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ASSESSMENT OF SLUDGES FROM RAIL FREIGHT CAR WASH WASTEWATERS. THE PRIMARY SLUDGES

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Abstract: This article presents the assessment results concerning sludges after sedimentation generated under full scale technical conditions on the system for pretreatment of sludges formed as a result of water washing of usable areas of railway freight transport of category: G, H and T in accordance with the International Union of Railways classification. The sludges were separated in a storage and average tank, being the first processing node of sludge pretreatment system to which the raw wastewaters were discharged. Due to significant diversification of the pollutants load, the sludges were characterised by significant inhomogeneity. The article presents the results of leaching procedure (TCLP) carried out for selected samples and the risk assessment using RAC code performed on the basis of the analysis of fractional composition of selected heavy metals such as: Cu, Ni, Pb and Zn. It was found out that gravitationally post-sedimentary sludges, generated during randomly selected three operational months of the installation, indicated a low risk (LR) in relation to Cu and a moderate one (MR) regarding Ni, Pb and Zn. In accordance with TCLP criteria, primary sludge - being the effect of raw sewage retention and sedimentation of its dispersed solids was classified as a non-toxic waste.

Keywords: wastewaters from railway freight car wash, post-sedimentary sludges, TCLP test, fractional composition of heavy metals in sediments, risk assessment code (RAC)

Introduction

The use of railway rolling stock of commodity type is inseparably connected with car surface cleaning and generating wastewaters and sludges formed in the processes of their physico-chemical treatment [1-10]. The composition, diversity and the amount of the pollutants load in wastewaters generated in freight car wash is a function of the composition of transported commodities [1-10]. In a specific development, the recorded load levels of individual pollutions depend on i.a.: a physical state and chemical composition, solid dispersion, humidity, heterophase state, methods of packaging and sealing of packages as well as repeatability of the transported commodities categories in long-term quantification [11, 12]. The composition and the amount of the pollutants load in wastewaters may also be a result of incidental cases of mechanical damage of protective packages for transported commodities during their shipment or transportation [12]. In the processes of wastewater pretreatment, post-processing sludges are generated. The sludges are characterised by specific and variable physico-rheological features and chemical composition that has to be disposed ultimately [13].

The aim of this study was to assess the risk on the basis of the analysis of fractional composition of selected heavy metals and leaching tests (TCLP) concerning settled primary

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sludges separated at the first step of raw effluents pretreatment after their retention and sedimentation of dispersed solid fractions, generated as the result of surface cleaning of railway cars of classes G, H and T, according to the International Union of Railways classification [14].

Experimental part

Basic characteristics of the source of primary sludges generation and sampling

The post-sedimentary sludges were sampled from the first processing volume of physico-chemical wastewater treatment plant with daily capacity up to 50 m³/day [15]. It was designed for water cleaning of rail freight cars of class E, F, G, H, K, L, R and T according to the International Union of Railways classification [14]. Raw effluents from washing surfaces of transport rolling stock were directed to flow gravitationally to the first retention-averaging tank. There the treated wastewaters were kept for at least 90 minutes to separate the sludges after sedimentation. Periodically accumulated sludges were pumped onto a unit of its gravity drainage that consisted of open sack filters. Sample groups of sludges dewatered separately each month were marked with: A, B and C indices. Specimens for analyses were collected after 7 days of final dewatering, counting from the moment that the last batch of raw sludges onto the filter unit. The filtrate pH recorded from the start of filtration and within seven days of final gravity filtering, counting from the moment of introducing the last batch of raw sludge onto the filter unit, formed as follows: a) A pH 6.4 ±0.5, b) B pH 7.2 ±0.5, c) C pH 7.3 ±0.6.

Collected sludge specimens were subject to 5-stage sequential extraction procedure in accordance with Tessier's methodology [16] and TCLP (Toxicological Characteristic Leaching Procedure) [17], then concentrations of selected heavy metals were determined.

