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Original Research

Using Sodium Trithiocarbonate to Precipitate Heavy Metals from Industrial Wastewater – from the Laboratory to Industrial Scale

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Abstract

This paper presents the possibility of using sodium trithiocarbonate to remove heavy metals such as copper, nickel, and tin from industrial wastewater generated by the production of printed circuit boards (PCBs). Initial metal removal studies aimed at selecting an effective precipitant and optimizing the precipitation process were conducted on an laboratory scale. The smallest concentrations of copper, nickel, and tin in treated wastewater (Cu 0.09 mg/L, Ni 0.009 mg/L, Sn <0.005 mg/L) were obtained after using a stoichiometric sodium trithiocarbonate dose at pH 9.0-9.5. Optimizing the metal removal process was possible by using the surface response method to obtain a good adjustment of the experimental data to the data obtained from the model ($R^2 = 0.9307$, $R^2_{adj.} = 0.8845$). The results of laboratory and model studies were used during industrial-scale testing in a wastewater treatment plant located in a PCB manufacturing plant. Optimization the wastewater treatment process on an industrial scale allowed us to obtain treated wastewater with very low copper (<0.005-0.014 mg/L), nickel (<0.005-0.008 mg/L), and tin (<0.005 mg/L) concentrations.

Keywords: heavy metals, copper, nickel, tin, wastewater, sodium trithiocarbonate, complexing agents, industrial wastewater

Introduction

The intensive development of industry is related to the increasing degree of pollution of the natural environment by emitting organic and inorganic pollutants into the air, water, and soil. Among inorganic substances, chemicals containing heavy metals are particularly dangerous because they are not biodegradable and can accumulate in living organism's causing many adverse changes. It is assumed that heavy metals are elements with atomic mass between 63.5 and 200.6 u and density greater than 5 g/L [1]. Adoption of the above criteria causes the inclusion of such elements as copper, nickel, and tin. Copper ions (II) are on the one hand a vital microelement essential for the functioning of living organisms, but on the other hand, even at low concentrations they cause a reduction of vital functions of the organisms responsible for the biodegrading organic pollutants in wastewater treatment processes such as: denitrifying bacteria, heterotrophic

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bacteria-decomposing glucose, and nitrifying bacteria [2]. High copper concentrations were recorded in water from copper mines (1,550 mg/L) and in wastewater originating from the production of semiconductors (5-100 mg/L) [3-4]. Also, in wastewater from the production of PCBs, the presence of copper (II) ions in the range of 0.1-60 mg/L was noted, depending on the type of process from which the wastewater originated. The highest concentration of copper was found in wastewater from acid and ammonia etching and the brushing process [5].

Nickel is an element commonly used in industry and it is therefore also a constituent of water systems where it is present, similarly to nickel, in the form of many chemical compounds. Nickel (II) ions also have toxic effects on many aquatic organisms, including freshwater fish such as: rainbow trout (*Oncorhynchus mykiss*), three-spined stickleback (*Gasterosteus aculeatus*), roach (*Rutilus rutilus*), perch (*Perca fluviatilis*), and dace (*Leuciscus leuciscus*). A lethal concentration of nickel (II) ions (LC_{50}, 96 hours) for the above-mentioned species was 19.3-61.2 mg/L [6]. Nickel (II) ions may have a toxic impact on aquatic organisms, possibly by the disturbance of Ca^{2+} homeostasis, Mg^{2+} homeostasis, Fe^{2+}/Fe^{3+} system homeostasis, oxidative damage caused by reactive oxygen forms, and allergic response of respiratory epithelium [7]. Nickel concentrations in industrial wastewater vary, but in the case of this element, that wastewater is highly toxic and possibly carcinogenic. In addition, only 30-40% of all metals used in galvanic processes are effectively used and placed as galvanic coatings.

