with 20 ml of 1 M sodium acetate (CH_3COONa) solution (pH = 8.2) at room temperature and shaken for one hour. In this step, a portion of exchangeable metals was obtained.
2. The residue from step 1 was leached at room temperature by 20 ml of 1 M CH_3COONa (adjusted to pH = 5 with acetic acid, CH_3COOH). Samples were shaken until carbonates dissolved. Metals bound to carbonates were acquired.
3. The residue from step 2 was extracted with 20 ml of 0.04 M $NH_2OH.HCl$ in 25% acetic acid at 96 ± 4 °C with occasional agitation. The time needed for a complete dissolution of free iron oxides was evaluated. Metals bound to Fe-Mn oxides were obtained.
4. 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 (adjusted to pH = 2 with HNO_3) were added to the residue from the previous step at 85 ± 2 °C. A second 3 ml equivalent of 30% H_2O_2 (adjusted to pH = 2 with HNO_3) was added and the sample was kept at the same temperature

for 3 hours with intermittent agitation. After cooling, 5 ml of 3.2 M ammonium acetate (CH_3COONH_4) in 20% HNO_3 were added and the sample was diluted to 20 ml and agitated continuously for 30 minutes. Metals bound to organic matter were acquired.
5. Metals fixed in mineral structure of silicates were released after digestion by 5 : 1 HF – $HClO_4$ mixture in platinum crucible.

Results and discussion

The steady state in columns

Samples in columns were exposed to recirculating water for more than 250 days. Concentrations of most main cations reached the steady state. Stationary concentrations of several elements in pore water are shown in Tab. 3. Experiments were performed on two parallel columns in order to estimate the uncertainty and error.

Sediments with the finest grain sizes possess the highest porosity (it means the biggest bulk volume of small-size pores), the lowest infiltration rate and reach the highest degree of mineralization of pore fluids within relatively short periods of time (1 year). In the case of our samples, the degree of mineralization increased in a series: HBS 2 < Žd < HBS 6 < Le 4 < HBV 4. Mineralization is a result of water interaction with mineral surfaces.

Fine-grained samples have the largest specific mineral surfaces (surface/weight) and reach the steady state earlier than coarser-grained samples of the same mineral composition. The size of specific surface plays an important role in the process of adsorption.

Batch tests – sorption isotherms

Results of the interpolation for Cu static sorption are presented in Tab. 4, for Cd in Tab. 5 and in figures on Plate I.

The value of Δ^2 is a residual of the least square method. A smaller number indicates a better agreement of experimental data with theoretical Langmuir or Freundlich curves.

Tab. 4. Sorption parameters for sorption of Cu

Cu	Γ_{max} (meq/100 g)	K_L	Δ^2	K_F	n	Δ^2
HBS 2	8.01	2057.09	1.40	23.77	0.23	2.18
HBS 6	11.74	1785.93	7.89	51.90	0.30	2.32
HBV 4	62.45	17.60	31.88	96.09	0.46	4.79
Le 4	97.09	874.90	126.66	1495.73	0.51	28.37

Tab. 5. Sorption parameters for sorption of Cd

Cd	Γ_{max} (meq/100 g)	K_L	Δ^2	K_F	n	Δ^2
HBS 2	5.95	984.47	0.60	25.00	0.32	0.16
HBS 6	7.69	984.47	1.00	32.32	0.32	0.27
HBV 4	15.56	821.41	9.26	85.42	0.37	4.61
Le 4	29.29	128.33	23.71	73.26	0.35	1.09
Žd	12.80	22.99	2.88	30.87	0.52	0.70

An unusual data distribution was acquired in the case of sample Žd (Fig. 2). The results could not be fitted by any absorption isotherm because the precipitation dominated the sorption.

The lowest sorption capacity for Cd was detected on sample HBS 2. This sample consists mainly of quartz, which is not favourable for adsorption of heavy metals due to the absence of functional groups such as -OH and -COOH, and its small specific surface. Moreover, HBS 2 is carbonate-free and possesses a low content of organic matter.

Fig. 3 shows points of the initial $CuSO_4$ solution mixed with the pore fluids in the batch experiment (The Geochemist's Workbench). All of them occur in the supersaturated field with respect to malachite.

Favourable properties such as the content of carbonates, organic matter content and fine grain size predetermined the highest sorption capacity of sample Le 4 for both Cu (97.09 meq/100 g) and Cd (29.29 meq/100 g).

A relatively high value of sorption capacity was also found in batch tests for Cu on HBV 4, probably due to the strong Cu affinity with organic matter (Morera et al. 2001).

Sorption, desorption and sequential extraction analyses of Cu and Cd onto HBS 2 and HBS 6 under dynamic conditions

Sorption capacities obtained from column experiments were of higher value than those acquired from batch tests.

Results of the sorption on sample HBS 2 are shown in Plate II, those on sample HBS 6 sample are shown in Plate III and the results of desorption of both metals from both samples are shown in Plate IV. Column diagrams for the SEA are presented in Plate V.