TCLP leaching tests procedure

The assessment of gravitationally sampled dewatered sludges was made in compliance with TCLP methods in accordance with the USEPA Method 1311 [17] determining leachable forms of metals such as Cu, Ni, Pb and Zn, because only those metals were found in the raw sewage flow. The final determinations in the extracts were made using the Jobin Yvon EMISSION JY 38S ICP-OES emission spectrometer and the standard for the determination of metals PN-EN ISO 11885:2009E [18]. The proceedings used in the TCLP leaching procedure included the following stages:

- a) sampling of sludge of particles size < 9.5 mm, homogenising and sieving;
- b) the reaction of sludge was checked: 96.5 cm³ of distilled water was added up to 5.0 g of "non-anhydrous" sample and mixed for 5 minutes and then pH was measured. When pH < 5.0, the extraction solution L no. 1 was used, and when pH > 5.0 then 3.5 cm³ of 1 M HCl was added. Then, the covered content was heated up to 50°C for 10 minutes. After cooling to room temperature, pH was measured to determine a type of extraction solution L. If pH < 5.0 extraction solution L no. 1 was applied. If pH > 5.0, extraction solution L no. 2 was used (extraction solution L no. 1 was a mixture of the following composition: 11.4 cm³ HOAc + 128.6 cm³ 1 M NaOH and topped up with distilled water to 2.0 dm³, and its final reaction was at the level of the

- pH = 4.93 ± 0.05 . Extraction solution L no. 2 was prepared by diluting 11.4 cm^3 HOAc with distilled water up to 2.0 dm^3 due to which its final reaction was at the level of pH = 2.88 ± 0.05);
- preparing the composition for extraction - for the determination of components: 100.0 g of “non-anhydrous” of sludge samples (S) in duplicates, to which suitable extraction solution (L) as described in point (b) was added in relation of the liquid to solid sludge (S), respectively $(L/S) = 20:1$ were used;
 - shaking during 18.0 ± 2.0 hours at room temperature;
 - separating the phases by filtering;
 - the analysis of metals concentration in the filtrate with $\text{pH} < 2$ (acidifying with HNO_3).

In the event of noticing the incidentally high concentrations of metals in the influencing raw sewage, for the relevant batch of settled sludge from such a stream of the effluents, an additional leaching procedure was run and its results are presented in the list of results.

The analysis of fractional composition of selected metals according to Tessier's procedure

Gravitationally settled deposits were submitted to sequential extraction consisting in determining five fractions in accordance with Tessier's basic procedure specified in item [16]. 100.0 g of “non-anhydrous” sludge in two replications was used for the extraction. The conditions of sequential extraction are set in Table 1.

Table 1

The proceedings in the sequential extraction was adopted on the basis of position [16]

Fractions	Quantities of used reagents for the sample of 100.0 g	Details of the proceedings
(F1) Exchangeable	<ul style="list-style-type: none"> 800 cm^3 1 M CaCl_2 (pH 7) 	<ul style="list-style-type: none"> shaking 1.0 h at room temperature
(F2) Carbonate	<ul style="list-style-type: none"> 800 cm^3 1 M $\text{CH}_3\text{COONH}_4$ (pH 7) (acidification with 25% $\text{CH}_3\text{COOH}^{\text{a)}$) 	<ul style="list-style-type: none"> shaking 5.0 h at room temperature
(F3) Fe-Mn oxides bound	<ul style="list-style-type: none"> 2000 cm^3 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% $\text{CH}_3\text{COOH}^{\text{a)}$ (v/v) (pH 2) 	<ul style="list-style-type: none"> shaking 5.0 h at 96°C
(F4) Organic	<ul style="list-style-type: none"> 300 cm^3 0.02 M HNO_3 and 500 cm^3 30% $\text{H}_2\text{O}_2^{\text{b)}$ (pH 2), 500 cm^3 3 M $\text{CH}_3\text{COONH}_4$ in 20% HNO_3 (v/v) (pH 2) 	<ul style="list-style-type: none"> shaking 3.0 h at 85°C shaking 0.5 h at room temperature
(F5) Residual	<ul style="list-style-type: none"> a mixture of aqueous solutions of HNO_3 and H_2O_2 was added twice within an hour (a mixture of pH 2 was prepared from 300 cm^3 $\text{HNO}_3^{\text{c)}$ and 500 cm^3 30% $\text{H}_2\text{O}_2^{\text{b)}$), 500 cm^3 30% $\text{H}_2\text{O}_2^{\text{b)}$ was added 	<ul style="list-style-type: none"> shaking during 1.0 h at boiling point up to a moment of the emission of white vapours, shaking during 0.5 h at boiling point

