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**CONSTRUCTION CHEMICALS PRODUCTION
WASTEWATERS TREATMENT.
PART 2. SLUDGE FROM TWO-STAGE PRETREATMENT
OCZYSZCZANIE ŚCIEKÓW Z PRODUKCJI CHEMII BUDOWLANEJ.
CZĘŚĆ 2. OSADY Z DWUSTOPNIOWEGO PODCZYSZCZANIA**

Abstract: The need for two-stage physicochemical pretreatment resulted out of necessity changes of the BOD₅/COD, COD(BOD₅)/TN, COD(BOD₅)/TP and TN/TP ratios on beneficial in streams directed at final treatment with biological methods. Hence also in pretreatment at the second stage was carried out with the use of oxidation or deep oxidation methods, which was reflected in the composition of sludge being subject to assessment in this part of research. Wastewaters came mainly from the line of different-tonnage producing fugal mass and sealing coatings, gypsum surfacers and putties, self-levelling compounds and grouts, paints for façades of concrete structures and interiors, cements and glazes, protective and decorative plasters. The first stage pretreatment on installations was being led applying coagulation methods based on the application of iron sulphate coagulants of PIX[®] category or the aluminium ones of ALS[®] category. At the second one - oxidation with the use of KMnO₄ or Fenton's system were applied. Sludge for the assessment were being allocated as a result of dewatering them on pressurized sets of chamber presses. For generated in this way sludge the TCLP (Toxicological Characteristic Leaching Procedure) procedure and the risk assessment with the use of risk assessment code (RAC) was made. It was found that dewatered by pressure mixed sludge present low risk (LR) in case of Cd, Cr, Cu, Ni, Pb and Zn and the moderate risk (MR) concerning Mn, in case of application of potassium permanganate at the second stage of pretreatment. In case of application of Fenton's system at the second stage of pretreatment, the mixed sludge presented low risk (LR) concerning all analysed heavy metals. In accordance with TCLP criteria, mixed sludge from two-stage physicochemical pretreatment of process wastewaters from manufacturing of the selected products of construction chemicals were classed as non-toxic wastes.

Keywords: construction chemicals manufacturing, process wastewaters, two-stage pretreatment, physicochemical pretreatment, sludge, TCLP procedure, risk assessment code (RAC)

Introduction

The necessity of double-stage physicochemical pretreatment of post-production effluents from manufacturing construction chemicals results from the need of their preliminary preparation before final biological treatment [1, 2]. After eliminating mainly the dispersed phases at the first stage, the second stage includes a treatment of soluble pollution load. Usually there are the oxidation or advanced oxidation processes to regulate basic indicative ratios: BOD₅/COD, COD(BOD₅)/TN, COD(BOD₅)/TP and TN/TP towards achieving the values that enable the biological decay using e.g. the methods of activated sludge in several variants of technical solutions [1, 3-6]. While manufacturing the construction chemicals, technological wastewater is generated during cleaning appliances and production surfaces. The wastewater contain two essential categories of pollution load: the contaminants of dispersed pool and the contaminants of dissolved pool [1, 2].

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The composition of pollution load and the size of several load pools in the effluents are generally determined by the nature and purpose of manufactured products [1, 2].

Wastewater pretreatment, single- and double-stage one, is applied according to the requirements outlined by a final recipient or in case of the use of final biological methods in the same production facility that generates the industrial wastewater. In literature described until now, the pretreatment of wastewater from the production of construction chemicals is carried out using coagulation methods, mostly by applying a single-stage coagulation with pH correction and final flocculation. The separation of precipitated phases is conducted using gravity thickening and/or on filtration units [1, 2]. Coagulation methods belong to relatively effective ways of eliminating the dispersed phases (colloids and suspensions) at the first, physicochemical stage of wastewater treatment. However, they do not allow to eliminate the loads of the following dissolved pools: COD and BOD₅ and the nitrogen ones (TN and AN), as well as to reduce effectively the general toxicity of the pretreated wastewater caused mainly by the residues of biocidal substances. This results in relatively low values of BOD₅ with reference to COD and the ratio BOD₅/COD, and to the other parameters (TN and TP) [7]. After the single-stage coagulation, it is not always possible to apply further, direct biological treatment due to the unfavourable values of the following relationships: BOD₅/COD, COD(BOD₅)/TN and COD(BOD₅)/TP in physicochemically pretreated wastewater, hence there is a need for additional pretreatment using oxidation or advanced oxidation processes (AOP) [3-6].