In general, desorption of Cu and Cd by distilled water is rather slow (see Plate IV). Concentrations of metals (in the outflow from the column) decrease steeply at the beginning

Fig. 2. Data for Cu and Cd static sorption onto sample Žd.
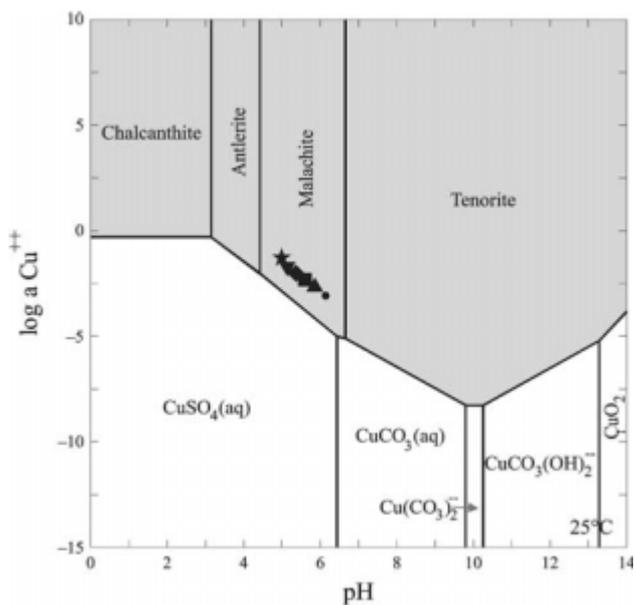
Fig. 3. Equilibrium diagram of Cu forms, $T = 23\ ^oC$, $\log a\ (HCO_3^-) = -2.7$ (equilibrium concentration at the steady state, column experiment, sample Žd), $\log a\ (SO_4^{2-}) = -2.34$ (average initial concentration in the batch experiment) and f $(O_2) = 0.2$, symbols – Cu concentration in the beakers, batch experiment.

Tab. 6. The sorption capacity of samples HBS 2 and HBS 6 for Cu

Cu	Arrangement	meq/100 g	mmol/100 g	mg/100 g
HBS 2	batch test	8.010	4.005	254.502
HBS 2	dynamic – solution contamination	16.350	8.175	519.489
HBS 2	dynamic – point contamination	17.870	8.935	567.784
HBS 6	batch test	11.740	5.870	373.015
HBS 6	dynamic – solution contamination	18.240	9.120	579.540
HBS 6	dynamic – point contamination	21.580	10.790	685.661

Tab. 7. The sorption capacity of samples HBS 2 and HBS 6 for Cd.

Cd	Arrangement	meq/100 g	mmol/100 g	mg/100 g
HBS 2	batch test	5.948	2.974	334.300
HBS 2	dynamic – solution contamination	5.859	2.929	329.300
HBS 2	dynamic – point contamination	7.104	3.552	399.300
HBS 6	batch test	7.690	3.845	432.220
HBS 6	dynamic – solution contamination	13.789	6.894	775.000
HBS 6	dynamic – point contamination	14.894	7.447	837.100

(wash-out of contaminated pore fluids) and then stabilise at relatively low levels (real desorption).

Through desorption by distilled water, about 6 % of the sorbed Cu and 44 % of the sorbed Cd were released from HBS 2. About 6 % of sorbed Cu and 9 % of Cd were released (by desorption) from HBS 6. These data do not correspond very well to the results of the SEA performed on the same samples before and after desorption (Plate 5). Desorption by distilled water should result in a wash-out of the exchangeable metals fraction. However, the SEA results indicate that the relative ratio of metals bonded to different fractions remains the same even after desorption. The question is, whether a redistribution among the five SEA fractions takes place or whether all the fractions release the metal simultaneously.

Fig. 3 on Plate V indicates that Cu was probably redistributed among the mineral surfaces during its desorption from sample HBS 6. In this particular case, the amount of Cu bonded to organic matter has increased at the expense of the phases preceding the organic matter in the SEA.

Conclusions

Generally, mineral surfaces tend to adsorb Cu more efficiently and firmly than Cd. Cadmium is therefore released more easily from sediments to the environment (Plate V, Figs 2 and 4). After the second step of the SEA (pH ≈ 5), more than 80 wt% of Cd in samples is mobilised (compare to about 50 wt% of Cu).

Sorption capacities obtained from column experiments were of higher value than those acquired from batch tests.

Carbonates in samples Le 4 and Žd affected the mobility of metal cations both in a direct and indirect way.

In a direct way by precipitation of secondary carbonate minerals and in an indirect way by buffering the pH over the point of zero charge for most minerals.

Numerous examples of competitive sorption of heavy metals onto monomineral surfaces have been published. The competition for the same sorption sites can be pursued among metals with similar ionic radius, surface charge density, electronegativity, hydrated radius and similar number of water molecules in the solvation sphere. This fact, in agreement with the trend observed by Trivedi et al. (2001) (see Introduction), indicates that Ca and Mg (the main cations in pore solution) should not compete with Cd and not at all with Cu for the same sorption sites.

