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WASTEWATERS TREATMENT FROM RAIL FREIGHT CAR WASH. ASSESSMENT OF PHYSICO-CHEMICAL TREATED SLUDGES

OCZYSZCZANIE ŚCIEKÓW Z MYJNI WAGONÓW TOWAROWYCH. OCENA OSADÓW PO FIZYKO-CHEMICZNYM OCZYSZCZANIU

Abstract: The process of physico-chemical pretreatment of wastewaters produced in the rail freight car wash was carried out under flow conditions in two-chamber reactor of accelator type with a final fine purification on multi-layer gravel filter. The post-processing sludge were generated as a result of the use of coagulation and flocculation and, to a minimum degree, from washings formed due to a periodic backwash of gravel filters. This article presents the results concerning assessment of gravitationally dewatered post-coagulation sludge and sludge from backwashing of gravel filters, released after sedimentation, and dewatered mixture of these two types of sludge. These all precipitates were subject to leaching with the use of TCLP procedure and risk assessment based on the analysis of fractional composition of selected heavy metals. It was found that sludge from wastewater treatment after the use of the two-stage acid-alkaline (PIX[®] 116 - SAX[®] 18) or alkaline-acid coagulation (SAX[®] 18 - PAX[®] 18) with a final flocculation and phase separation in a flow type accelator are characterised by a distinctly lower leachability levels of heavy metals than in case of post-sedimentary primary sludge and they manifest low risk considering Cu, Ni, Pb and Zn determined by the adopted level of risk assessment code (RAC). According to the criteria adopted for TCLP classification, the analysed sludge are neither toxic nor hazardous waste.

Keywords: treatment of wastewaters from railway freight car wash, sludge after coagulation, sludge from gravel filter backwashing, TCLP test, fractional composition of metals in sludge, risk assessment code (RAC)

Introduction

Water cleaning of usable surfaces of rail freight cars of class E, F, G, H, K, L, R and T in accordance with the International Union of Railways classification creates significant quantities of wastewaters that are predominantly loaded with the specific and rarely repeatable levels of pollutants [1]. The low-loaded wastewaters, with a rational use of water, may be effectively pretreated with physico-chemical methods and returned to be reused in the cleaning processes of railway transport rolling stock [2, 3]. The size and composition of the pollutants load depend, among other things, on physical state and chemical composition of residues after transported goods and their fineness, sealing of different types of packaging used to secure the transported goods etc. [4, 5]. In raw sewage, there can also be microbiological, mycological contamination and other forms of biologically active organisms [6-9]. Moreover, incidentally or periodically heavy metals in various speciation forms may become a significant load in contamination pools generated in effluents [10].

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Bio-activity and eco-toxicity of heavy metals primarily depend on their fractional speciation [11-13]. Sequential extraction is a group of known and widely used methods to determine fractions of metals in different environmental components and other matrices containing these contaminants. A method that uses Tessier's procedure, enables an interesting risk estimation of speciation forms by dividing them into five different fractions on the basis of a criterion linked to their leachability with the use of various solvents revealing different activity and ionic strength. For example, the pools of metal marked and classified as exchangeable and carbonate forms are easily released under acidic environmental conditions. This fact causes a considerable interest in search for different forms of relationships between the results obtained by TCLP methods and sequential extraction for different matrices, e.g.: soil ones [14], ashes from the incineration of medical wastes [15], residues from the incineration of municipal solid wastes [16], residues from metallurgical leaching of zinc [17] or waste paints from protective covering of bridge structures [18].

The aim of this study was to assess the risk on the basis of the analysis of fractional composition of selected heavy metals and (TCLP) leaching tests concerning mixed post-processing sludge (after-coagulation ones, from backwashing of gravel filters) generated as the result of physico-chemical pretreatment of water used for surface cleaning of railway cars of classes G, H and T for the post part, according to the International Union of Railways classification [1]. The research focused on the analysis of fractional composition of such heavy metals as Cu, Ni, Pb and Zn, because their presence was found in the influent raw wastewaters during the randomly selected three months of operation of the wastewaters pretreatment plant. The results obtained using TCLP method with values assigned to the risk assessment code (RAC) were also compared in this paper.

