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IMMOBILIZATION OF CADMIUM FROM CONTAMINATED  
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**Keywords:** Contaminated sediment; cadmium; remediation; stabilization; cardboard mill sludge; leaching mechanism; leaching test.

**Abstract:** Sludge from cardboard mill is most commonly landfilled, but it could also be recycled on-site into production or reused in some other way. In this study the use of sludge from cardboard mill as stabilizing agent in the stabilization treatment of cadmium polluted sediment was examined. The effectiveness of treatment and long-term leaching behavior of cadmium was evaluated by determining the cumulative percentage of cadmium leached, diffusion coefficients ( $D_e$ ) and by applying different leaching tests (semi-dynamic test, toxicity characteristic leaching procedure, waste extraction test). In order to simulate the “worst case” leaching conditions, the semi-dynamic leaching test was modified using 0.014 M acetic acid ( $\text{pH} = 3.25$ ) and humic acids solution ( $20 \text{ mg l}^{-1}$  TOC) as leachants instead of deionized water. A diffusion-based model was used to elucidate the controlling leaching mechanisms. Applied treatment was effective in immobilizing cadmium irrespective of high availability in the untreated sample. The controlling leaching mechanism appeared to be diffusion, which indicates that a slow leaching of cadmium could be expected when the cardboard mill sludge as stabilization agent is applied.

## INTRODUCTION

Cadmium (Cd) is ubiquitous heavy metal pollutant in the environment due to its wide-spread use that has received a great deal of attention because of its toxic effects. Sediments are the final sink for cadmium input to the water environment, originating from both natural and/or anthropogenic sources. However, they may also act as endogenous contamination sources for aquatic systems [33].

Toxicity and mobility of elements depend strongly on their distribution in sediment and its identification helps in understanding geochemical processes in order to evaluate remobilization potential and the risks induced [32]. Most commonly used methods for that are the extraction procedures. Based on Tessier procedure [27], the three-stage sequential extraction procedure proposed by the European Community Bureau of Reference (BCR) was developed in an attempt to standardize the various schemes described in the literature

[24]. This method partitions heavy metals into four fractions: exchangeable (weakly bound and bound to carbonates), reducible (bound to iron and manganese oxides), oxidizable (bound to organic matter and sulphides) and residual (bound to the mineral matrix).

In some studies [14, 16, 18] the Risk Assessment Code (RAC) has been used to estimate possible damage to benthic organisms caused by contaminated sediments based on the results of sequential extraction procedures. The RAC considers the percentage fraction of metals that are exchangeable and associated with carbonates. In this fraction, the metals are weakly bound to the sediment, and pose a greater environmental risk since they are more available to the aquatic system. According to RAC, if this fraction is < 1% there is no risk for the aquatic system, 1–10% exhibits low risk, 11–30% medium risk, 31–50% high risk and > 75% very high risk. [16, 24].

In this study stabilization was used in order to remediate cadmium contaminated sediment, since this is a widely accepted treatment process for the immobilization of heavy metals contained in wastes [11, 21, 31].

Stabilization of contaminated sediment with sludge originating from cardboard industry is a potential tool to stimulate correct industrial sludge disposal in a safe and profitable manner. In this regard, we propose the incorporation of this sludge into contaminated sediment. Currently in Serbia, dredged sediment, contaminated or non-contaminated and cardboard mill sludges are deposited in landfills.

Paper and cardboard mill sludges are generated by various processes in the production of paper and cardboard, and increasing quantities produced make the disposal of these sludges a problem [4, 20]. Waste is mainly generated from pulping, deinking unit operations and wastewater treatment. The amount and the composition of the waste depends on the paper grade produced, the raw materials used, the process techniques applied and the paper properties achieved. The paper and cardboard mill sludges could be effective in sediment remediation treatments because of their organic matter, silicate and carbonate content. Organic matter is able to form stable complexes with several metals; the silicates are materials of high cation exchange capacity (CEC) and the bicarbonate/carbonate system is able to increase the pH value of soil. These chemical features were able to reduce the harmful mobile metals in polluted soils when the paper mill sludge was added to them [6].