Free metals in bulk solution were washed out of pores at the very beginning of the desorption tests. Then, weakly adsorbed metals (electric double layer) were washed out, and finally, a low steady state metal concentration was established. Such behaviour should result in a slow release of small amounts of a heavy metal, which should not pose significant danger to the environment.

References

Koubová M. (2002): Mineralogická charakteristika vzorků. In: P. Müller et al.: Závěrečná zpráva programu výzkumu a vývoje MŽP/630/3/00 – Komplexní geochemický výzkum interakcí a migrací anorganických a organických látek v horninovém prostředí. Report, Czech Geol. Surv., Brno.

Kruml O. (2002): Záchyt a uvolňování mědi na vybraných vzorcích sedimentárních hornin. Diploma Thesis. Report, Masaryk University, Brno.

Morera M. T., Echeverría J. C., Mazkiarán C., Garrido J. J. (2001): Isotherm and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils. Environmental Pollution 113, 135–144.

Steele H. M., Wright K., Nygren M. A., Hillier I. H. (2000): Interactions of the (001) surface of muscovite with Cu(II), Zn(II), and Cd(II): A computer simulation study. Geochim. Cosmochim. Acta 64, 257–262.

Stumm W., Morgan J. J. (1996): Aquatic chemistry. John Wiley & sons, Inc. New York, USA.

Tessier A., Campbell P., Bisson M. (1979): Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. Analytical Chemistry 51, 844–851.

Trivedi P., Axe L., Dyer J. (2001): Adsorption of metal ions onto goethite: single-adsorbate and competitive systems. Colloids and Surfaces 191, 107–121.

Vybíhal K. (2002): Záchyt a uvolňování kadmia na vybraných vzorcích sedimentárních hornin. Diploma Thesis. Report, Masaryk University, Brno.
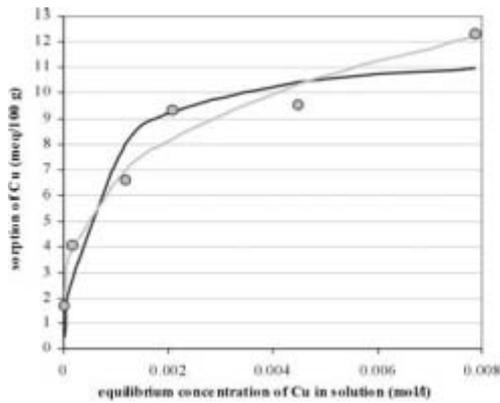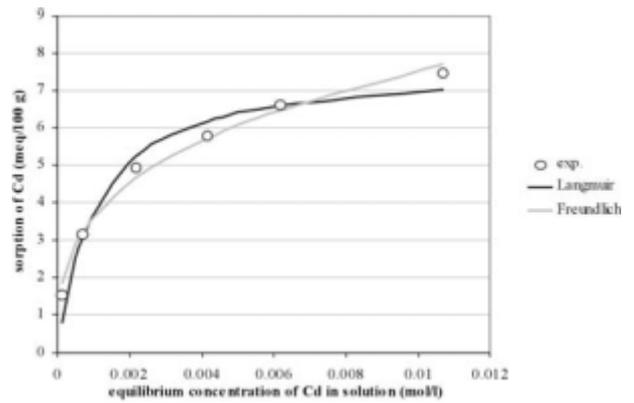
Handling editor: Petr Dobeš
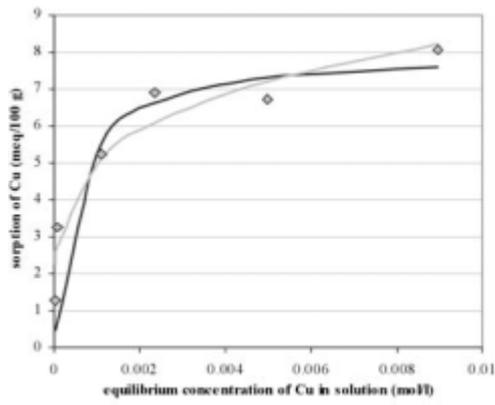
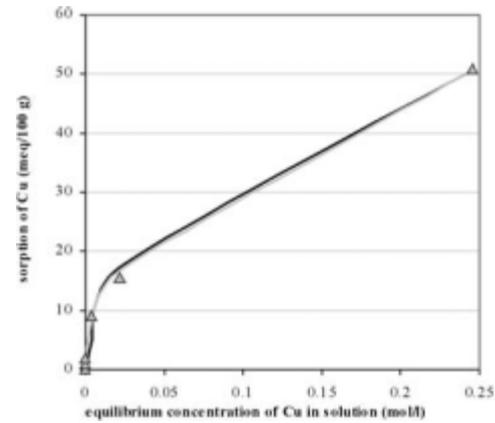1 – Isotherms for Cu sorption onto HBS 2.
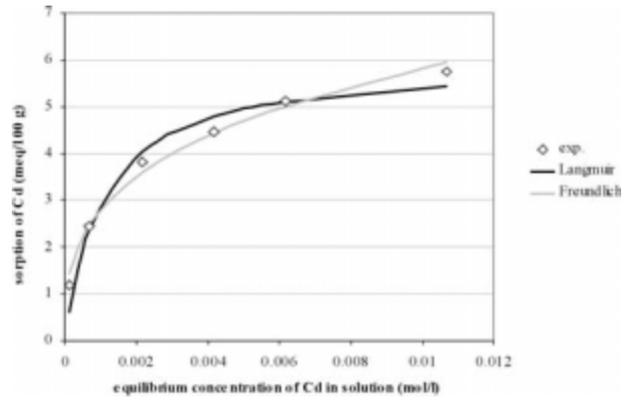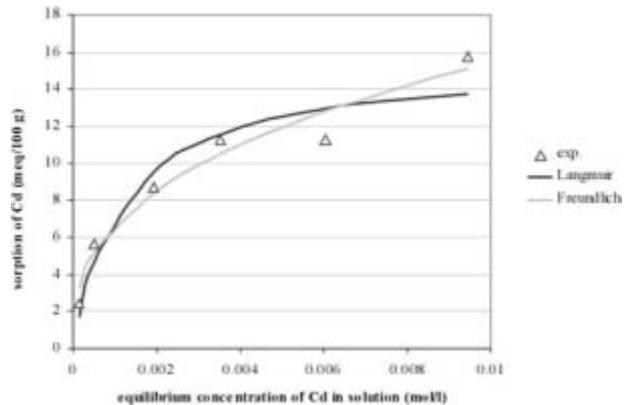