The remaining amount (60-70%) pollutes rinse water, which may contain toxic metals in concentrations even up to 1,000 mg/L [8]. Non-organic tin (II) and tin (IV) compounds, as opposed to copper (II) and nickel (II) compounds, are characterized by low toxicity in relation to aquatic and terrestrial organisms, mainly due to their low solubility, poor absorption, frequently low accumulation in tissue, and rapid excretion [9]. Despite its low toxicity compared to other metals, tin compounds must also be removed from industrial wastewater to protect the natural environment from excessive pollution, as required by law. Removal of heavy metals from wastewater can be accomplished by the use of unit processes such as: chemical precipitation, coagulation, flocculation, complexing, adsorption on activated carbon, ion exchange, solvent extraction, foam flotation, cementation, and others. Chemical precipitation processes are one of the most common methods used in industry for the removal of heavy metals from non-organic wastewater due to the speed of the process and its simplicity [10]. Heavy metal precipitation processes take place as a result of wastewater alkalisation with $Ca(OH)_2$ slurry or NaOH solution to a certain pH value required to precipitate metal ions present in wastewater in the form of hydroxides. Typically, pH 8-11 is used, where the solubility of most metal hydroxides is the lowest. Metal hydroxide precipitated in the form of sediment can be removed by flocculation, sedimentation, and filtration. The method of metals precipitation by wastewater alkalisation is easy to use, but it tends to be ineffective as far as precipitation of amphoteric hydroxides is concerned, and the presence of complexing agents in wastewater, which prevent quantitative precipitation of metal ions [11]. These problems can be eliminated by the use of metal sulphides in a soluble (Na_2S, NaHS) or insoluble (FeS) form for precipitation, which at acid pH (pH<3) release H_2S and allow precipitation of heavy metal ions in the form of sulphides.

It is known that the solubility product of metal sulphides is much lower than the solubility product of metal hydroxides, and therefore the use of sulphides enables us to obtain treated wastewater with a lower content of heavy metals than in the case of metal hydroxide precipitation. The method with the use of sulphides is effective for wastewater containing metal (Cr, Ni, Zn) mixtures as well as in the presence of complexing compounds (CN^-), but its use is associated with the formation of large amounts of sludge and requires the use of more reagents. Despite these inconveniences, it is still used due to its high efficiency and low installation costs [12]. When using this method, there is a risk of H_2S gas release, as precipitation of metals is carried out in acidic environments. This risk can be eliminated by using other sulphur-containing compounds for precipitation, such as: dimethyl-, diethyl-, diphenyl-dithiocarbamic sodium salt, its derivatives [13-14], or trimercaptotriazine sodium salt [15-17] in an inert or alkaline medium. The purpose of the present study was to determine the efficacy of sodium trithiocarbonate (Na_2CS_3) as a precipitation reagent of Cu (II), Ni (II), and Sn (II) ions from industrial wastewater from PCB production and containing complexing compounds. The research was conducted on a laboratory and industrial scale.

The testing in the laboratory in the first stage involved the selection of the most effective precipitant and in the second stage, the optimization of metal removal using the RSM method. The obtained results of model tests carried out on a laboratory scale were used to optimize the heavy metals precipitation process on the industrial scale, at the wastewater treatment plant located in the production of PCBs.

Material and Methods

Material and Chemical Reagents

Laboratory-scale research was carried out on a sample of actual wastewater collected in a wastewater treatment plant of a PCB plant located in Poland. Samples of raw wastewater were collected for five consecutive days, after which their composition was averaged by mixing. The collected wastewater samples and the averaged test sample were not fixed and their physico-chemical composition is shown in Table 1. The following precipitants were used: $Na_2S{\cdot}9H_2O$ (analytical grade, POCH, Poland), Furosep CW3 (40% solution of sodium dimethyldithiocarbamate, Chemische Fabrik Wocklum GmbH & Co. KG, Germany), TMT 15 (15% solution of sodium trimercapto-s-triazine, Donauchem, Poland), and 44.26% and 10.00% solution of Na_2CS_3 (sodium trithiocarbonate, KiZChS Siarkopol S.A., Poland). Moreover, we used the following reagents: $Ca(OH)_2$ (Chempur, Poland), NaOH (POCH, Poland), HCl (POCH, Poland), Praestol 2500 (Ashland Deutschland GmbH, Germany) and $FeCl_3 \cdot 6H_2O$ (Chempur, Poland). All reagents had analytical purity and 30% NaOH (technical grade), 36% HCl (technical grade), FeCl3 (Donau Klar Smart, Donauchem, Poland), and anion flocculant (Furoflock CW277, Chemische Fabrik Wocklum GmbH & Co. KG, Germany) were used at the stage of industrial testing.