The mechanisms governing heavy metals leachability of contaminants from waste forms and evaluation of the long-term behaviors of stabilized wastes can be effectively examined using the American Nuclear Society's (ANS) semi-dynamic leaching test [1]. The ANS 16.1 provides substantially more information regarding the “real time” rate at which heavy metals are released from the stabilized product as compared to other leaching tests. The leaching results extend over a 90-day period instead of a single result at the end of the test. The most often used leaching test, recommended by the USEPA, which provides only one result for defining the waste toxicity, is the Toxicity Characteristic Leaching Procedure – TCLP test [30]. TCLP was specifically designed to mimic acidic conditions in a sanitary landfill and identify wastes that have a potential to contaminate ground water. The Waste Extraction Test – WET is used in California [8], US, in a similar manner as the TCLP (determination of whether a solid waste is a hazardous waste), with the exception of the liquid-to-solid (L/S) ratio (10:1) and the leaching time.

In view of the above, the objectives of this study were: 1) to define cadmium distribution in dredged sediment and evaluate environmental risk based on the results of

sequential extraction procedure; 2) to assess the effectiveness of cadmium immobilization, stabilization treatments with cardboard mill sludge; 4) to evaluate the effectiveness of cadmium immobilization and stabilization treatments under the conditions that mimic the landfill environment; and 5) to determine the controlling leaching mechanisms of cadmium in untreated and treated sediment samples.

## MATERIALS AND METHODS

### *Sediment sampling procedure*

Fresh sediment was collected, using Eijkelkamp core sampler, from a middle of sediment reach Great Backa Canal (Serbia) and was placed in a sealed plastic, acid-rinsed box (15×15 cm and 20 cm deep) immediately after sampling.

### *Analytical methods*

The cardboard mill sludge used was obtained from cardboard mill situated in Belgrade (Serbia) after physico-chemical wastewater treatment and its chemical characterization was: pH  $8.6 \pm 0.3$ , CEC  $14.8 \text{ (cmol kg}^{-1}\text{)}$ , water content 19%, organic matter 31%, carbonates 25%, silicates 47%, Cd  $0.9 \text{ mg kg}^{-1}$ . The sludge was dried, crushed and passed through a 2.0 mm sieve, then characterized and used in the experiment.

Sediment initial water content was 75%. The organic matter content was determined as ignition loss, and it was  $4.48 \pm 0.1\%$ . The sediment pH was measured according to ASTM D 4972-01 [3] and it was  $7.3 \pm 0.4$ . The given values represent the means of three measurements.

Pseudo-total cadmium content was assessed on a sample triplicate after digestion [15] and determined by atomic absorption spectrometer (AAS) or inductively coupled plasma mass spectrometer (ICP-MS). The standard deviations (% R.S.D.) obtained ( $n=3$ ) were below 10%. The results of sediment cadmium pseudo-total concentrations are discussed in reference to Dutch regulation standards and Canadian guidelines, since Serbia has neither an established system of continual monitoring of sediment quality nor regulations concerning the quality standards [7, 19].

Microwave assisted sequential extraction procedure (MWSE) was performed as described by Jamali et al. [17], using identical operating conditions applied in each individual BCR fraction. Mean values were used and the RSDs ( $n=3$ ) were below 5%. The sum of the four steps sequential procedure and the pseudo-total cadmium content differed in less than 10%.

Pseudo-total sediment metal content and cadmium content in sequential extraction procedure steps were analyzed by AAS (Perkin Elmer AAnalyst™ 700) or ICP-MS (Perkin Elmer Sciex Elan 5000) according to the standard procedures [23]. All results are expressed with respect to sediment dry matter.

TCLP test was done according to the USEPA protocol [30]: 0.1 M acetic acid solution with a pH of 2.88 was used to extract control sample and treated samples since the pH was above 5. The sediment samples were extracted at a liquid to solid (L/S) ratio of 20 in capped polypropylene bottles on a rotary tumbler at 30 rpm for 18 hours. After the extraction, the final pH of the leachate was measured and the liquid was separated from the solids by filtration through a  $0.45 \text{ }\mu\text{m}$  pore size membrane filter. This test was applied on every sample in triplicate and the RSDs were below 5%.