2 – Isotherms for Cd sorption onto HBS 2.

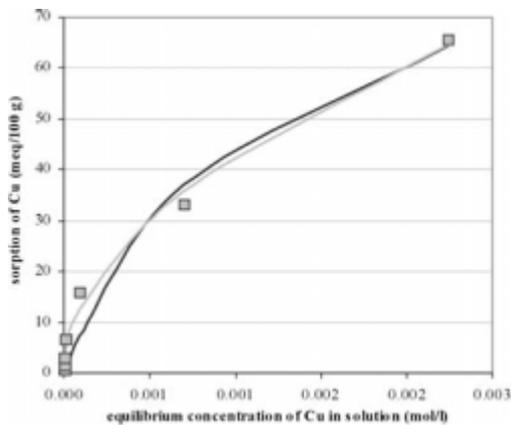3 – Isotherms for Cu sorption onto HBS 6.
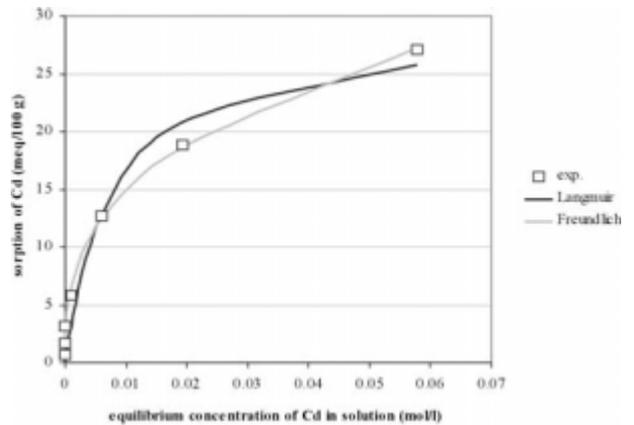

4 – Isotherms for Cd sorption onto HBS 6.

5 – Isotherms for Cu sorption onto HBV 4.
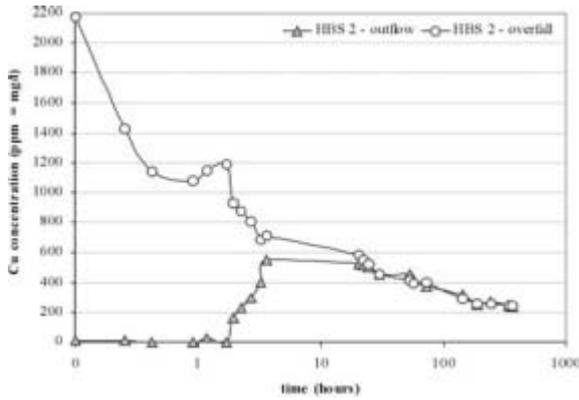