Experimental part

Basic technical characteristics of physico-chemical pretreatment installation

The post-processing sludge used for the analyses were sampled from the physico-chemical wastewater pretreatment plant with daily capacity up to 50 m³/day [19]. It was designed for water cleaning of rail freight cars of class E, F, G, H, K, L, R and T in accordance with the International Union of Railways classification [1]. Raw sewage originating from washing the surface of the railway rolling stock of freight type were gravitationally drained to a retention-averaging tank, to its sedimentary-settling section, where they were kept, the result of which were post-processing primary sludge assessed in the first part of this study. Then, the sludge was directed to the flow installation for physico-chemical pretreatment of accelerator type, where post-coagulation sludge (SC) were generated as a result of metering the 1st-stage coagulant and then the 2nd-stage coagulant; the sludge were accumulated gravitationally in sediment pockets of sedimentary zone of the accelerator. This part presents the results for sludge generated after applying the associated acid-alkaline coagulation with the use of a system coagulants of Kemira Kemipol Sp. z o.o. class [20], respectively: PIX[®] 116 - SAX[®] 18 (acidic ferric coagulant - alkaline aluminium coagulant) or alkaline-acidic ones, respectively: SAX[®] 18 - PAX[®] 18 (alkaline aluminium coagulant - acidic ferric coagulant) (Table 1). Thickening of dispersed precipitated fractions was carried out by means of 0.3% flocculant solution (aqueous solution of FLOPAM[™] FO

4800 SNF Floerger S.A.S. ZAC de Milieux). After the sedimentation phase, cleared pretreated sewage was directed onto the process unit of open, multilayer gravel gravity filter, on which periodic backwashing was conducted, resulting in generation of backwash sludge marked with index SG (Table 1). The mentioned above streams of post-processing sludge were periodically transported using sludge pumps onto the drainage system equipped with open gravity bag filters, where a concentration of solid fractions was performed under conditions of gravitatively forced filtration. The application of such a method of filtration enabled to isolate individual types of sludge after coagulation on separated units of their gravity drainage. The separated sludge were marked with indexes in further parts of this text as follows:

- a) post-coagulation sludge obtained using system PIX[®] 116 - SAX[®] 18 (SC_(PIX[®] 116 - SAX[®] 18)),
- b) post-coagulation sludge obtained using system SAX[®] 18 - PAX[®] 18 (SC_(SAX[®] 18 - PAX[®] 18)),
- c) sludge from backwashing the gravel filter (SG),
- d) mixed sludge (MS) containing post-coagulation sludge and gravel filter backwash sludge.

Short characteristics of the place of post-processing deposits generation and sampling

Post-coagulation sludge of classes SC_(PIX[®] 116 - SAX[®] 18), SC_(SAX[®] 18 - PAX[®] 18) and mixed ones (MS) originating from coagulation systems PIX[®] 116 - SAX[®] 18 and SAX[®] 18 - PAX[®] 18 with the participation of sludge from gravel filter backwash (SG) without specifying the percentage fraction of them, accumulating in precipitate pockets of sedimentary-depositional zone of the accelator were periodically transported using a sludge pump onto the unit of gravity drainage of them, consisting of open bag filters. Such technical solution of the filtration enabled to particular types of sludge to be dewatered. After seven-day period of gravity drainage (counting from the moment that the last batch of sludge was input onto the filtration unit), samples for further analyses were collected and the results obtained are summarized in Table 1. The pH of the individual filtrates also measured during the final, seven-day drainage was registered at a stable level and was the following for the individual types of sludge:

- a) SC1 and SC2 (from coagulation with system PIX[®] 116 - SAX[®] 18) pH_{SC1} = 7.7±0.3 and pH_{SC2} = 8.2±0.2,
- b) SC3 (from coagulation with system SAX[®] 18 - PAX[®] 18) pH_{SC3} = 8.4±0.3,
- c) SG1 (post-filtering sludge from filter backwash SC1) pH_{SG1} = 7.9±0.1,
- d) SG2 (post-filtering sludge from filter backwash SC2) pH_{SG2} = 8.3±0.1,
- e) SG3 (post-filtering sludge from filter backwash SC3) pH_{SG3} = 8.5±0.1,
- f) SM1, SM2 and SM3 (mixed post-coagulation and post-filtration sludge) pH_{SM1} = 8.8±0.1, pH_{SM2} = 8.2±0.2 and pH_{SM3} = 8.4±0.1.