The aim was to estimate a risk on the basis of the analysis fractional composition of selected heavy metals and TCLP (Toxicological Characteristic Leaching Procedure) leachability tests of a mixture of post-processing sludge from two-stage physicochemical pretreatment of technological effluents. In the research, it was focused on the analysis of fractional contents of such heavy metals such as: Cd, Cr, Cu, Ni, Mn, Pb and Zn. As a part of this research, it was also compared the results obtained with TCLP method with the values determined for risk assessment code (RAC) for the sludge generated after applying KMnO₄ at the second stage of the wastewater pretreatment.

Experimental part

Basic characteristics of the place of post-processing sludge generation and sampling

Sludge from the first and second stage of physicochemical pretreatment were generated in the full technological scale installations, two-stage pretreatment of processing effluents of technical characteristics presented in Table 1 and in daily flow capacities up to 30 m³ (installation D) and up to 25 m³ (installation E) [7]. These installations were designed for the needs of mixed processing effluents from different tonnage production divisions of building industry chemicals, including the production of water-based paints and silicone plasters for the façades of concrete structures and interiors, protective and decorative plasters, gypsum surfacers and putties, as well as self-levelling compounds and sealing coats. The raw processing effluents of basic characteristics shown in Table 2 were flown down gravitationally to the first ground retention basin, in which their averaging was conducted with pumps and bypasses, and then the pretreatment was carried out according to the sequences given in Table 1. Sludge precipitated and thickened by flocculation after the

first and second stage, were pumped into a common vertical thickening tank and then, after metering additional doses of flocculant and thickening, onto the pressurized sets of plate and frame chamber filter presses. Pressure dewatered groups of sludge were marked for the individual installations of double-stage pretreatment with indices, respectively, shown in Table 3.

Table 1

Basic characteristics of double-stage wastewater pretreatment installations

No.	Installation	Installation setup and pretreatment method [7]
1	D	<p>The installation included:</p> <ol style="list-style-type: none"> a) the first stage: a coupled unit of vertical tube reactor with a central cylindrical-tapered processing reactor equipped with a low-speed frame agitator, stations metering the reagents which were the following coagulants: iron(III) sulphate based PIX[®] or aluminum based ALS[®] and 0.3 % aqueous solution of flocculant 8398 Optifloc Cytec Industrie Inc. Kemipol Sp z o.o.; b) the second stage: the cylindrical-tapered oxidation reactor fitted with a low-speed frame agitator, stations metering the reagents (30 % aqueous solution of H₂SO₄, 3.5 % aqueous solution of KMnO₄ and 30 % aqueous solution of NaOH). The dewatering set of post-processing sludge was common and included: a vertical thickening tank to which a flocculant was metered, and a pressurized chamber press. <p>The course of physicochemical pretreatment:</p> <ul style="list-style-type: none"> • the raw sludge averaged in the ground basin were pumped through the 1st stage cylindrical-tapered reactor directly onto the reactor with metering the acidic coagulant (PIX[®] 113 or PIX[®] 122 or ALS[®]) into the tube reactor in doses that enable the treatment environment obtaining a set value of the reaction at the level of pH = 7.8-8.5 under the conditions of circulation of the effluents within the volumes of these reactors; • the flocculation was conducted by metering 0.3 % solution of flocculant (8398 Optifloc Cytec Industrie Inc. Kemipol Sp z o.o.) directly onto the cylindrical-tapered reactor; • after sedimentary separation of the sludge phase from the over-sedimentary phase, the recent one was pumped onto the 2nd stage oxidation reactor to which 3.5 % aqueous solution of KMnO₄ was metered, previously acidifying the environment with 30 % aqueous solution of H₂SO₄ to obtain the reaction level within pH = 3.5-4.0; • after oxidation, the neutralization was made by metering 30 % solution of NaOH in doses to enable the reaction to achieve pH = 8.0-8.5; • the flocculation of dispersed phases was conducted by metering 0.3 % solution of flocculant (8398 Optifloc Cytec Industrie Inc. Kemipol Sp. z o.o.) directly onto the reactor; • thickened in the two stages of the pretreatment were discharged onto the vertical thickening tank equipped with a low-speed frame agitator, to which 0.3 % aqueous solution of flocculant (8398 Optifloc Cytec Industrie Inc. Kemipol Sp. z o.o.) was metered and then, after additional thickening by flocculation the sludge were supplied onto the pressurized dewatering set.
2	E	<p>The installation included:</p> <ol style="list-style-type: none"> a) the first stage: a coupled unit of vertical tube reactor with a central cylindrical-tapered processing reactor equipped with a low-speed frame agitator, stations metering the reagents which were the following coagulants: iron(III) based PIX[®] or aluminium based ALS[®] and 0.3 % aqueous solution of flocculant 8398 Optifloc Cytec Industrie Inc. Kemipol Sp. z o.o.; b) the second stage: the cylindrical-tapered oxidation reactor fitted with a low-speed frame agitator, stations metering Fenton's reagents (acid solution of