Analytical Methods

The reaction was determined using the WTWinolab pH/IONCond 750 device using the combination electrode SenTix81according to PN-EN ISO 10523:2012, specific electrical conductivity using the TetraCon325 electrode according to EN 27888:1999 and the redox potential was determined using the Elmetron CPC411 with the platinum electrode ErPt-11 (Hydromet, Poland). Turbidity was determined by nephelometric method using a Cyberscan IR Turbidimeter TB1000 according to PN-ISO 7027:2003 and colour using a SPEKOL 1200 Spectrophotometer according to PN-ISO 7887:2012. Chemical oxygen demand (COD) was determined by spectrophotometric method using sealed tubes and a Spekol 1200 spectrometer according to PN-ISO 15705:2005, and total organic carbon (TOC) by high-temperature combustion at 680ºC with IR detection using a Shimadzu TOC-L_{CPH} analyzer according to PN-EN 1484:1999. Chlorides were determined by titrimetric method according to PN-ISO 9297:1994 and sulphates (VI) by weight method according to PN-ISO 9280:2002. Heavy metals (Cu, Ni, Sn) were determined by the ISP-OES method using an Optima 5300DV spectrometer (Perkin Elmer) according to PN-EN ISO 11885:2009. Complexing compounds were determined by spectrophotometry using a Nanocolor Organische Komplexbildner 10 (Bi(III)/xylenol orange, Macherey-Nagel GmbH, Germany), according to DIN 38409-H26, using the following bismuth complex index calculation (I_{BiK}): 1mg/L I_{BiK} = 1.61 mg/L Na_2EDTA. Finally, sulphides were determined by spectrophotometric method, using Visocolor Sulfides 0.1-0.8 mg/L (sulphides/N,N-dimethyl-1.4-phenylenediamine/Fe (III) sulphides, Macherey-Nagel GmbH, Germany).

Methodology of Research

Comparative studies of precipitation efficiency of copper (II), nickel (II), and tin (II) ions from wastewater were conducted using Na_2S, Furosep CW3, TMT 15, and 44.26% solution of Na_2CS_3. Precipitation of metals in the case of using Furosep CW3 and TMT 15 was carried out strictly according to the instructions in the specification sheets of these products, using 1 L wastewater samples. Precipitation using Na_2S was carried out at pH 6.5 (the highest theoretical efficiency of copper precipitation in the form of sulphide), using a stoichiometric amount of $Na_2S \cdot 9H_2O$. After 10 min, the pH was adjusted to 7.5, and 2 mL of 0.05% Furoflock CW277 was added and then poured into a measuring cylinder of 1L capacity and subjected to 30 min. sedimentation. Likewise, precipitation was performed using Furosep CW3 by adding the stoichiometric amount of Furosep CW3 after adjustment of pH to 7.5. Precipitation using TMT 15 was carried out in two stages according to the manufacturer's guidelines for wastewater containing Cu^{2+} and Ni^{2+} ions.