TCLP leaching tests procedure

The assessment of wastes generated after the process of their gravity drainage was performed by determining leachable forms of metals (Cu, Ni, Pb and Zn) in accordance with the TCLP methods (Toxicological Characteristic Leaching Procedure) in compliance

with US EPA procedure, Method 1311 [21], for 100.0 g of “non-anhydrous” sludge in two replications with the use of Jobin Yvon EMISSION JY 38S emission spectrometer ICP-OES and standard ISO 11885:2007 [22] for the determination of metals in the filtered extracts.

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

Post-processing sludge, including the ones after coagulation (SC1-SC3), from the backwash of gravel filter (SG1-SG3) and mixed sludge (MS1-MS3) were subject to sequential extraction consisting in determining five fractions in accordance with basic Tessier's procedure specified in detailed description in [23] and in the first part of this study. 100.0 g of the sludge of the "non-anhydrous" sample in two replications was applied for the extraction.

Results and discussion

In recent decades, there have been developed different methods of a simple one- and multi-stage sequential extraction [23, 24]. The use of sequential extraction in accordance with the proposal of Tessier et al. [23] provides the possibility to obtain information concerning potential mobility and bioavailability of heavy metals in a hypothetical environment. The data obtained from the use of fractionation procedures, provide i.a. the information on speciation of heavy metals and their origin, occurrence, bioavailability, mobility and a possible pool for migration [25, 26]. Table 1 shows the results of 5-stage sequential extraction (acc. to Tessier), which were obtained for the samples of post-processing sludge: after coagulation (SC1-SC3) and after backwashing of gravel filter (SG1-SG3) and the mixed sludge (SM1-SM3). The sludge were generated on the full scale installation in the randomly selected time period of three months of continuous operation and the application of associated acid-alkaline coagulation using the PIX[®] 116 - SAX[®] 18 system or of alkaline-acid coagulation using the SAX[®] 18 - PAX[®] 18 system. The determined fractional composition of the analysed metals in sludge indicates an evident qualitative growth in fractional stability of post-processing sludge with reference to fractional composition determined in raw sludge separated as the result of sedimentation (characterised in the first part of this study). The use of associated coagulation especially affects the increase in a quantitative share of residual fraction F5 for nickel and lead. Those post-processing sludge may be classified as not posing risk considering Pb for samples after coagulation (SC) and mixed (SM) sludge. Sludge samples from backwashing gravel filter (SG) for lead are characterised by a high content of residual fraction (approx. 62%) and a relatively considerable content (1-5.1%) of mobile - carbonate fraction F2 which affects the qualification of sludge in the category presenting low risk to the environment. Other analysed samples feature a low risk considering Cu, Ni and Zn. A dominant speciation fraction in the tested post-processing sludge was residual F5 for Cu, Ni, Pb and Zn. In terms of chemical composition and structure, you can interpret the size of the F5 pool as a permanently composed mixture (mainly preferred in terms of pH) of sparingly soluble hydroxide pools of the following type: Cu(OH)_{2(s)}, Ni(OH)_{2(s)}, Pb(OH)_{2(s)} and Zn(OH)_{2(s)} in quantitatively dominant vicinity of solid conglomerates generated as a result of precipitation of iron and aluminum forms.

Table 1

Example of fractional composition [%] of selected heavy metals, determined according to Tessier's procedure in the following dewatered sludge: sludge after coagulation (SC), sludge from backwashing of gravel filter (SG) and mixed sludge (SM) generated as a result of the physico-chemical treatment of wastewaters from the rail freight car wash, and the risk assessment code (RAC) adopted for the individual types of sludge ^{a-c)}