No.	Installation	Installation setup and pretreatment method [7]
		<p>FeSO₄ in H₂SO₄, 30 % solution of H₂O₂ and 30 % solution of NaOH). The dewatering set of post-processing sludge was common and included: a vertical thickening tank to which a flocculant was metered, and a pressurized chamber press.</p> <p>The course of physicochemical pretreatment:</p> <ul style="list-style-type: none"> • at the 1st stage of the pretreatment, all operations and elementary processes were conducted in the same way as for installation D; • when sedimentary separation of sludge phase from over-sediment phase was made, the recent phase was pumped onto the 2nd stage oxidation reactor to which the acidic solution of FeSO₄ was metered in doses to obtain pH = 2.5-3.0, then 30 % aqueous solution of H₂O₂ was metered; • after oxidation, the neutralization was made by metering 30 % solution of NaOH in doses to enable the reaction to achieve pH = 8.0-8.5; • the flocculation of dispersed phases was conducted by metering 0.3 % solution of flocculant 8398 Optifloc Cytec Industrie Inc. Kemipol Sp. z o.o., directly onto the reactor; • the sludge thickened by sedimentation in the two stages of pretreatment were supplied onto the vertical thickening tank equipped with a low-speed frame agitator, to thicken them finally by flocculation in directed to the pressurized dewatering set.

Table 2

Basic characteristics of raw effluents treated in the installations D and E

No.	Installation	Effluent origin	Characteristics ^{a, b)} (median) ^{c)}
1	D	Mainly from low-tonnage production of paints and silicone plasters the façades of concrete structures and interiors, as well as decorative gypsum finishing agents and putties. In lower volume fraction from high-tonnage production of cements and glazes, as well as self-levelling compounds and grouts.	<p>pH = 9.2-12.1 (10.3) TSS = 975.9-4622.3 (3244.7) COD = 1109.0-4082.9 (2892.3) BOD₅ = 283.9-620.3 (407.3) TN = 20.4-202.5 (98.7) TP = 6.6-40.2 (13.7)</p>
2	E	Mainly from the low-tonnage production of water-based paints and silicone plasters for the façades of concrete structures and interiors, cements and glazes, protective and decorative plasters. In lower volume fraction from medium-tonnage production of gypsum surfacers and putties, as well as self-levelling compounds and sealing coats.	<p>pH = 8.9-11.7 (10.8) TSS = 670.4-6048.0 (4804.9) COD = 1870.9-4803.9 (3772.0) BOD₅ = 209.6-503.8 (345.9) TN = 32.5-122.0 (78.9) TP = 2.2-26.8 (17.4)</p>

^{a)} parameters TSS, COD, BOD₅, TN and TP were given in [mg/dm³]

^{b)} determined acc. to the following standards, respectively: pH (PN-EN ISO 10523:2012) [8], TSS (PN-EN 872:2007) [9], COD (PN-ISO 15705:2005) [10], BOD₅ (PN-EN 1899-1:2002) [11], TN (PN-EN 12260:2004) [12] and TP (PN-EN ISO 6878:2006) [13]

^{c)} median ("middle value") (m_{1,2}) of the order: ½

Test specimens of sludge were sampled after pressurized dewatering (up to 12 atm.) using frame chamber filtering presses. The sludge specimens were submitted to the procedures of fractionation by 5-step sequential extraction acc. to Tessier's methodology [14] and TCLP [15], and then the determination of concentrations of selected heavy metals was made. Table 3 presents the established indices of markings for the individual post-processing sludge categories.