In the first step, Ca $(OH)_2$ was dosed to pH 7.0, then 50% of NaOH to pH 9.0 to precipitate free metals in the form of hydroxides. Then 1 mL of 0.05% Praestol 2500 was added and subjected to 30 min. sedimentation. $V_{of\ sludge}$ was measured at this stage and concentrations of Cu, Ni, and Sn were measured in pre-treated wastewater, which after sedimentation was decanted and purification was continued by adding a stoichiometric amount of TMT 15 in relation to the amount of metals remaining in the wastewater. After 30 min. of reaction, 1 mL of $FeCl_3$ (10 g Fe/L) solution and 0.2 mL 0.05% of Praestol 2500 was added and subjected to sedimentation for 60 min. Precipitation using Na_2CS_3 was carried out by adding 1 mL 40% of FeCl3 to the sample of 1 L wastewater, correcting the pH to 9.0 (30% NaOH) and adding a stoichiometric amount of 44.26% Na_2CS_3 solution. After adjusting the pH to 9.0-9.5, 2 mL of 0.05% Furoflock CW277 was added and subjected to 30 min. sedimentation. After completion of the described precipitation processes, a sample of supernatant fluid was collected in each case (after 30 or 60 minutes of sedimentation, according to the recommended procedure) to determine the pH and Cu, Sn, Ni, and S^{2-} concentrations. $V_{of\ sludge}$ was measured after 30 min. of sedimentation or in the case of TMT 15 precipitation after 60 min. of sedimentation. Based on the analysis of Cu^{2+}, Ni^{2+}, and Sn^{2+} precipitation results performed on a laboratory scale, a mathematical model was developed to remove metals from the treated wastewater using the RSM method. The results of the model tests were used during continuous industrial tests in a wastewater treatment plant located in a PCB plant and shown schematically in Fig. 1.

The process of wastewater treatment in the wastewater treatment plant of 350 L/h capacity, shown in Fig. 1, was as follows: (i) the averaged wastewater was pumped into the first chamber of the flow reactor where pH was measured and at pH greater than 5.5 the HCl was dosed with simultaneously dispensed coagulant (Donau Klar Smart) in the amount of 1 L/1,000 L of wastewater, (ii) in the second chamber the wastewater was alkalised to pH ca. 9 with 30% NaOH to precipitate metal hydroxides, (iii) in the third chamber 44.26% of Na_2CS_3 at a constant dose of 0.3 L/1,000 L of wastewater was dosed to precipitate the complexed heavy metals, and (iv) in the fourth chamber, 0.05% of Furoflock CW277 solution was dosed in the amount of 2 L/1,000 L of wastewater. Subsequently, the wastewater together with the precipitated sediments flowed through