Metals	Sample (kind of sludges) ^{d)}	F1	F2	F3	F4	F5	ΣF1-F2	RAC ^{e)}
Zn	SC1(PIX® 116 - SAX® 18)	1.3	0.8	9.1	19.5	69.3	2.1	LR
	SC2(PIX® 116 - SAX® 18)	1.2	0.8	12.3	22.4	63.3	2.0	LR
	SC3(SAX® 18 - PAX® 18)	0.6	0.6	15.2	16.3	67.3	1.2	LR
	SG1(PIX® 116 - SAX® 18)	0.3	1.3	18.1	9.1	71.5	1.3	LR
	SG2(PIX® 116 - SAX® 18)		0.9	15.5	11.2	72.1	1.2	LR
	SG3(SAX® 18 - PAX® 18)		1.1	19.2	10.3	69.4	1.1	LR
	SM1	1.2	1.4	13.6	14.1	70.9	1.4	LR
	SM2		1.1	11.4	18.8	68.7	1.1	LR
	SM3		1.2	12.5	14.1	72.2	1.2	LR
Pb	SC1(PIX® 116 - SAX® 18)		5.1 ^{o)}	2.5	29.5	62.9	5.1	LR
	SC2(PIX® 116 - SAX® 18)		3.2	2.1	36.6	58.1	3.2	LR
	SC3(SAX® 18 - PAX® 18)		1.3	2.3	34.3	62.1	1.0	LR
	SG1(PIX® 116 - SAX® 18)			7.4	28.5	64.1		NR
	SG2(PIX® 116 - SAX® 18)			9.2	29.1	61.7		NR
	SG3(SAX® 18 - PAX® 18)			8.5	28.3	63.2		NR
	SM1				38.3	61.7		NR
	SM2				37.6	62.4		NR
	SM3				39.1	60.9		NR
Cu	SC1(PIX® 116 - SAX® 18)	0.8	1.4		13.1	85.5	1.4	LR
	SC2(PIX® 116 - SAX® 18)		0.9		13.2	85.9	0.9	NR
	SC3(SAX® 18 - PAX® 18)				8.1	91.1	0.8	NR
	SG1(PIX® 116 - SAX® 18)		1.2		16.7	82.1	1.2	LR
	SG2(PIX® 116 - SAX® 18)		1.1		17.2	81.7	1.1	LR
	SG3(SAX® 18 - PAX® 18)				19.6	80.4		NR
	SM1		0.5		15.1	84.4	0.5	NR
	SM2		0.8		13.7	85.5	0.8	NR
	SM3				11.8	88.2		NR
Ni	SC1(PIX® 116 - SAX® 18)	1.1	1.3	7.4	12.1	79.2	1.3	LR
	SC2(PIX® 116 - SAX® 18)			8.1	14.1	76.7	1.1	LR
	SC3(SAX® 18 - PAX® 18)		1.1	6.9	12.9	79.1	1.1	LR
	SG1(PIX® 116 - SAX® 18)		1.7	7.5	14.1	76.7	1.7	LR
	SG2(PIX® 116 - SAX® 18)			6.5	16.3	77.2		NR
	SG3(SAX® 18 - PAX® 18)		1.1	7.7	15.1	76.1	1.1	LR
	SM1	0.9		7.8	11.1	80.2	0.9	NR
	SM2		1.4	7.1	12.4	79.1	1.4	LR
	SM3		1.1	7.3	13.2	78.2	1.1	LR

^{a)} the process of coagulation in the accelerator was conducted with the control of the reagent uniform mixing using pH-meters process at the inlet (pH1) and outlet (pH2) of tube reactor installed at the upstream of the flow chamber of high speed mixing of the accelerator, setting the dose of coagulant PIX® 116 in metering mode "up to pH" with reference to the algorithm of pH-meter readouts (pH1), and the dose of alkaline coagulant SAX® 18 according to the dose of coagulant PIX® 116 in preset relations while meeting the conversion relationship of pH, respectively: $pH_{(PIX\ 116)} = 1.2 \cdot pH_{(SAX\ 18)}$, but with keeping the preset value of upper limit after neutralization at pH = 8.8

^{b)} analogous to the one given in ^{a)} metering procedure was adopted for coagulation system SAX® 18 - PAX® 18

^{c)} retention time of wastewaters treated by sedimentation (total flow time) in processing chambers of slow and fast mixing of the accelerator, established for the procedures of this series of experiments at the level of 90-95 minutes

^{d)} adopted indices SC1-SC3, SG1-SG3 and SM1-SM3 mean, respectively, sludges after coagulation (after coagulation using the following systems: PIX® 116 - SAX® 18 or SAX® 18 - PAX® 18), from the backwash of gravel filter, and mixed sludge

^{e)} adopted indices mean, respectively: NR - no risk and LR - low risk (Table 2)

These structures can be presented by the simplified stoichiometric notation (e.g.: $x_{(1)}\text{Fe}(\text{OH})_{3(s)} \cdot y_{(1)}\text{Al}(\text{OH})_{3(s)} \cdot z_{(1)}\text{H}_2\text{O}$), or aluminoferric (e.g.: $x_{(2)}\text{Al}(\text{OH})_{3(s)} \cdot y_{(2)}\text{Fe}(\text{OH})_{3(s)} \cdot z_{(2)}\text{H}_2\text{O}$), where: the value of coefficients $x_{(1)}$, $x_{(2)}$, $y_{(1)}$ and $y_{(2)}$ depends on a dose of coagulants and a final pH value of the post-processing sludge, $z_{(1)}$, $z_{(2)}$ - the number of bounded water molecules (e.g. constitutional and/or crystallisation water and/or water in other forms) [27].