densities of chemical reagents used were as follows: ^{a)} 25% CH_3COOH ($\rho = 1.0320 \text{ g/cm}^3$), ^{b)} 30% H_2O_2 ($\rho = 1.1110 \text{ g/cm}^3$), ^{c)} 65% HNO_3 ($\rho = 1.4020 \text{ g/cm}^3$)

Results and discussion

Both fractions: the exchange one (F1) and the carbonate (F2) one, are considered to be loosely associated with matrices of sludge, and sensitive even to minor changes of environmental conditions, i.a. changes in pH or ionic strength [19]. In most known methods

of sequential extraction, fraction F1 is obtained using mild extraction solvents such as mild solutions of acids or salts.

Table 2

The content [%] of metals in various fractions of 5-stage sequential extraction carried out in compliance with Tessier's methodology for gravitationally dewatered post-sedimentary primary sludge from wastewater treatment generated in rail freight car wash ^{a)}

Metals	Sample (pH)	F1	F2	F3	F4	F5
Zn	B1 (7.2)	3.1	9.6	9.7	25.5	52.1
	B2 (7.1)	17.7	10.3	14.9	21.0	36.1
	B3 (7.3)	2.9	9.9	9.6	25.8	52.4
	A1 (6.4)	6.2	6.8	10.3	26.1	50.6
	A2 (6.5)	5.8	27.0	29.8	27.1	10.3
	A3 (6.4)	17.1	5.8	10.1	26.6	50.4
	C1 (7.2)	5.8	5.2	9.6	22.3	57.1
	C2 (7.3)	5.9	14.9	9.3	28.0	41.9
	C3 (7.3)	5.2	5.1	10.1	21.9	56.7
Pb	B1 (7.2)	4.7	2.5	0.9	7.7	84.2
	B2 (7.1)	5.1	7.6	1.1	7.9	78.3
	B3 (7.3)	5.5	7.3	1.6	7.4	78.2
	A1 (6.4)	2.8	9.1	1.6	7.4	79.1
	A2 (6.5)	2.5	9.3	1.3	7.7	79.2
	A3 (6.4)	3.1	9.7	1.1	7.2	78.9
	C1 (7.2)	8.5	3.8	0.8	7.6	79.3
	C2 (7.3)	4.5	3.1	1.5	7.8	83.1
	C3 (7.3)	8.2	4.9	1.2	7.9	77.8
Cu	B1 (7.2)	5.8	0.2	1.9	67.6	24.4
	B2 (7.1)	5.5	0.5	2.1	67.8	24.1
	B3 (7.3)	4.0	1.9	2.3	68.5	23.3
	A1 (6.4)	9.8	2.3	47.9	28.1	11.9
	A2 (6.5)	2.8	3.1	2.2	68.2	23.7
	A3 (6.4)	3.3	2.9	2.1	62.6	29.1
	C1 (7.2)	3.9	2.2	1.8	67.7	24.4
	C2 (7.3)	3.6	2.5	1.9	67.8	24.2
	C3 (7.3)	3.8	2.3	1.8	67.7	24.4
Ni	B1 (7.2)	6.8	9.3	16.8	35.6	31.5
	B2 (7.1)	16.6	9.8	6.6	35.3	31.7
	B3 (7.3)	6.3	9.8	16.9	30.0	37.0
	A1 (6.4)	6.1	10.2	7.4	39.8	36.5
	A2 (6.5)	6.3	10.6	7.5	36.2	39.4
	A3 (6.4)	7.8	9.8	7.1	35.1	40.2
	C1 (7.2)	4.2	12.6	5.9	34.7	42.6
	C2 (7.3)	4.3	12.5	5.7	35.2	42.3
	C3 (7.3)	9.9	10.2	19.7	38.1	22.1