Table 3

The genesis and the markings of sludge dewatered by pressure, generated in the installations: D and E

No.	Installation	Reagents used in the pretreatment stages ^{a-c)}	Marking of mixed sludge
1	D	a) The 1st stage: ● coagulants: PIX [®] 113 or PIX [®] 122, or ALS [®] b) The 2nd stage with oxidation: ● oxidiser 3.5 % aqua solution of KMnO ₄ ● 30 % solution of NaOH	DC _(PIX 113) - Ox(KMnO ₄) DC _(PIX 122) - Ox(KMnO ₄) DC _(ALS) - Ox(KMnO ₄)
2	E	a) The 1st stage: ● coagulants: PIX [®] 113, PIX [®] 122, or ALS [®] b) The 2nd stage with deep oxidation: ● Fenton system (FeSO ₄ in H ₂ SO ₄ and 30 % H ₂ O ₂) ● 30 % NaOH	EC _(PIX 113) - Ox(Fs) ^{d)} EC _(PIX 122) - Ox(Fs) ^{d)} EC _(ALS) - Ox(Fs) ^{d)}

^{a)} the sludge were obtained using commercial coagulants made by Kemira Kemipol Sp. z o.o., of detailed characteristics given in [16]

^{b)} at 1st stage, only acidic sulphate coagulants were used to reduce a risk of molecular chlorine generation and a synthesis of chloro derivative compounds at 2nd oxidation stage of the pretreatment

^{c)} in each case, the same 0.3 % solution of flocculant 8398 Optifloc Cytec Industrieec Inc. Kemipol Sp. z o.o. was used to thicken the precipitated dispersed solid phases

^{d)} Fs - Fenton system (used at the 2nd stage of the pretreatment)

Procedure of TCLP leaching tests

The evaluation of mixed and pressure dewatered sludge from double-stage physicochemical pretreatment of the post-production wastewater from “non-anhydrous” samples were performed according to TCLP methodology of USEPA Method 1311 [15] by the determination of leachable forms of metals such as: Cd, Cr, Cu, Mn, Ni, Pb and Zn. Final determinations in the extracts were made using Jobin Yvon EMISSION JY 38S ICP-OES emission spectrometer and the standard for the determination of metals: EN ISO 11885:2009 [17]. The proceedings used in TCLP leaching procedure included steps presented and characterised in Table 4 of the part one of this study.

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

Sludge dewatered by pressure in chamber presses, mixed in the thickening tank, were submitted to sequential extraction consisting in determining five fractions in accordance with Tessier's basic procedure specified in item [14]. For the extraction 100.0 g of “non-anhydrous” samples of sludge were used in two replications. The conditions of the sequential extraction were the same as given in our studies [18-21].

Results and discussion

The necessity of the use of double-stage physicochemical pretreatment of processing effluents from the production of construction chemicals results from the need to prepare the wastewater flow of the remaining and dissolved pollution load after the first pretreatment stage which has to be biodegradable to possibly the highest degree at a final stage of biological treatment. This applies, in particular, to the wastewater from the manufacture of the products of more complex chemical composition and a significant participation in the total pollution load of the pool of compounds and/or substances soluble in the aqueous

phase. The processing wastewater from the manufacture of a very wide range of construction chemicals in the total pollution load, to simply put, include primarily the dispersed particles of different type basic substances and the so-called additives and admixtures from the production lines such as from the production of paints for different purposes, varnishes and cleaning agents, adhesives for tiles and styrofoams, grouts, primers, floor underlays, waterproof membranes, silicones, impregnating agents etc. [22-25]. Another composition can have the wastewater from the production of all kinds of plasters and mortars [26-30]. Still another types of pollutions may their origin in manufacturing admixtures and additions for concretes and waterproof, anti-freezing, colouring renders, retarding or accelerating the setting of cement paste [22]. The general and processing effluents from such productions usually contain predominant amounts of colloids and suspensions of varying stability degree [1, 31]. This group contains generally mineral fillers: chalk, dolomites, titanium white, talcum, kaolin, silica dust and mica [32-35]. This group of chemical compounds and substances is mainly separated at the 1st stage of wastewater pretreatment and does not form any essential part of the effluent dissolved load. At the level of much lower concentrations but significant in the aspect of the choice an optimal wastewater pretreatment method are the substances the origin of which is from plasticisers, e.g. sodium and/or magnesium lignosulphonates [36]. The group of super plasticisers may include sulphonated naphthalene and melamine polycondensates, starch hydrolyzates and polycarboxyethers, that occur in a pool of dissolved load [37, 38]. From the quick-set admixtures: calcium nitrate and calcium chloride, and from the hydrophobizing agents: calcium stearate [39, 40]. From the group of air-entrainers: synthetic tensides and modified rosin resins that enrich the dissolved load of pollutants in the processing effluents [41]. Colouring admixtures (pigments) are the source of heavy metals (e.g., Cr, Cu, Ni, Ti) originating mostly with the use of these metals. Biocides protect construction chemicals, but in the effluents they significantly increase their general toxicity [1, 42]. In the total pollutants load may also be residues of non-reacted resins: acrylic, epoxy, epoxy-polyurethane, polyurethane, polyester or vinyl [43].