Speciation forms determined by fractional analysis are essential to estimate the potential mobility and toxicity of heavy metals identified in the tested post-processing sludge. Depending on the further proceedings, wastes may involve even the risk of releasing the metals into the environment by a spontaneous run of natural or anthropogenic processes [28]. The quantitative distribution in different fractional pools, determined with the use of sequential extraction in accordance with Tessier's or BCR procedures, provides an estimate for their availability which, in turn, affects the risk associated with the potential migration of metals into the aquatic environment from the post-processing wastes under discussion. Historically, the RAC classification for 5-stage sequential Tessier's extraction was introduced by Perin et al. [29], whereas Sundaray et al. introduced this classification for standardized 3-stage BCR sequential extraction [13], which is presented in Table 2 in a form of indices.

Table 2

Scale according to risk assessment code criteria (RAC)

Risk category	Risk level (adopted index)	% of metal in fraction F1 ^{a)} or the sum of fraction F1+F2 ^{b)}
I	No risk (NR)	< 1
II	Low risk (LR)	1-10
III	Medium risk (MR)	11-30
IV	High risk (HR)	31-50
V	Very high risk (VHR)	> 50

^{a)} soluble in acid/exchangeable in BCR procedure [13]; ^{b)} in Tessier's procedure [29].

Table 3

Exemplary concentrations of the leachable metals on the basis of TCLP procedure for sludge after coagulation (SC1-SC3), sludge from the backwash of gravel filter (SG1-SG3) and mixed sludge (SM1-SM3) generated as a result of physico-chemical treatment of wastewaters from the rail freight car wash

Samples (kind of sludge)	TCLP test results [mg/dm ³] ^{a)}			
	Zn	Pb	Cu	Ni
SC1(PIX [®] 116 - SAX [®] 18)	0.31	0.065	0.1	0.017
SC2(PIX [®] 116 - SAX [®] 18)	0.25	0.03	0.067	0.038
SC3(SAX [®] 18 - PAX [®] 18)	0.062	0.008	0.059	0.013
SG1(PIX [®] 116 - SAX [®] 18)	0.43	ND	0.11	0.089
SG2(PIX [®] 116 - SAX [®] 18)	0.15	ND	0.1	ND
SG3(SAX [®] 18 - PAX [®] 18)	0.17	ND	ND	0.081
SM1	0.23	ND	0.054	0.008
SM2	0.55	0.01	0.079	0.036
SM3	0.25	ND	ND	0.009

^{a)} ND - below the method determination threshold for Zn, Pb, Cu and Ni at the level of 7 µg/dm³

However, the risk assessment code (RAC) shows the potential of possible availability to migrate on the basis of the percentage of the metal content in the exchangeable and

carbonate fractions [29]. These fractions are considered to be weakly bounded chemically that they are able to migrate into aqueous phase, and in this way they may constitute a pool that is directly available for biocenoses of aquatic ecosystems [30, 31]. Therefore, the RAC can be treated as an analytical scale which can be used to evaluate the potential mobility and at the same time the potential risk based on the estimated percentage of metal associated with both exchangeable and carbonate fractions, determined quantitatively for the sediments [24, 25, 32, 33]. According to RAC criteria, deposits may be classified as not posing or posing a threat to a hypothetical ecosystem [25, 28, 30].

In order to assess the potential toxicological risk of the wastes or sludge caused by the presence of heavy metals, the quantity of metals bonded in mobile fractions, i.e. the total of exchangeable and carbonate fraction are taken into account more frequently than the total contents of metals, which for the presented waste are listed in Table 3 [17, 29, 35-38].