^{a)} the raw wastewater was generated as a result of water cleaning of usable surface of transport railway rolling stock, mainly of: G, H and T classes according to the International Union of Railways classification [14]

The forms of metals associated with reducible fraction (F3) are considered as thermodynamically labile and available under anaerobic or anoxic conditions [19]. Therefore, fractions F1-F3 are considered as the pools of metals from direct effects and involving a direct toxicity. In oxidizing conditions that are obtained for the determination of fraction F4, metals which are connected with organic matter and metals that react with

sulphides may be released or converted from the forms of preferred for fractions F1-F3. Fraction F4 is also identified as a pool of speciation forms of potential effect and potential toxicity. But the residual fraction F5 is regarded as chemically stable and durable because it contains mainly primary and secondary mineral forms and the metals are firmly bonded in their structures with predominant participation of crystallized forms as well. Currently, it is usually assumed that metals from residual fraction are not easily released to different components of the environment and do not represent any potential toxic risk for the biosphere [20]. Table 2 shows the data obtained from the 5-stage sequential extraction (according to Tessier's methodology) for settled dewatered post-sedimentary sludges collected at monthly intervals within the period of 3 months of the operation of the physico-chemical treatment plant for sewage generated from water cleaning of usable surfaces of railway transport rolling stock, mainly of classes: G, H and T according to the International Union of Railways classification [14]. Samples for the research were collected after seven days of gravity settling of sludges on the sets of open sack filters, counting from the moment of pressing the last volume of post-sedimentary sludge. Differences in pH of filtrates recorded every day in the time of sludges dewatering are given in part of basic characteristics of the source of primary sludges generation and sampling of this stage of the work.

An interesting and useful criterion for assessing the waste is the risk assessment code (RAC). RAC classification for 5-stage sequential Tessier's extraction was introduced by Perin et al. [21], whereas Sundaray et al. introduced this classification for standardized 3-stage sequential extraction BCR [19]. RAC methodological guidelines are used to determine the risk with reference to each metal contained in the waste. The risk assessment code is determined on the basis of the percentage of total heavy metals content in the exchangeable fraction and the one associated with carbonates. In the exchangeable fractions, metals are associated with a solid phase of the waste by different kind of weak bonds. Therefore, the higher the percentage of metal in these fractions, the greater the likelihood of its release from the solid phase of the waste to the adjacent water phase having direct physical contact with it. In accordance with RAC classification, if a sum of two fractions F1+F2 (in 5-stage extraction) or if the content of F1 (in BCR extraction) is less than 1%, then the sludge does not constitute a threat (NR) carrying the risk (I) for the aquatic environment by the individual metal. When the total percentage of metal in the fraction F1 or in the sum of the fractions F1+F2 is, respectively: 1-10, 11-30, 31-50%, and more than 50%, it means, respectively: low (LR) risk (II), moderate (MR) risk (III), high (HR) risk (IV) and very high (VHR) risk (V). It is suggested that basing on the criterion defined in such way, you can estimate the easiness of introducing the metal into the food chain [21-25].

Analysing fractional composition of heavy metals in the post-sedimentary primary sludge, you can notice (Table 2 and Fig. 1) that in case of Zn, the labile fractions, including exchangeable, carbonate, reduction and organic ones, are quantitatively similar to the contents of a stable residual fraction F5, the share of which varies between 40 to 50%. It can be assumed that the analytically evaluated primary deposits are characterised by a moderate risk (MR 11-30%) for aquatic environment due to the recorded concentration level of mobile forms of Ni, Zn and Pb (the exceptions are two sludge samples with reference to lead: B1 and C2, of low risk (LR)). The nature of low risk (LR 1-10%) is

characteristic of “non-anhydrous” samples of sludge in relation to Cu, with the exception of sample A1 of moderate character. Moderate risk (MR) and moderate likelihood of introducing metals into the food chain concerns 70% (25 of 36) of the analysed samples of sludge and a low risk: 30% (11 analysed samples of 36 in total). The sludge samples of slightly acidic pH 6.4 indicate the moderate nature of risk for the aquatic environment concerning Ni, Pb and Zn and low nature of risk in relation to Cu. This can be interpreted by higher availability of mobile metals forms in more acidic pH, which results in a higher level of their extraction.