For evaluated pressure dewatered groups of sludge, the analytically determined leachability level of metals was recorded at low threshold of the values, and the contents of e.g. Cd, Cr and Pb was below the determination limit of the method used to make analyses. At the same time, the concentrations of randomly selected samples of raw effluents were recorded only in a few cases at trace levels, i.e. below 0.2 mg/dm^3 . Pigments constituted the main source of heavy metals in the investigated wastewater. Their contents in the total mass of dispersed fractions was at trace level, which was observed by the recorded low levels of concentrations or the levels below the determination limit of analytical method used for quantitative determination. The results of the procedure made acc. to TCLP methodology [15] indicate the manifestly more stable mixed sludge that were obtained using Fenton's system at the 2nd oxidation stage of the pretreatment. The leachability recorded for some of analysed samples, was at the level not exceeding 0.2 mg/dm^3 , and the concentrations determined above the limit of determination for Cr, Cu, Ni or Zn, were stated for post-processing sludge, for which pH values of filtrates determined during sampling were within the range 7.0-7.5. The higher pH of the mixed sludge in the thickener favours bonding these metals in the mass of sludge and, at the same, minimizes their leachability from the dehydrated sludge in the filtering presses. Practically, it should be aimed to

maintain higher pH in the tank designed to thicken the sludge before their discharge onto the set of pressure dewatering. In the case of using Fenton's system, the dewatered sludge of a significantly lower total leachability level of heavy metals were achieved. The use of this system at the 2nd stage of the pretreatment results in the occurrence also some amount of residual hydrogen peroxide in the thickening tank. Its presence in the mass of mixed sludge can generate the forms of metals more oxidised and more prone to precipitate in this processing volume, reducing their leachability from the after-filtering sludge cakes. This phenomenon may include some of the analysed metals and the transformations with the participation of H_2O_2 can be shown with the following simplified scheme: $M^{+\odot} + H_2O_2 \rightarrow M^{+(\odot + x)}$, where: $M^{+\odot}$: Cu^+ , Ni^{+2} , Mn^{+2} or Pb^{+2} , whereas x - means a numeric increase in the oxidation state under the effect of H_2O_2 . In the case of Cr this phenomenon can be reversed and may result in the occurrence of more difficultly precipitable forms of Cr^{6+} , and thus more leachable ones.

Table 4

Examples of concentrations of leachable metals on the basis of TCLP procedure for pressure dewatered mixed sludge generated as the result of two-stage, physicochemical pretreatment of effluents discharged from the selected production of construction chemicals

Samples (sludge type)	Results of TCLP [mg/dm ³] ^{a)}						
	Cd	Cr	Cu	Ni	Mn	Pb	Zn
1. DC _(PIX 113) - Ox(KMnO ₄)	ND	ND	ND	0.017	4.85	ND	ND
2. DC _(PIX 113) - Ox(KMnO ₄) ^{c1)}	ND	0.037	0.067	0.088	9.88	ND	0.11
1. DC _(PIX 122) - Ox(KMnO ₄) ^{c2)}	ND	0.008	0.059	0.083	7.03	ND	0.101
2. DC _(PIX 122) - Ox(KMnO ₄)	ND	0.062	ND	ND	5.81	ND	0.107
1. DC _(ALS) - Ox(KMnO ₄)	ND	ND	ND	ND	2.89	ND	ND
2. DC _(ALS) - Ox(KMnO ₄)	ND	ND	ND	0.064	1.63	ND	ND
1. EC _(PIX 113) - Ox(Fs) ^{d1)}	ND	ND	0.11	0.019	0.09	ND	ND
2. EC _(PIX 113) - Ox(Fs)	ND	ND	ND	ND	ND	ND	ND
1. EC _(PIX 113) - Ox(Fs) ^{d2)}	ND	ND	0.101	0.031	0.11	ND	ND
2. EC _(PIX 113) - Ox(Fs) ^{d3)}	ND	ND	0.069	ND	0.08	ND	0.069
1. EC _(PIX 122) - Ox(Fs) ^{d4)}	ND	ND	0.044	ND	ND	ND	0.063
2. EC _(PIX 122) - Ox(Fs)	ND	ND	ND	ND	ND	ND	ND
1. EC _(ALS) - Ox(Fs) ^{d5)}	ND	0.017	0.027	ND	0.16	ND	0.011
2. EC _(ALS) - Ox(Fs)	ND	ND	ND	ND	0.05	ND	ND