6 – Isotherms for Cd sorption onto HBV 4.
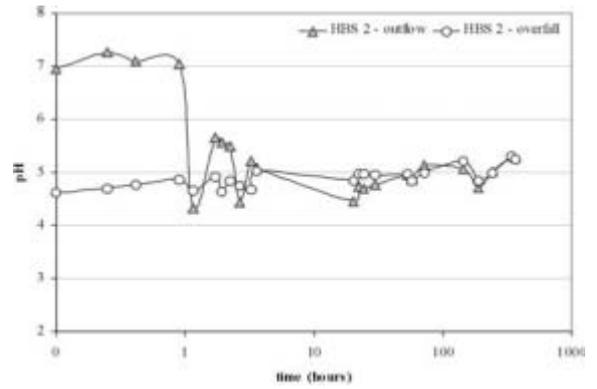

7 – Isotherms for Cu sorption onto Le 4.
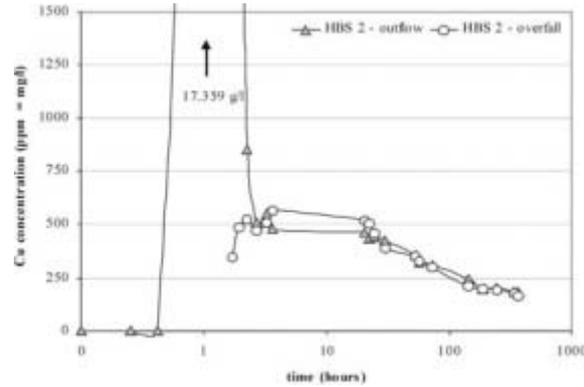

8 – Isotherms for Cd sorption onto Le 4.

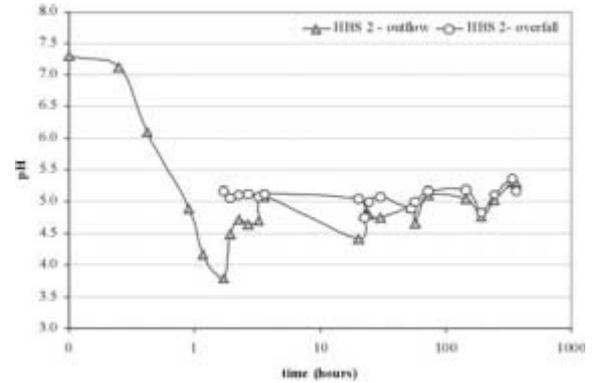Plate I. Langmuir and Freundlich isotherms for sorption of Cu and Cd onto different types of sediments (soils).

1 – Cu migration through the column with HBS 2 filling – stock solution contamination.

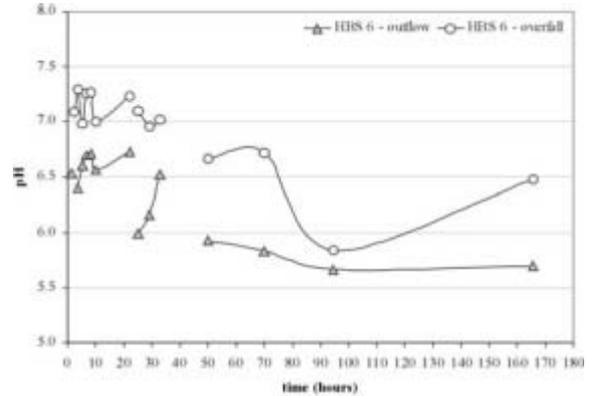2 – Progress of pH during experiment – Cu contamination of the stock solution.

3 – Cu migration through the column with HBS 2 filling – point contamination.
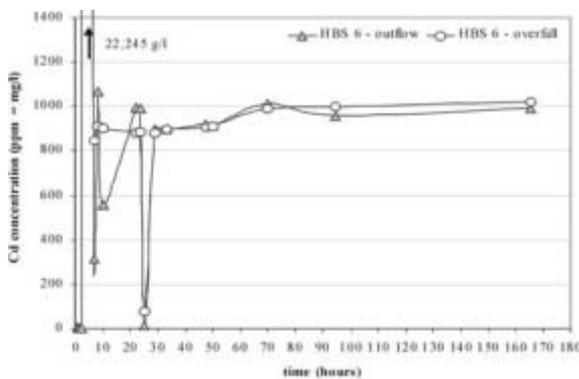

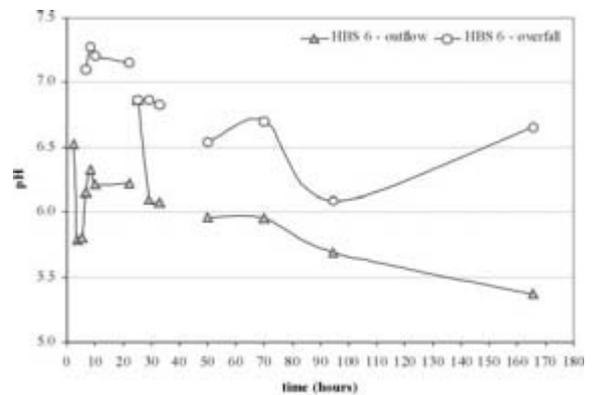4 – Progress of pH during experiment – Cu contamination on the surface of the solid phase.
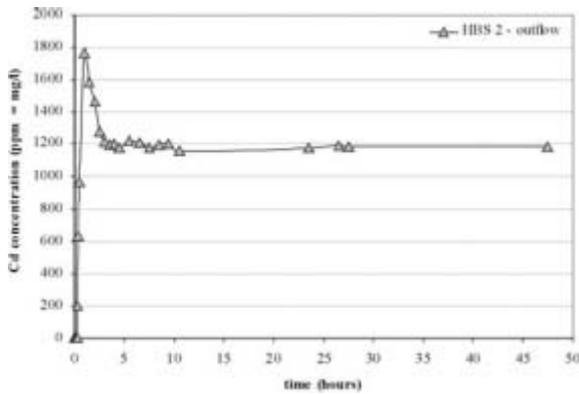
5 – Cd migration through the column with HBS 2 filling – stock solution contamination.