The WET test [8] is similar to the TCLP in that it uses a buffered organic acid solution as the extraction fluid. This test uses a pH buffered citrate acid solution with sodium hydroxide, a 10:1 L/S ratio, and a 48-hour testing period. The WET extraction solution is prepared with a combination of 0.2 M citric acid solution and 4.0 N NaOH to pH  $5.0 \pm 0.1$ . One liter of this solution is added to a 100 g sample and rotated for 48 hours. After rotation, the final pH is measured, and the samples are filtered through a 0.45  $\mu\text{m}$  pore size membrane filter. This test was applied on every sample in triplicate and the RSDs were below 5%.

The ANS 16.1 test was applied in duplicate only on the M2 sample, with deionized water as leachant, and the RSDs were below 10%. The ANS 16.1 method was modified by including 0.014 M acetic acid (AA) pH 3.25 and humic acid (HA) solutions (20 mg TOC l<sup>-1</sup>, pH 6.55) as leachant instead of deionized water (DI). This was applied with the objective to mimic the worst possible conditions of the stabilized waste disposed in the environment (influence of acidic rains or increased organic loads). All materials in contact with the leachant were pre-cleaned with HNO<sub>3</sub> and subsequently rinsed with deionised water.

### **Experimental set-up**

Sediment and cardboard mill sludge were dried at 105°C to a constant mass. The sediment and cardboard mill sludge were mixed in proportion of 95:5 (M1), 90:10 (M2), 80:20 (M3), 70:30 (M4) and 50:50 (M5) by wt. Samples were prepared in the form of cubes ( $(3 \pm 0.1) \times (3 \pm 0.1) \times (3 \pm 0.1)$  cm) by compaction. The compaction was performed according to ASTM D1557-00 [2], providing a compactive effort of 2700 kN m m<sup>-3</sup>. Samples were cured for 28 days at 20°C in sealed sample bags and then subjected to the leaching tests: TCLP, WET and ANS 16.1.

### **Evaluation of Leaching Behavior**

The long-term leachability of cadmium from the treated sediments was evaluated using the ANS method 16.1 [1]. By applying this test we get the cumulative fraction of cadmium leached versus time. The ANS has standardized the Fick's law-based mathematical diffusion model as follows:

$$D_e = \pi \left[ \frac{a_n}{A_0} \right]^2 \left[ \frac{V}{S} \right]^2 T_n \quad (1)$$

where  $a_n$  is the contaminant loss (mg) during the particular leaching period with subscript  $n$ ;  $A_0$  is the initial amount of contaminant present in the specimen (mg);  $V$  is the specimen volume (cm<sup>3</sup>);  $S$  is the surface area of specimen (cm<sup>2</sup>);  $Dt_n$  is the duration of the leaching period in seconds;  $T_n$  is the time that elapsed to the middle of the leaching period  $n$  (s), and  $D_e$  is the effective diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>).

The relative mobility of cadmium can be evaluated by this coefficient, which varies from  $D_e = 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, (very mobile) to  $D_e = 10^{-15}$  cm<sup>2</sup> s<sup>-1</sup> (immobile).

### ***Determination of the controlling leaching mechanism***

The type of leaching mechanism that controls the release of metals can be determined based on the values of the slope of the plot of the logarithm of cumulative fraction release,  $\log(B_t)$ , versus the logarithm of time,  $\log(t)$ :

$$\log(B_t) = \frac{1}{2} \log(t) + \log \left[ U_{\max} d \sqrt{\left( \frac{D_e}{\pi} \right)} \right] \quad (2)$$

where  $D_e$  is the effective diffusion coefficient in  $\text{m}^2 \text{s}^{-1}$  for component  $x$ ;  $B_t$  is the cumulative maximum release of the component in  $\text{mg m}^{-2}$ ;  $t$  is the contact time in seconds;  $U_{\max}$  is the maximum leachable quantity in  $\text{mg kg}^{-1}$ , and  $d$  is the bulk density of the product in  $\text{kg m}^{-3}$ .