To assess the potential toxicity of individual metals, it is worth considering the test results for samples with pH = 6.4 which is the nearest to pH found in TCLP method. The concentrations of mobile metals forms released in the exchangeable and carbonate fractions are comparable with the concentrations determined in accordance with TCLP procedure with acidic values of pH. According to a broad group of authors, to estimate the potential risk of toxicological wastewaters or sludges, the number of metals bound in mobile fractions, i.e. the sum of exchangeable fraction and carbonate one, instead of the total contents of metals [21, 26-30] are taken into account.

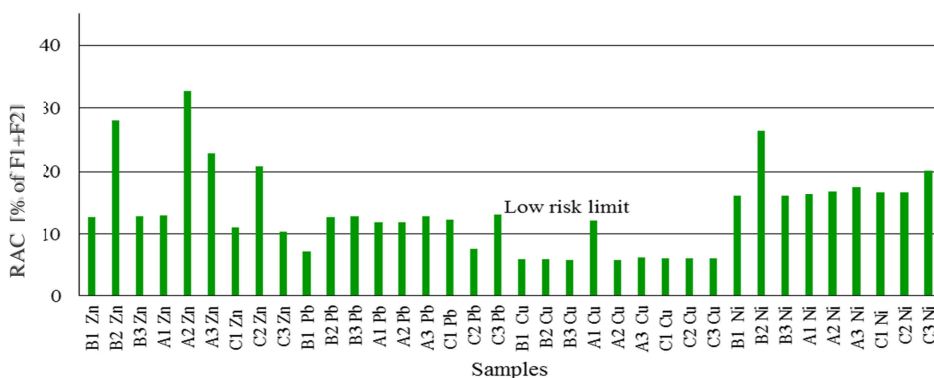


Fig. 1. Comparison of the risk assessment code (RAC) determined in relation to Cu, Ni, Pb and Zn for the gravitationally dewatered samples of post-sedimentary primary sludge from the first stage treatment of wastewaters generated as a result of water cleaning of rail freight cars, mainly of: G, H and T classes; where: indexes A-C indicate the groups of sludge samples taken in consecutive months from the sludge dewatering stage with simultaneous registration of pH values and pH of filtrates were at the level, respectively for: A - 6.4 ± 0.5 , B - 7.2 ± 0.5 and C - 7.3 ± 0.6

Exemplary results of leaching Cu, Ni, Pb and Zn from gravitationally dewatered post-sedimentary primary sludge, obtained after the application of TCLP procedure, is set in Table 3. The highest concentrations of all metals were leached for sediments with pH 6.4 that were, respectively for Pb and Zn, at levels: 0.041-0.13 and 0.54-0.99 mg/dm³, whereas in case of Cu and Ni at the same pH of leaching, the concentration limits were the following: 0.05-0.93 and 0.60-0.67 mg/dm³.

In accordance with US EPA, the leaching limit value has been defined only for lead, on the basis of which a nature of waste toxicity is determined. For this metal, the concentration limit is set at the level of 5 mg/dm³ [17]. In case of post-sedimentary deposits

from the first stage of wastewater treatment, an incidental value of leached lead concentration at the level of 6 mg/dm^3 was determined in a separated “non-anhydrous” additional sample during the last month of this research. The additional procedure was applied due to the found out incidentally increased concentration of this metal in the raw sewage which was at the level of 1.06 mg/dm^3 . Considering a final value of Pb concentration from the TCLP test for assessment, it was assumed that the incidental cases of unusual short-term concentrations for random sampling test specimens cannot be taken into account for assessing the final value of leachability of representative samples for the whole mass of the waste. Therefore, in previous months (groups of samples marked with indices A and B), no concentrations of leached Pb above the assumed criterion threshold values were found and Pb concentrations in the influent raw sewages were recorded at definitely lower levels.