The limit leachability value for Pb in accordance with US EPA was determined at the level of 5.0 mg/dm^3 and on this basis the nature of the waste toxicity is determined (for Cu, Ni and Zn, no limit values were determined). In all samples of the analysed groups of sludge: SC1-SC3, SG1-SG3 and SM1-SM3 no exceedance of limit value for leachable Pb, determining toxicity in accordance with US EPA criteria, was analytically found. It is an argument for the effective physico-chemical treatment of wastewaters and obtaining post-processing sludge with a low leachability level and it also suggests to consider the further practical use of dewatered sludge. The listed results include the assessment of post-processing sludge generated over a short, three-month period of operation of the installation for physico-chemical pretreatment of wastewaters and they are a part of a certain level of values recorded in real conditions. In that period, the pretreated wastewaters were generated as a result of water cleaning of usable surfaces of transport railway rolling stock, mainly of classes: G, H and T according to the International Union of Railways classification [1]. Therefore, the results obtained might be the derivatives of the composition of residues left by the transported commodities for a category referred to by the International Union of Railways classification, only from this operational period of the rail freight car wash. Therefore, the presented here results should be treated as an approximation of the inadequately described in literature problem of assessment of post-processing sludges generated as a result of physico-chemical treatment of effluents from water cleaning of the surfaces of freight type railway rolling stock.

Conclusions

Post-processing sludge generated from physico-chemical pretreatment of wastewaters from the water cleaning of freight railway rolling stock surfaces are particularly characterised by:

- a) comparable values of the results obtained in case of TCLP leaching procedure and comparable fractional composition of the selected heavy metals;
- b) prevailing content of stable residual fraction determined in accordance with Tessier's procedure for each type of sludge;
- c) non-toxic nature according to the criteria obtained from TCLP procedure.

Mixed streams of post-processing sludge (MS) might be classified in accordance with the risk assessment code, as not posing any risk considering Cu and Pb, and as carrying low risk for aquatic ecosystems considering Ni and Zn.

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References

- [1] Railway Technical Publications, UIC Code: Catalogue of UIC Leaflets, 2015. www.uic.org.
- [2] Etchepare R, Zaneti R, Azevedo A, Rubio J. Application of flocculation-flotation followed by ozonation in vehicle wash wastewater treatment/disinfection and water reclamation. *Desalination Water Treat.* 2015;56(7):1728-1736. DOI: 10.1080/19443994.2014.951971.
- [3] Rubio J, Zaneti RN. Treatment of washrack wastewater with water recycling by advanced flocculation-column flotation. *Desalination Water Treat.* 2009;8(1-3):146-153. DOI: 10.5004/dwt.2009.679.
- [4] Anderson P, Cunningham CJ, Barry DA. Efficiency and potential environmental impacts of different cleaning agents used on contaminated railway ballast. *Land Contam Reclamat.* 2002;10(2):71-77. DOI: 10.2462/09670513.609.
- [5] Anderson P, Cunningham CJ, Barry DA. Gravimetric analysis of organic contamination in railway ballast. *Land Contam Reclamat.* 2000;8(2):71-74. DOI: 10.2462/09670513.559.
- [6] Kaptsov VA. Deontological issues in railway hygiene. *Gigiena i sanitariia.* 2015;94(3):40-43. <http://www.medlit.ru/en/journal/1297> or <http://europepmc.org/abstract/med/26302557>.
- [7] Krivulia SD, Kaptsov VA, Korotich LP. Real problems of conducting social-hygienic monitoring on railroads. *Gigiena i sanitariia.* 2003;2:65-67. <http://europepmc.org/abstract/med/12861701>.
- [8] Kaptsov VA, Pankova VB, Elizarov BB, Mezentsev AP, Komleva EA. Hygienic optimization of the use of chemical protective means on railway transport. *Gigiena i sanitariia.* 2004;2:37-40. <http://europepmc.org/abstract/med/15141627>.
- [9] Malomo O. Future for food technology in Nigeria. *Int J Current Microbiol Appl Sci.* 2015;4(2):1067-1076. <http://www.ijcmas.com/vol-4-2/Olu.%20Malomo.pdf>.
- [10] Wasay SA, Tokunaga S, Haron MJ, Uchiumi A, Nagahiro T, Puri BK. Removal of Cu, Ir, Pd and Os ions in the form of chelates from wastewaters by naphthalene. *J Environ Sci Health A - Tox Hazard Subst Environ Eng.* 1994;29(9):1817-1828. DOI: 10.1080/10934529409376149.
- [11] Quevauviller P. Operationally defined extraction procedures for soil and sediment analysis I. Standardization. *TrAC - Trend Anal Chem.* 1998;17(5):289-298. DOI: 10.1016/S0165-9936(97)00119-2.
- [12] Chen M, Li X, Yang Q, Zeng G, Zhang Y, Liao D, et al. Total concentrations and speciation of heavy metals in municipal sludge from Changsha, Zhuzhou and Xiangtan in middle-south region of China. *J Hazard Mater.* 2008;160(2-3):324-329. DOI: 10.1016/j.jhazmat.2008.03.036.
- [13] Sundaray SK, Nayak BB, Lin S, Bhatta D. Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments - a case study: Mahanadi basin, India. *J Hazard Mater.* 2011;186:1837-1846. DOI: 10.1016/j.jhazmat.2010.12.081.
- [14] Wu F, Liu Y, Xia Y, Shen Z, Chen Y. Copper contamination of soils and vegetables in the vicinity of Jiuhuashan copper mine, China. *Environ Earth Sci.* 2011;64(3):761-769. DOI: 10.1007/s12665-010-0897-4.
- [15] Xie Y, Zhu J. Leaching toxicity and heavy metal bioavailability of medical waste incineration fly ash. *J Mater Cycles Waste Manage.* 2013;15:440-448. DOI: 10.1007/s10163-013-0133-x.
- [16] Chiang KY, Tsai CC, Wang KS. Comparison of leaching characteristics of heavy metals in APC residue from an MSW incinerator using various extraction methods. *Waste Manage.* 2009;29(1):277-284. DOI: 10.1016/j.wasman.2008.04.006.