^{a)} ND - below the method determination threshold for Zn, Pb, Cu and Ni

^{b)} Fs - Fenton system (used at the 2nd stage of the pretreatment)

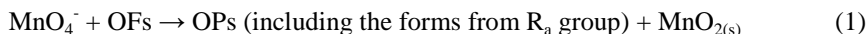
^{c)} the reactions (pH) of filtrates after the press were recorded at levels, respectively: c1) 7.14 and c2) 7.37

^{d)} in those specimens after the oxidation with Fenton system, no neutralisation was made and the acidic sludge were directed into the thickening tank before the pressure dewatering, whereas the pH of the filtrate was measured during sampling and was as follows: d1) 7.11, d2) 7.30, d3) 7.18, d4) 7.03, and d5) 7.46

High concentrations of manganese in the extracts occurred in the mixed sludge that were generated as the result of the application of KMnO₄ at the 2nd stage of the oxidation pretreatment. Recorded concentrations of leachable forms may be a result of coordination of Mn at its state (II) by ligands present in the environment, e.g. mineral ligands from pool F1, mainly sulphate ions ($[Mn(SO_4)_m]^{(+2 - 2 \cdot m)}$, where: m - number of binding sulphate ligands) and carbonate ions ($[Mn(CO_3)_n]^{(+2 - 2 \cdot n)}$, where: n - number of binding carbonate ligands), which are the result of oxidation and mineralisation of organic fractions to CO₂ and the generation of the coordination forms of HCO₃⁻, particularly CO₃²⁻, that form the

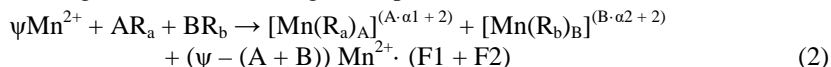
essential part of pool F2. The organic ligands, being a part of pool F4, were probably a source of the generation of low-molecular products as a result of the oxidation of organic components in the dissolved part of the load discharged from the 1st stage onto the further stage of their treatment. In view of the finding the presence of manganese at +2 oxidation state, the coordination forms of this metal in pool F4 may have their general complexation of $[\text{Mn}(\text{R})_{\mu}]^{(\mu-\alpha+2)}$, where: R - organic ligands that are the products of oxidation by KMnO_4 , μ - number of binding ligands R, α - valency of ligand R). In these two processing volumes there are generated various coordination forms of the following type: $[\text{Mn}(\text{R}_a)_A]^{(A-\alpha_1+2)}$ and $[\text{Mn}(\text{R}_b)_B]^{(B-\alpha_2+2)}$, where: A and B - number of binding ligands, respectively, R_a and R_b , α_1 - valencies of organic ligands from group R_a , generated in the oxidation reactor, α_2 - valencies of organic ligands from group R_b , generated in the thickening tank. Transformation products of the stages of wastewater physicochemical pretreatment that may be formed at the final phases of sludge processing are probably generated in accordance with the following simplified schemes (1) and (2):

a) in the 2nd stage oxidation reactor:



where: OFs - organic fractions of the load after the 1st stage of physicochemical pretreatment, OPs - oxidation products of organic fractions;

b) in the thickening tank (where the residual reduction of $\text{MnO}_{2(s)}$ occurs to obtain Mn^{2+} in the mixed sludge), before dewatering in the press:



where: ψ , A and B - numbers resulting from the rules of stoichiometry for Mn(II), binding ligands R_a and R_b , R_a - fractions which are oxidation products using KMnO_4 at the 2nd stage of pretreatment, R_b - fractions that are the products of transformations in the mixed sludge occurring in the thickening tank, $\text{Mn}^{2+} \cdot (\text{F1} + \text{F2})$ - manganese(II) contained in fraction pools F1 and F2.

The group of oxidation products R_a and the group of transformations in the thickening tank R_b may be a significant part of the determined pool of fraction F4 of manganese leached from the sludge mixed in the thickening tank and separated when KMnO_4 (Table 5) was applied at the 2nd physicochemical stage of the wastewater pretreatment.