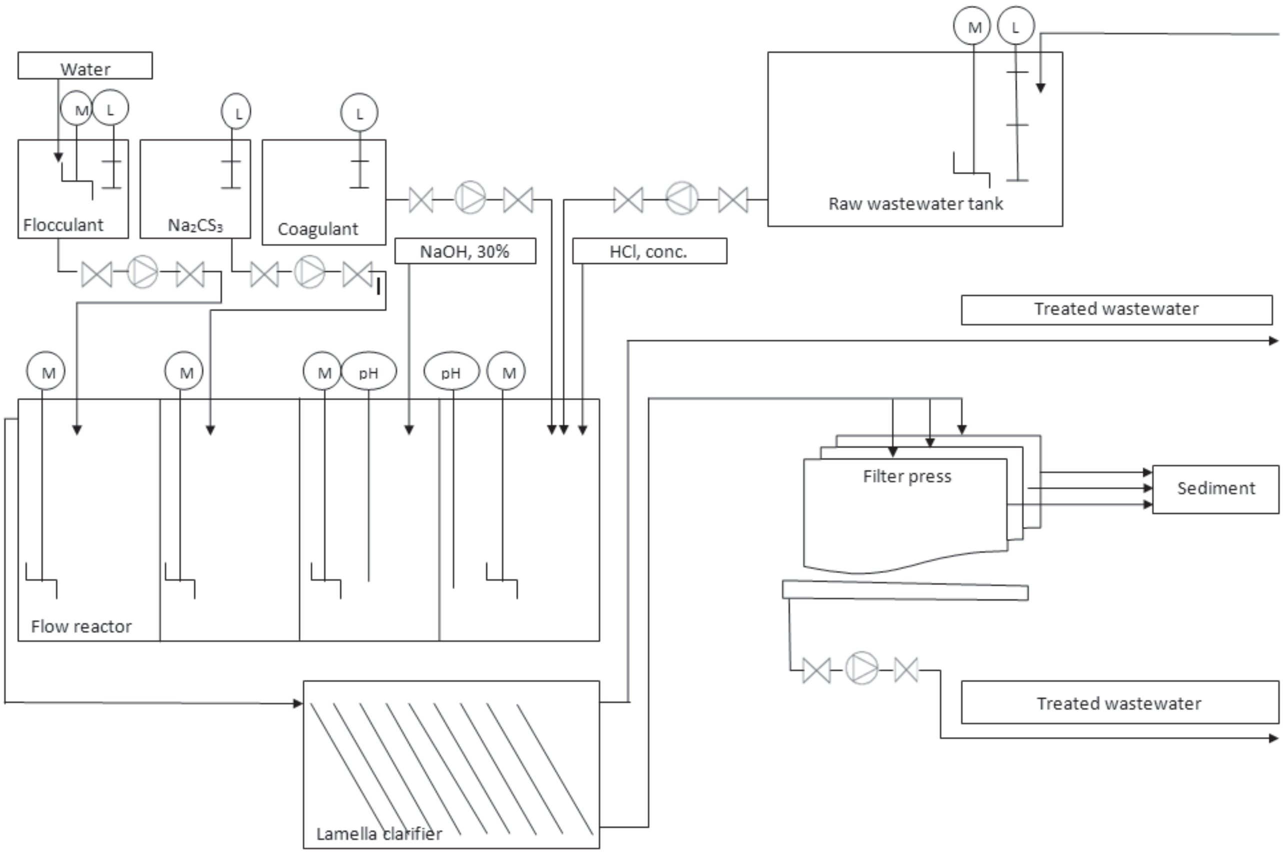

Fig. 1. Schematic diagram of the wastewater treatment plant (L-level sensor, M-stirrer, pH-pH electrode).

the lamellar settler, where sedimentation of sediment took place, which was then directed by means of a spiral pump to the chamber press, while the treated wastewater was discharged into the well of treated wastewater.

Each of the flow reactor chambers was equipped with either fast- or low-speed agitators, and the first and second chamber additionally in the pH electrodes. The amount of dosed 30% of NaOH (final pH in the second chamber) was adjusted in such a way that after dosing 44.26% of Na_2CS_3, the final pH of the wastewater was about 9-9.5 and nearly complete precipitation of the metals occurred. Once the correct dosage was accomplished, for six consecutive days during normal plant operation, a sample of raw wastewater was pumped to the flow reactor and treated wastewater flowing from the well of treated wastewater to the municipal sewer system in order to determine pH, turbidity, colour, and concentration of Al, Fe, Cu, Ni, Sn, and S^{2-}.