When the slope of the plot of the logarithm of cumulative fraction release,  $\log(B_t)$ , versus the logarithm of time,  $\log(t)$  is close to 1 (0.60-1), the process is defined as dissolution. In that case, the dissolution of the material proceeds faster than the diffusion. If the slope of the plot of the logarithm of cumulative fraction release,  $\log(B_t)$ , versus the logarithm of time,  $\log(t)$  is around 0.50 (0.40–0.60), the controlling leaching mechanism is diffusion. If the slope is close to zero (0.00–0.40) the controlling leaching mechanism is surface wash-off. [12].

## RESULTS AND DISCUSSION

### ***Pseudo-total metal concentrations and sequential extraction of untreated sample***

Pseudo-total cadmium concentration in sediment was  $40.6 \pm 1.9 \text{ mg kg}^{-1}$ . According to the Dutch regulation standards, sediment is polluted with cadmium (class 4). Class 4 sediments are of unacceptable quality and need most urgent actions, dredging, disposal in special storage reservoirs, and, if possible, sediment clean-up measures [19].

Compared with the Canadian Sediment Quality Guidelines [7] for aquatic life protection, Cd content is above the PEL. Sediment concentrations above PEL values are expected to be frequently associated with adverse biological effects. Although PEL is considered to be applicable to a variety of sediment types, it cannot define uniform values of sediment pollution as the bioavailability (and hence toxicity) of contaminants may be different.

Percentage of extracted cadmium in most available, mobile, step was 31.4%. The percentage of cadmium in the other modified BCR fractions according to their relative contents is as follows: 24.5% in reducible fraction, 32.4% in oxidizable form, and 13.2% in residual fraction.

According to the RAC, cadmium comes under the high risk category [16]. Cd also showed the high content in the oxidizable fraction. Cd is strongly complexed in sediments, and could be released following degradation of the organic matter or oxidation of sulfides to sulfates. The observed behavior was probably due to the affinity of the metals for the OM present in water, given the high anthropogenic loadings in the region under study [24, 25]. Reports in the literature for regions of high inputs from human activity are indicative of the presence of significant percentages of Cd in this sediment fraction [16, 24, 26].

The nonresidual fractions (exchangeable+reducible+oxidizable) of cadmium were 88.3%. This is an indication that these fractions of cadmium in sediment are potentially available for exchange and/or release into the environment.

### **Leaching Tests: ANS 16.1, TCLP and WET**

Samples of sediment-cardboard mill sludge mixtures were subjected to the semi-dynamic leaching test ANS 16.1 [1]. This test has not been previously applied on the mixtures of metal-contaminated sediment with cardboard-mill sludge. A total cumulative fraction of cadmium leached (%) after ANS 16.1 test completion using deionized water (DI), acetic acid (AA) and humic acid (HA) solutions as leachants are presented in Table 1.

Table 1. Total cumulative fraction of cadmium leached (CFL, %) after ANS 16.1 test completion using deionized water (DI), acetic acid (AA) and humic acid (HA) solutions as leachants, mean effective diffusion coefficient  $D_e$  ( $\text{cm}^2 \text{s}^{-1}$ ) for untreated (SO) and treated sediment samples (M1, M2, M3, M4, M5)

<b>DI</b>	<b>SO</b>	<b>M1</b>	<b>M2</b>	<b>M3</b>	<b>M4</b>	<b>M5</b>
CFL (%)	17.4	6.13	5.92	5.80	5.75	5.78
$\overline{De}$	$4.74 \cdot 10^{-7}$	$5.14 \cdot 10^{-11}$	$4.07 \cdot 10^{-11}$	$3.11 \cdot 10^{-11}$	$3.21 \cdot 10^{-11}$	$3.27 \cdot 10^{-11}$
<b>AA</b>						
CFL (%)	19.6	8.17	7.55	7.23	7.20	7.28
$\overline{De}$	$1.26 \cdot 10^{-6}$	$4.12 \cdot 10^{-9}$	$3.11 \cdot 10^{-9}$	$1.94 \cdot 10^{-9}$	$2.05 \cdot 10^{-9}$	$2.12 \cdot 10^{-9}$
<b>HA</b>						
CFL (%)	18.2	6.96	6.92	6.46	6.48	6.52
$\overline{De}$	$7.92 \cdot 10^{-7}$	$7.96 \cdot 10^{-11}$	$7.24 \cdot 10^{-11}$	$6.26 \cdot 10^{-11}$	$6.39 \cdot 10^{-11}$	$6.48 \cdot 10^{-11}$