Table 3

Recorded concentrations of leachable pools of metals [mg/dm^3] after applying TCLP procedure for “non-anhydrous” samples of gravitationally dewatered post-sedimentary primary sludge of the wastewater generated in the installation of rail freight cars wash

Samples (pH)	TCLP [mg/dm^3]			
	Zn	Pb	Cu	Ni
B1 (7.2)	0.33	ND	0.109	0.041
B2 (7.1)	0.53	0.029	0.18	0.061
B3 (7.3)	0.062	0.008	0.095	0.047
A1 (6.4)	0.54	0.041	0.1	0.6
A2 (6.5)	0.76	0.089	0.05	0.61
A3 (6.4)	0.99	0.13	0.93	0.67
C1 (7.2)	0.71	0.082	0.076	0.049
C2 (7.3)	0.061	ND	0.107	0.053
C3 (7.3)	0.58	0.17 (6.0) ^{a)}	0.006	0.067

^{a)} This incidental value was determined for a sample of gravitationally dewatered sludge from isolated batch of raw wastewaters, in which Pb concentration was determined at the incidentally high level of 1.06 mg/dm^3

The post-sedimentary primary sludges from the first stage wastewater treatment may be classified as non-toxic, as the limit value of 5 mg/dm^3 of leached lead was not exceeded. Therefore, in accordance with the adopted criterion, the primary sludge may be qualified as non-toxic for the environment, taking into account the range of TCLP assessment proposed by the US EPA [17].

Conclusions

Gravitationally dewatered post-sedimentary sludges generated as a result of the pretreatment of effluents from water cleaning of usable surfaces of railway transport rolling stock transport are in particular characterised by:

- irregularity of leached quantities in accordance with the TCLP test procedure concerning such metals as: the Cu, Ni, Pb and Zn and a variable fraction of these metals pools determined as a result of conducting a sequential extraction procedure in accordance with the methods set out by Tessier,
- low-risk (LR) regarding Cu,
- moderate risk (MR) in case of Zn, Pb and Ni.

Analysed deposits may be classified as non-toxic waste with reference to Pb and Zn, Cu, Ni (which are unlimited) in accordance with the TCLP criteria of USEPA.

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OCENA OSADÓW Z OCZYSZCZANIA ŚCIEKÓW Z MYJNI KOLEJOWYCH WAGONÓW. OSADY WSTĘPNE

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Abstrakt: Przedstawiono wyniki oceny osadów posedymentacyjnych generowanych w warunkach pełnej skali technologicznej na instalacji do podczyszczania ścieków powstających w wyniku stosowania wodnego oczyszczania powierzchni użytkowej kolejowych środków transportu towarowego, głównie klas G, H i T według typologii International Union of Railways. Osady wydzielano w zbiorniku magazynująco-uśredniającym, będącym pierwszym węzłem procesowym instalacji podczyszczania, do której napływały ścieki surowe. Z uwagi na znaczące zróżnicowanie ładunku zanieczyszczeń kierowanych do tej objętości również osady charakteryzowały się istotną niejednorodnością. Zaprezentowano wyniki z przeprowadzonej procedury wymywalności TCLP dla wytypowanych próbek oraz przedstawiono ocenę ryzyka, stosując kod RAC na podstawie analizy składu

frakcyjnego wytypowanych metali ciężkich, takich jak Cu, Ni, Pb i Zn. Stwierdzono, że odwodnione grawitacyjnie osady posedymentacyjne, generowane w okresie losowo wytypowanych trzech miesięcy eksploatacji instalacji, wykazują niskie ryzyko (LR) względem Cu oraz umiarkowane (MR) względem Ni, Pb i Zn. Zgodnie z kryteriami TCLP, osad wstępny, będący efektem przetrzymania surowych ścieków i sedymentacji z nich frakcji zdyspergowanych, sklasyfikowano jako odpad nietoksyczny.

Słowa kluczowe: ścieki z myjni wagonów towarowych, osady posedymentacyjne, test TCLP, skład frakcyjny metali ciężkich w osadach, kod oceny ryzyka (RAC)