6 – Progress of pH during experiment – Cd contamination of the stock solution.

7 – Cd migration through the column with HBS 2 filling – point contamination.


8 – Progress of pH during experiment – Cd contamination on the surface of the solid phase.

Plate II. Sorption of Cu and Cd onto HBS 2 under dynamic conditions.

1 – Cu migration through the column with HBS 6 filling – stock solution contamination.
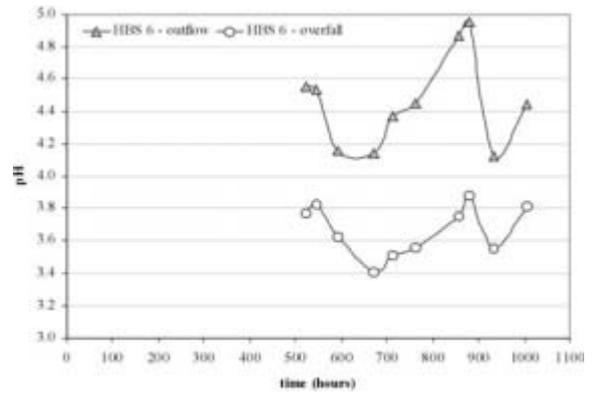
2 – Progress of pH during experiment – Cu contamination of the stock solution.

3 – Cu migration through the column with HBS 6 filling – point contamination.

4 – Progress of pH during experiment – Cu contamination on the surface of the solid phase.
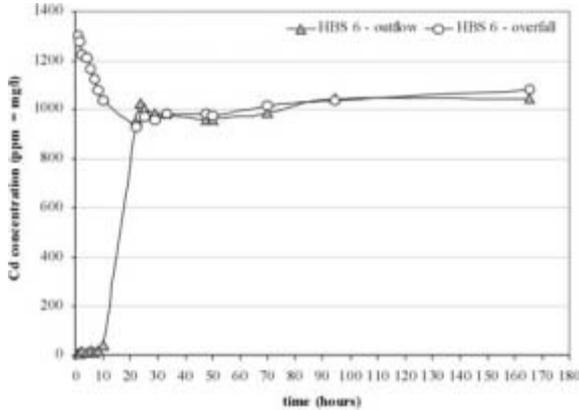

5 – Cd migration through the column with HBS 6 filling – stock solution contamination.

6 – Progress of pH during experiment – Cd contamination of the stock solution.

7 – Cd migration through the column with HBS 6 filling – point contamination.

8 – Progress of pH during experiment – Cd contamination on the surface of the solid phase.