- [17] Sethurajan M, Huguenot D, Lens PNL, Horn HA, Figueiredo LHA, van Hullebusch ED. Fractionation and leachability of heavy metals from aged and recent Zn metallurgical leach residues from the Três Marias zinc plant (Minas Gerais, Brazil). *Environ Sci Pollut Res*. 2016;23:7504-7516. DOI: 10.1007/s11356-015-6014-1.
- [18] Shu Z, Axe L, Jahan K, Ramanujachary KV. Metal leaching from the bridge paint waste in the presence of steel grit. *Chemosphere*. 2015;119:1105-1112. DOI: 10.1016/j.chemosphere.2014.09.061.
- [19] <http://www.projprzemeko.pl/oczyszczanie-wod-obiegowych.html>.
- [20] <http://www.kemipol.com.pl/products>.
- [21] US EPA Method 1311. Toxicity characteristic leaching procedure (TCLP), 1992. <https://www.epa.gov/hw-sw846/sw-846-test-method-1311-toxicity-characteristic-leaching-procedure>.
- [22] ISO 11885:2007. Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). <https://www.iso.org/standard/36250.html>.
- [23] Tessier A, Campbel P, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem*. 1979;51(7):844-851. DOI: 10.1021/ac50043a017.
- [24] Ghrefat H, Yusuf N. Assessing Mn, Fe, Cu, Zn, and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. *Chemosphere*. 2006;65(11):2114-2121. DOI: 10.1016/j.chemosphere.2006.06.043.
- [25] López-Sánchez JF, Rubio R, Samitier C, Rauret G. Trace metal partitioning in marine sediments and sludges deposited off the coast of Barcelona (Spain). *Water Res*. 1996;30(1):153-159. DOI: 10.1016/0043-1354(95)00129-9.
- [26] Pérez-Cid B, Lavilla I, Bendicho C. Application of microwave extraction for partitioning of heavy metals in sewage sludge. *Anal Chim Acta*. 1999;378(1-3):201-210. PII: S0003-2670(98)00634-5.
- [27] Duan J, Gregory J. Coagulation by hydrolysing metal salts. *Adv Colloid Interface Sci*. 2003;100-102:475-502. PII: S0001-8686(02)00067-2.
- [28] Ghrefat H, Yusuf N. Assessing Mn, Fe, Cu, Zn, and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. *Chemosphere*. 2006;65(11):2114-2121. DOI: 10.1016/j.chemosphere.2006.06.043.
- [29] Perin G, Craboledda L, Lucchese M, Cirillo R, Dotta L, Zanetta ML. Heavy metal speciation in the sediments of northern Adriatic Sea. A new approach for environmental toxicity determination. In: Lakkas TD, editor. *Heavy Metals in the Environment*, vol. 2. Edinburg: CEP Consultants; 1985.
- [30] Pardo R, Barrado E, Perez L, Vega M. Determining and association of heavy metals in sediments of the Pisurgra river. *Water Res*. 1990;24(3):373-379. DOI: 10.1016/0043-1354(90)90016-Y.
- [31] Hseu ZY. Extractability and bioavailability of zinc over time in three tropical soils incubated with biosolids. *Chemosphere*. 2006;63(5):762-771. DOI: 10.1016/j.chemosphere.2005.08.014.
- [32] Jain CK. Metal fractionation study on bed sediments of River Yamuna, India. *Water Res*. 2004;38(3):569-578. DOI: 10.1016/j.watres.2003.10.042.
- [33] Karak T, Abollino O, Bhattacharyya P, Das KK, Paul RK. Fractionation and speciation of arsenic in three tea gardens soil profiles and distribution of As in different parts of tea plant (*Camellia sinensis* L.). *Chemosphere*. 2011;85(6):948-960. DOI: 10.1016/j.chemosphere.2011.06.061.
- [34] Ikem A, Adisa S. Runoff effect on eutrophic lake water quality and heavy metal distribution in recent littoral sediment. *Chemosphere*. 2011;82(2):259-267. DOI: 10.1016/j.chemosphere.2010.09.048.
- [35] Sakan S, Grzetić I, Dordević D. Distribution and fractionation of heavy metals in the Tisa (Tisza) river sediments. *Environ Sci Pollut Res*. 2007;14(4):229-236. DOI: 10.1065/espr2006.05.304.
- [36] Ntakirutimana T, Du G, Guo JS, Gao X, Huang L. Pollution and potential ecological risk assessment of heavy metals in a lake. *Pol J Environ Stud*. 2013;22(4):1129-1134. <http://www.pjoes.com/pdf/22.4/Pol.J.Enviro.Stud.Vol.22.No.4.1129-1134.pdf>.
- [37] Pan Y, Wu Z, Zhou J, Zhao J, Ruan X, Liu J, Qian G. Chemical characteristics and risk assessment of typical municipal solid waste incineration (MSWI) fly ash in China. *J Hazard Mater*. 2013;261:269-276. DOI: 10.1016/j.hazmat.2013.07.038.
- [38] Singh J, Lee BK. Reduction of environmental availability and ecological risk of heavy metals in automobile shredder residues. *Ecol Eng*. 2015;81:76-84. DOI: 10.1016/j.ecoleng.2015.04.036.