In a typical proceeding to assess the potential risk, the quantity of metals bonded in mobile fractions, i.e. the total of exchangeable and carbonate fractions are taken into account instead the total contents of metals which are listed in Table 5 for the investigated sludge samples [44, 45]. The nature of waste toxicity in accordance US EPA is determined by the level of Pb concentration and on this basis a waste category is defined. In all samples of the analysed groups of sludge: DC - Ox(KMnO_4) and EC - Ox(Fs) no exceedance of limit value for leachable Pb (5.0 mg/dm^3), decisive of toxicity in accordance with US EPA criterion, was analytically found. This not only an argument for the effective physicochemical processing wastewater treatment technology, but also demonstrates acquiring the post-processing sludge of a low leachability level. It also indicates an opportunity to consider a further use of them for the purposes of commercial nature. Therefore, in this case, the speciation forms determined using fractional analysis are essential to estimate a potential lability, mobility and toxicity of analysed metals.

The quantitative distribution in different fractional pools, determined using sequential extraction in accordance with Tessier's procedures, provides an estimate for their availability and informs about the risk associated with the potential migration of metals into the aquatic environment.

Table 5

Fraction content [%] of manganese determined using Tessier's procedure in pressure dewatered mixed sludge from the 2nd stage processing effluent pretreatment from the production of construction chemicals and the risk assessment code (RAC) assumed for the case when the oxidation using KMnO_4 was applied ^{a)}

No.	Sludge type ^{b)}	F1	F2	F3	F4	F5	Σ F1+F2	RAC ^{c)}
1	1. DC _(PIX 113) - Ox(KMnO ₄) ¹⁾	6	10	ND	13	71	16	MR
	2. DC _(PIX 113) - Ox(KMnO ₄) ²⁾	2	9	2	17	70	11	MR
2	1. DC _(PIX 113) - Ox(KMnO ₄) ³⁾	7	11	1	8	73	18	MR
	2. DC _(PIX 113) - Ox(KMnO ₄) ⁴⁾	9	9	3	17	62	18	MR
3	1. DC _(PIX 122) - Ox(KMnO ₄) ⁵⁾	7	9	9	6	69	16	MR
	2. DC _(PIX 122) - Ox(KMnO ₄) ⁶⁾	3	4	ND	16	77	7	LR
4	1. DC _(PIX 122) - Ox(KMnO ₄) ⁷⁾	11	8	2	10	69	19	MR
	2. DC _(PIX 122) - Ox(KMnO ₄) ⁸⁾	7	7	4	16	66	14	MR
5	1. DC _(ALS) - Ox(KMnO ₄) ⁹⁾	12	8	5	7	68	20	MR
	2. DC _(ALS) - Ox(KMnO ₄) ¹⁰⁾	4	14	2	15	65	18	MR
6	1. DC _(ALS) - Ox(KMnO ₄) ¹¹⁾	2	11	ND	18	69	13	MR
	2. DC _(ALS) - Ox(KMnO ₄) ¹²⁾	13	7	ND	8	72	20	MR

^{a)} individual fractions were marked, respectively: F1 (exchangeable), F2 (carbonate), F3 (Fe-Mn oxides bound), F4 (organic) and F5 (residual)

^{b)} adopted indices: DC_(PIX 113) - Ox(KMnO₄), DC_(PIX 122) - Ox(KMnO₄) or DC_(ALS) - Ox(KMnO₄), mean respectively the mixed sludge obtained: using the coagulation at the first stage with acidic sulphate coagulants: PIX[®] 113 or PIX[®] 122, or ALS[®] and oxidation at the second stage using KMnO₄ in the acidic environment

^{c)} adopted indices mean, respectively: MR - medium risk and LR - low risk

^{1) - 12)} the reaction (pH) of filtrates directly after the press, measured during the sampling of sludge for tests was as follows: 1) 8.7 ±0.2, 2) 7.9 ±0.1, 3) 8.3 ±0.1, 4) 8.4 ±0.2, 5) 8.6 ±0.1, 6) 8.4 ±0.2, 7) 9.1 ±0.1, 8) 9.4 ±0.2, 9) 9.5 ±0.1, 10) 8.8 ±0.1, 11) 9.0 ±0.1 and 12) 9.4 ±0.2

The results compiled include the assessment of sludge from double-stage physicochemical pretreatment of processing effluents from the production of selected construction chemicals and are a part of a scope of values that was recorded in an actual system when mixed general and technological wastewater made streams from different tonnage productions in the most part, such as: protective and decorative plasters, gypsum surfacers and putties, self-levelling compounds and grouts, paints for façades of concrete structures and interiors, cements and glazes. The results presented here should be regarded as the orientation level that is obtained for sludge being a secondary effect of physicochemical treatment of processing effluents from the production of construction chemicals - the assortment group that is poorly described in literature. The double-stage pretreatment is a complex way of processing and it is operated in the developed installations. The reagents used, apart from the history of which they introduce to the stream of wastewater, e.g. in a form of anions of used coagulants, undoubtedly generate considerable fractions of sparingly soluble products of hydrolysis with a developed surface and sorption properties of metals, which may also affect the final level of leachability results. It should be noted that an important aspect for practice that determines the

leachability level is the control of pH of mixed sludge in the thickening tank before their pumping onto chamber filtering presses.