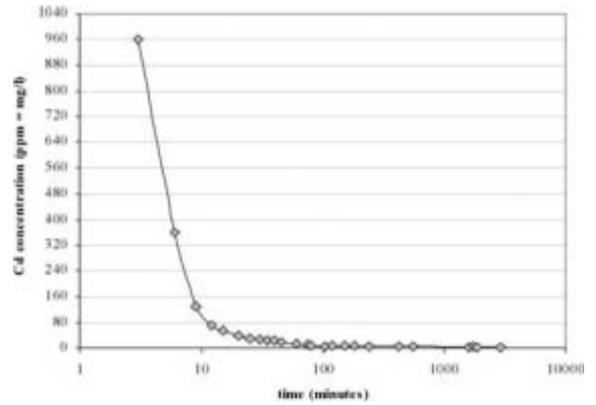Plate III. Sorption of Cu and Cd onto HBS 6 under dynamic conditions.
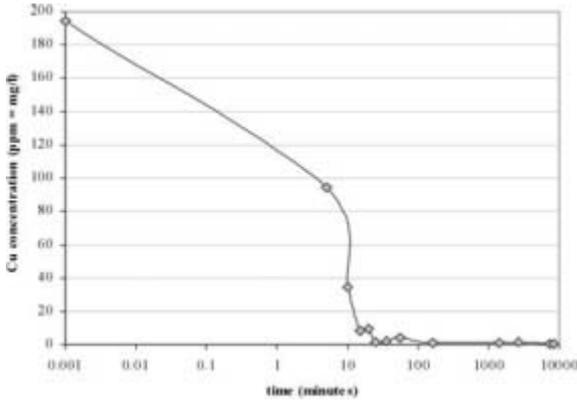
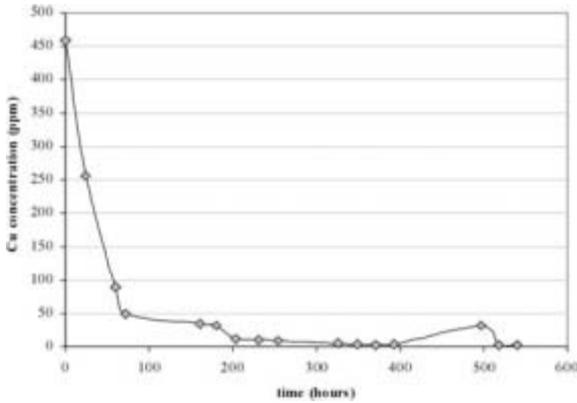1 – Cu desorption from HBS 2 after the sorption – stock solution contamination.
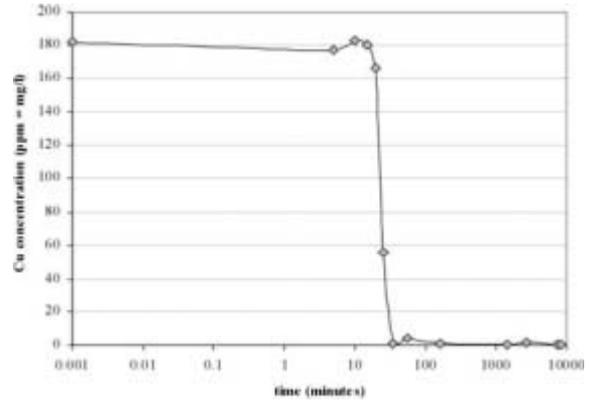
2 – Cu desorption from HBS 2 after the sorption – point contamination.
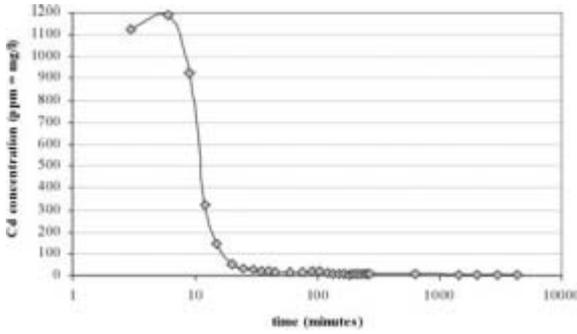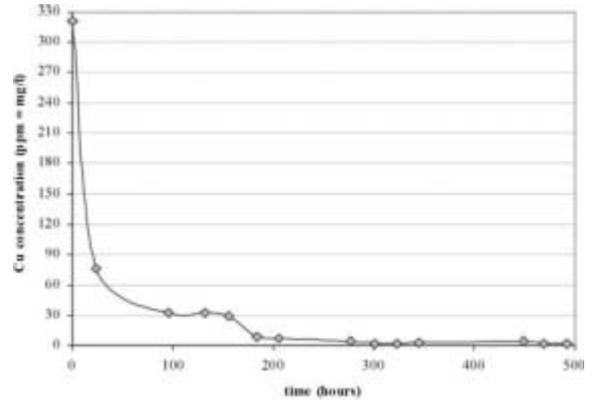

3 – Cd desorption from HBS 2 after the sorption – stock solution contamination.
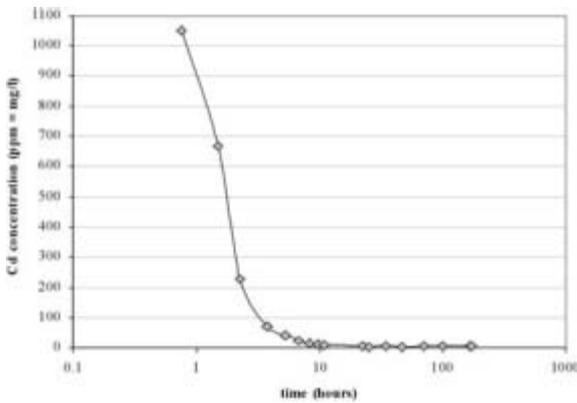

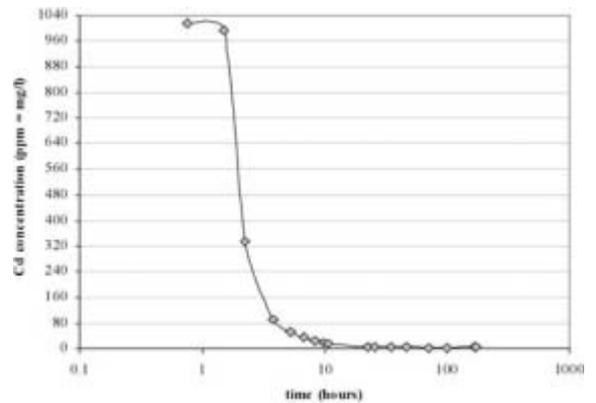4 – Cd desorption from HBS 2 after the sorption – point contamination.