Experimental Design

Optimizing heavy metal precipitation from industrial wastewater was carried out using the surface response method and *Statistica 10* software. The following values were adopted for determining dependent and independent variables: $\mathbf{x_1}$ – pH, $\mathbf{x_2}$ – Na_2EDTA concentration, mg/L, $\mathbf{x_3}$ – 44.26% dose of Na_2CS_3, mL/L wastewater and $\mathbf{Z_1}$ - $\sum_{\text{of metals}}$, i.e.: sum of Cu^{2+}, Ni^{2+} and Sn^{2+} concentrations in treated wastewater, in mg/L. Based on the analysis of the preliminary research carried out by the authors and literature review, it was assumed that one of the conditions for obtaining low concentrations of metals in treated wastewater was wastewater pH 9, while a dose of 44.26% Na_2CS_3 per 1 L of examined wastewater ($\mathbf{x_3}$) should be 0.13-0.19 mL, which is about 50% of the stoichiometric dose. On the basis of raw wastewater tests it was found that the concentration of complex compounds expressed as Na_2EDTA is 20.9 mg/L. Therefore, while planning the experiment, the concentration of Na_2EDTA ($\mathbf{x_2}$) in the range of 25-75 mg/L was adopted, while taking into account the possibility of increasing the concentration of complexing compounds in industrial wastewater, and the necessity of demonstrating the effectiveness or ineffectiveness of the proposed technology, also in the case of increased concentrations of substances hindering the precipitation of heavy metals. At pH ($\mathbf{x_1}$), the values of 8.75-9.25 were adopted to precipitate the predominant amount of heavy metals contained in the wastewater in the form of hydroxides. Finally: $\mathbf{x_1} \in \langle 8.75; 9.25 \rangle$, $\mathbf{x_2} \in \langle 40.0; 60.0 \rangle$, and $\mathbf{x_3} \in \langle 0.13; 0.19 \rangle$ were adopted. It was assumed that the given ranges would be normalized in the range $\langle -1, +1 \rangle$, which means: $\mathbf{x_{1(-1)}} = 8.75$, $\mathbf{x_{1(0)}} = 9.00$, $\mathbf{x_{1(+1)}} = 9.25$, $\mathbf{x_{2(-1)}} = 40.0$, $\mathbf{x_{2(0)}} = 50.0$, $\mathbf{x_{2(+1)}} = 60.0$, $\mathbf{x_{3(-1)}} = 0.13$, $\mathbf{x_{3(0)}} = 0.16$, and $\mathbf{x_{1(+1)}} = 0.19$. The initially adopted ranges were extended, which

Table 1. Physicochemical parameters of wastewater from PCB production.

Parameter	Unit	Value
pH	-	1.80
Electrical conductivity at 20ºC	µS/cm	6,570
Turbidity	NTU	26
Colour	mg Pt/L	20
Chemical oxygen demand (COD)	mg O_2/L	150
Total organic carbon (TOC)	mg/L	48
Chlorides	mg/L	460
Sulfates	mg/L	200
Copper	mg/L	70.80
Tin	mg/L	3.36
Nickel	mg/L	1.10
Complexing agents (as Na_2EDTA)	mg/L	20.9

resulted from normalization in the range of <-α, α> instead of the predefined normalization in the range <-1,1>, for which α = 1. After accepting α = 1.6818 from the experiment plan, the ranges of the given parameters assumed the following values: $\mathbf{x}_{1(-\alpha)} = 8.58$, $\mathbf{x}_{1(0)} = 9.00$, $\mathbf{x}_{1(+\alpha)} = 9.42$, $\mathbf{x}_{2(-\alpha)} = 33.2$, $\mathbf{x}_{2(0)} = 50.0$, $\mathbf{x}_{2(+\alpha)} = 66.8$, $\mathbf{x}_{3(-\alpha)} = 0.11$, $\mathbf{x}_{3(0)} = 0.16$, and $\mathbf{x}_{1(+\alpha)} = 0.21$. The experiment was planned using the experimental planning module in the Statistica 10 programme. Central composite design was used for planning, and 16 experiments were performed for three independent factors, i.e.: pH, Na_2EDTA concentration, and Na_2CS_3 dose as shown in Table 3. According to the presented plan, 16 experiments were performed, including two experiments (15C and 16C) in design centre using raw wastewater of the composition shown in Table 1.

Concentrations of individual metals determined in the treated wastewater were used to calculate the sum of metals expressed in mg/L. In the case of Sn^{2+} concentration (values <0.05 mg/L), the value 0 mg/L was used to calculate total concentration.

Table 2. Physicochemical parameters of wastewater treated using stoichiometric doses of Na_2S, Furosep CW3, TMT 15, and Na_2CS_3.