Conclusions

The sludge mixed in the thickening tank, generated as the result of two-stage physicochemical pretreatment of effluents from the production of construction chemicals and dewatered in pressurized chamber filtering presses, are particularly characterised by:

- very low leachability levels of heavy metals in the case of application of Fenton's system at the second stage of effluent pretreatment;
- elevated leachability level of Mn in the case of using potassium permanganate at the second stage of effluent pretreatment;
- minimally increased tendency of metal detectability, in particular: Cr, Cu, Ni and Zn, in cases where neutralization was not applied after the phase of the oxidation with Fenton's system at the second stage of wastewater pretreatment.

It should be noted that an important aspect is to monitor the reaction (pH) of mixed sludge in the thickening tank before their pumping onto the chamber filtering presses in order to maximally precipitate them and to conduct other residual reduction processes, e.g. using sorption and ion exchange of the residual quantities of heavy metals after the operations of neutralisation and coagulation.

Mixed streams of post-processing sludge might be classified in accordance with the risk assessment code (RAC) as not involving risk in respect of determined metals while using Fenton's system at the 2nd stage of the physicochemical wastewater pretreatment, and of a low risk for aquatic ecosystems against Mn in the case of using potassium permanganate at the 2nd, oxidation stage.

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OCZYSZCZANIE ŚCIEKÓW Z PRODUKCJI CHEMII BUDOWLANEJ. CZEŚĆ 2. OSADY Z DWUSTOPNIOWEGO PODCZYSZCZANIA

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Abstrakt: Potrzeba fizykochemicznego podczyszczania dwustopniowego wynikała z konieczności zmiany relacji BZT₅/ChZT, ChZT(BZT₅)/N, ChZT(BZT₅)/P i N/P na korzystne w strumieniach kierowanych do końcowego oczyszczania metodami biologicznymi. Stąd też w podczyszczaniu na drugim stopniu zastosowano metody utleniania lub głębokiego utleniania, co znalazło swoje odzwierciedlenie w składzie osadów poprocesowych poddanych ocenie w niniejszej części pracy. Ścieki pochodziły głównie z linii różnotonażowego wytwarzania mas fugowych i powłok uszczelniających, gładzi gipsowych i szpachlowych, zapraw samopoziomujących, wodorocieńczalnych farb i tynków silikonowych do elewacji konstrukcji betonowych i wnętrz, zapraw klejących i glazur, tynków ochronnych oraz ozdobnych. Na instalacjach podczyszczanie pierwszego stopnia prowadzono, stosując metody koagulacyjne oparte na wykorzystaniu siarczanowych koagulantów żelazowych klasy PIX[®] lub glinowych klasy ALS[®], na drugim natomiast utlenianie za pomocą KMnO₄ lub układem Fentona. Osady do oceny wydzielano w wyniku ich odwadniania na zespołach ciśnieniowych pras komorowych. Dla tak generowanych osadów przeprowadzono procedurę TCLP oraz wykonano ocenę ryzyka, stosując kod RAC. Przyjęto, że ciśnieniowo odwodnione osady mieszane wykazują niskie ryzyko (LR) względem Cd, Cr, Cu, Ni, Pb i Zn oraz umiarkowane (MR) względem Mn w przypadku stosowania nadmanganianu potasu na drugim stopniu podczyszczania. W przypadku stosowania układu Fentona na drugim stopniu mieszane osady charakteryzowały się niskim ryzykiem (LR) względem wszystkich analizowanych metali ciężkich. Zgodnie z kryteriami TCLP mieszane osady z dwustopniowego fizykochemicznego podczyszczania ścieków technologicznych z produkcji wytypowanego asortymentu chemii budowlanej sklasyfikowano jako odpady nietoksyczne.

Słowa kluczowe: produkcja chemii budowlanej, ścieki technologiczne, dwustopniowe podczyszczanie, podczyszczanie fizykochemiczne, osady, test TCLP, kod oceny ryzyka (RAC)