The amount of cadmium released during the ANS 16.1 tests for the untreated samples did not exceed 20% of the total mass of the contaminant in the waste, which is the upper limit for the diffusion model to be applicable [1]. The cardboard mill sludge exhibits good sorption properties significantly reducing its leachability compared to the untreated sample. This is in agreement with the literature data for soil remediation [4, 6].

Humic acid leachant releases more cadmium than deionized water in all samples. Humic acids are very important in the formation of stable organo-mineral complexes due to their physicochemical and biological stability. Due to their amphipathic nature and structural features, HAs play an important role in environmental processes governing the fate and transport of organic and inorganic pollutants in natural systems. They include binding sites with different complexation strength, able to form inert and labile complexes with inorganic cations and organic compounds. Based on some previous studies, cadmium shows pronounced tendency for complexing with humic acids [9, 13].

Amount of cadmium leached sometimes increases with higher sorbent loading (Table 1). Similar results have been reported by other authors [5, 13, 25]. This may be attributed to two reasons: (i) a large adsorbent amount effectively reduces the unsaturation of the adsorption sites and correspondingly, the number of such sites per unit mass comes down resulting in comparatively less adsorption at higher adsorbent amount, and

(ii) higher adsorbent amount creates particle aggregation, resulting in a decrease in the total surface area and an increase in diffusional path length both of which contribute to decrease in amount adsorbed per unit mass.

Diffusion coefficients  $D_e$  for treated samples, computed by Eq. (1), are listed in Table 1. The mobility of cadmium in this study was reduced by treatment. Diffusion coefficients are in agreement with the results of cumulative release of the cadmium from the treated samples. The diffusion coefficients for metals in the treated samples ranged from  $10^{-9}$   $\text{cm}^2 \text{s}^{-1}$  to  $10^{-11}$   $\text{cm}^2 \text{s}^{-1}$  (low mobility). The treatments employed may be considered efficient, even under the conditions of sediment exposure to the influence of, for example, acidic rains or increased organic loads.

At present, TCLP is used by the USEPA to evaluate whether a particular stabilization process is effective in treating a given waste in terms of the reduction of contaminant mobility and toxicity [30]. TCLP leaching test results are presented in Table 2.

Table 2. Results of the TCLP and WET leaching test ( $\text{mg L}^{-1}$ ) for untreated (SO) and treated sediment samples (M1, M2, M3, M4, M5)

	SO	M1	M2	M3	M4	M5
TCLP	1.7	0.50	0.43	0.38	0.41	0.42
WET	1.9	0.59	0.51	0.46	0.47	0.49

A comparison of the concentrations obtained in the TCLP test showed that cadmium concentration in the treated samples is below concentration obtained for untreated sediment, implying that cadmium is successfully incorporated in treated matrix. The TCLP Cd concentration was  $1.7 \text{ mg L}^{-1}$  of leachate for untreated sediment, which was higher than the regulatory limit of  $1 \text{ mg L}^{-1}$  for hazardous waste [30]. The treatments reduced the TCLP concentration to less than  $0.6 \text{ mg L}^{-1}$ , which was below the TCLP limit.

The WET extracted somewhat higher concentrations of Cd than the TCLP but below WET limit values [8]. This is consistent with the literature [28, 29]. TCLP is conducted at a 20:1 liquid-to-solid ratio and WET is carried out at 10:1 liquid to solid ratio; the TCLP is twice diluted compared to WET and in general higher leachate concentrations are observed at lower liquid-to-solid ratio [28, 29]. The greater element concentrations observed in the WET leachates relative to the leachates most likely result, however, from citrate's propensity to chelate Cd. Citric acid has multidentate ligands while acetic acid has monodentate ligands, and in general, complexes with monodentate ligands are less stable than those with multidentate ligands [28, 29].