OCZYSZCZANIE ŚCIEKÓW Z MYJNI WAGONÓW TOWAROWYCH. OCENA OSADÓW PO FIZYKOCHEMICZNYM OCZYSZCZANIU

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Abstrakt: Proces fizykochemicznego podczyszczania ścieków wytwarzanych na myjni kolejowych wagonów towarowych był prowadzony w warunkach przepływowych na dwukomorowym reaktorze typu akcelerator z końcowym doczyszczaniem na wielowarstwowym filtrze żwirowym. Osady poprocesowe były generowane w wyniku zastosowania koagulacji i flokulacji oraz w minimalnym stopniu z wód popłucznych w wyniku stosowania okresowego, wstecznego płukania filtrów żwirowych. Przedstawiono wyniki oceny odwodnionych grawitacyjnie osadów pokoagulacyjnych i osadów z wstecznego płukania filtrów żwirowych wydzielanych na drodze sedimentacji oraz odwodnionej mieszaniny tych dwóch rodzajów osadów. Przedmiotowe osady poddano ługowaniu za pomocą procedury TCLP oraz ocenie ryzyka na podstawie analizy składu frakcyjnego wytypowanych metali ciężkich. Stwierdzono, że osady pochodzące z procesu oczyszczania po zastosowaniu dwustopniowej koagulacji kwaśno-alkalicznej (PIX[®] 116 - SAX[®] 18) lub alkaliczno-kwaśnej (SAX[®] 18 - PAX[®] 18) z końcową flokulacją i separacją faz na układzie przepływowym typu akcelerator charakteryzują się zdecydowanie niższymi poziomami wymywalności metali ciężkich niż wstępne osady posedymentacyjne oraz wykazują niskie ryzyko względem Cu, Ni, Pb i Zn określone przyjętym poziomem kodu oceny ryzyka (RAC). Według kryteriów przyjętych dla klasyfikacji TCLP, analizowane osady nie są odpadami toksycznymi i niebezpiecznymi.

Słowa kluczowe: oczyszczanie ścieków z myjni wagonów towarowych, osady pokoagulacyjne, osady z wstecznego płukania filtrów żwirowych, test TCLP, skład frakcyjny metali zawartych w osadach, kod oceny ryzyka (RAC)