5 – Cu desorption from HBS 6 after the sorption – stock solution contamination.

6 – Cu desorption from HBS 6 after the sorption – point contamination.

7 – Cd desorption from HBS 6 after the sorption – stock solution contamination.

8 – Cd desorption from HBS 6 after the sorption – point contamination.

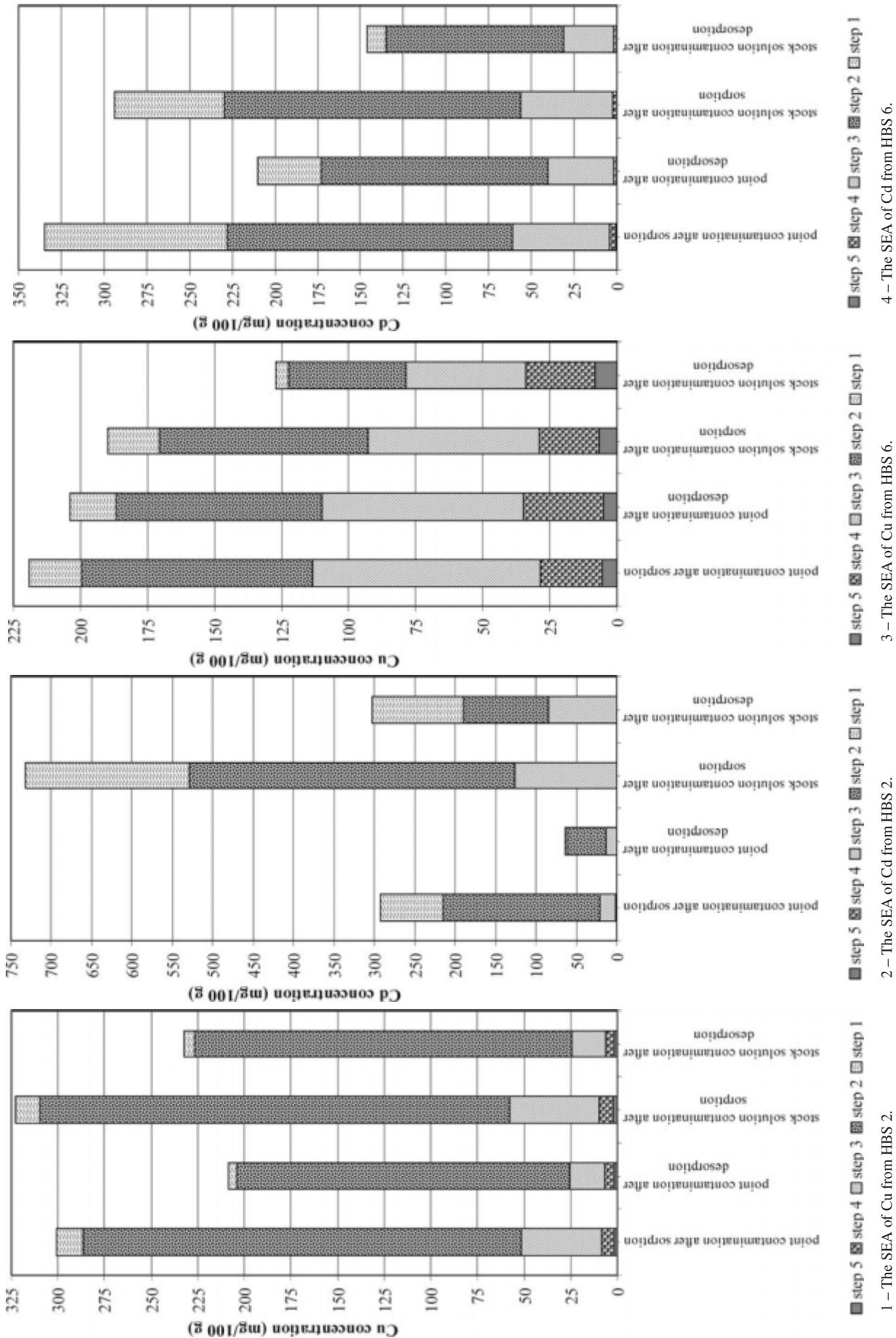Plate IV. Desorption of Cu and Cd from HBS 2 and HBS 6 by distilled water.

Plate V. The sequential extraction analysis (SEA) of Cu and Cd from HBS 2 and HBS 6. (Steps 1–5 of SEA are detailed respectively in the chapter Sequential extraction analysis.)

1 – The SEA of Cu from HBS 2.

2 – The SEA of Cd from HBS 2.

3 – The SEA of Cu from HBS 6.

4 – The SEA of Cd from HBS 6.