While the single leaching tests are rapid, they do not simulate complex environmental settings. Also, sequential extractions provide semi-quantitative information on element distribution between operationally defined geochemical fractions. Therefore, the fractions obtained from sequential extractions do not necessarily reflect true chemical distribution. One of the main limitations of sequential extraction procedures is that they are extremely time-consuming, so that they are less used for routine analysis. Although leaching techniques such as column leaching tests are probably more realistic to field conditions, sequential extractions and single step extractions can give an indication of the 'pools' or 'sinks' of heavy metals that are potentially available under changing environmental conditions.

Overall, the treatment was efficient having in mind that sediment sample had a high initial cadmium concentration. This may be difficult to readily explain due to the degree of complexity of the natural sediment samples. In nature there are many constituents that could participate in and influence cadmium leachability. Further research is required to obtain some of this information in order to evaluate the cadmium speciation and subsequent mechanisms of incorporation and release in these samples.

### ***Controlling Leaching Mechanism***

The controlling leaching mechanisms were evaluated using the diffusion model (Eq. (2)). All slopes of the plot of the logarithm of cumulative fraction release,  $\log(Bt)$ , versus the logarithm of time,  $\log(t)$  and  $R^2$  (correlation coefficient) values obtained from the diffusion model are presented in Table 3.

Table 3. Slope values of the plot of the logarithm of cumulative fraction release,  $\log(Bt)$ , versus the logarithm of time,  $\log(t)$  and  $R^2$  (correlation coefficient) values obtained from the diffusion model for untreated (SO) and treated sediment samples (M1, M2, M3, M4, M5)

Deionized water solution	SO	M1	M2	M3	M4	M5
Slope	0.18	0.42	0.45	0.51	0.42	0.44
$R^2$	0.99	0.93	0.96	0.99	0.91	0.92
Acetic acid solution						
Slope	0.12	0.47	0.50	0.53	0.57	0.52
$R^2$	0.98	0.92	0.94	0.96	0.95	0.92
Humic acid solution						
Slope	0.20	0.41	0.49	0.51	0.46	0.48
$R^2$	0.98	0.99	0.91	0.92	0.98	0.93

The slope values of the plot of the logarithm of cumulative fraction release,  $\log(Bt)$ , versus the logarithm of time,  $\log(t)$  for mixtures were in the range from 0.41 to 0.57 for all treated samples. That indicates diffusion is the dominant leaching mechanism. In the untreated sediment sample slope values were in the range from 0.18 to 0.20, which indicates that the dominant leaching mechanism was surface wash-off.

Further research should be focused on a more detailed analysis aiming at the elucidation of the incapsulation of cadmium into the structure and its leaching mechanism, relying on the studies of mineralogy (qualitative and quantitative X-ray diffraction) as well as micromorphology (scanning electron microscopy and optical microscopy).

## CONCLUSION

Assessment of the sediment quality based on the pseudo-total cadmium content and according to the corresponding Dutch standards and Canadian guidelines showed its severe contamination. Sequential extraction can be used as a valuable tool to provide

information on the mobility, bioavailability and potential toxicity of the trace metals in the environment. Cadmium seems to pose high risk based on the modified BCR sequential extraction and risk assessment code.

The immobilization treatment with cardboard mill sludge applied appeared to be efficient in the remediation of sediment contaminated with cadmium based on the diffusion coefficients, cumulative fraction of cadmium leached and the results of TCLP and WET tests. In all samples the controlling leaching mechanism of cadmium upon the stabilization treatment appeared to be diffusion. Hence, only small amounts of cadmium could be expected to leach into the environment over time.

Due to the large volumes of waste generated in the cardboard, paper and pulp industries, it is necessary to continue environmental awareness on different applications of wastes, while taking into account the environmental and economic factors of these waste treatments. Conventional waste management methods, which might have been acceptable in the past, may not be optimal to meet present and future requirements. Cardboard mill sludge utilization to “remediate” contaminated sediment could be an interesting approach.

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