Parameter	Unit	Value	
Precipitation using stoichiometric doses of Na_2S			
pH	-	7.51	
Cu	mg/L	1.51	
Sn	mg/L	<0.005	
Ni	mg/L	0.012	
S^{2-}	mg/L	< 0.1	
$V_{\text{of sludge after 30 min. sediment.}}$	mL	120	
Precipitation using stoichiometric doses of Furosep CW3			
pH	-	7.52	
Cu	mg/L	3.49	
Sn	mg/L	<0.005	
Ni	mg/L	0.054	
S^{2-}	mg/L	< 0.1	
$V_{\text{of sludge after 30 min. sediment.}}$	mL	230	
Precipitation using stoichiometric doses of TMT 15			
Precipitation stage		I stage	II stage
pH	-	8.95	9.03
Cu	mg/L	10.5	1.02
Sn	mg/L	<0.005	0.031
Ni	mg/L	0.0099	0.011
S^{2-}	mg/L	< 0.1	< 0.1
$V_{\text{of sludge after 30 min. sediment.}}$	mL	35	10
Precipitation using stoichiometric doses of Na_2CS_3			
pH	-	9.21	
Cu	mg/L	0.09	
Sn	mg/L	<0.005	
Ni	mg/L	0.009	
S^{2-}	mg/L	< 0.1	
$V_{\text{of sludge after 30 min. sediment.}}$	mL	95	

Results and Discussion

Table 2 shows the test results of treated wastewater obtained as a result of using stoichiometric doses of Na_2S, TMT 15, Furosep CW3, and Na_2CS_3 for precipitation. As a result of the tests carried out, treated wastewater was obtained which contained in each case small amounts of Ni^{2+} and Sn^{2+} ions in the range of 0.009-0.054 mg/L and <0.005-0.031 mg/L, respectively. Wastewater with the lowest content of Cu^{2+} ions, i.e., 0.09 mg/L, was obtained in an experiment where the stoichiometric amount of Na_2CS_3 was used to precipitate. In the remaining experiments, final concentrations of the Cu^{2+} ions ranged from 1.02 to 3.49 mg/L, which probably indicates the need to use some excess of these reagents to further reduce the concentration of Cu^{2+} ions. In the course of the study using Na_2S, a delicate smell of H_2S was felt during the initial precipitation phase, which was not observed in the other cases. The use of TMT 15 for precipitation of metals from wastewater containing both Cu^{2+} and Ni^{2+} ions was associated with the need for two-stage treatment and a long sedimentation time for precipitated sediments. The precipitated sediment, similar to

Table 3. Experimental conditions and results of central composite design.

The number of the experiment	Variables			Response			
	Factor 1	Factor 2	Factor 3				
	pH	Na_2EDTA, mL/L	Na_2CS_3 mL/L	Cu, mg/L	Ni, mg/L	Sn, mg/L	$\sum_{\text{of metals,}}$ mg/L
1	8.75	40.0	0.13	0.765	0.025	<0.05	0.49
2	8.75	40.0	0.19	0.605	0.025	<0.05	0.35
3	8.75	60.0	0.13	1.022	0.028	<0.05	0.78
4	8.75	60.0	0.19	0.923	0.027	<0.05	0.67
5	9.25	40.0	0.13	0.368	0.012	<0.05	0.31
6	9.25	40.0	0.19	0.309	0.011	<0.05	0.20
7	9.25	60.0	0.13	0.457	0.013	<0.05	0.45
8	9.25	60.0	0.19	0.398	0.012	<0.05	0.17
9	8.58	50.0	0.16	1.038	0.052	<0.05	1.17
10	9.42	50.0	0.16	0.365	0.015	<0.05	0.56
11	9.00	33.2	0.16	0.272	0.028	<0.05	0.31
12	9.00	66.8	0.16	0.649	0.040	<0.05	0.55
13	9.00	50.0	0.11	0.465	0.040	<0.05	0.40
14	9.00	50.0	0.21	0.049	0.020	<0.05	0.07
15(C)	9.00	50.0	0.16	0.165	0.025	<0.05	0.19
16(C)	9.00	50.0	0.16	0.176	0.023	<0.05	0.18

using Furosep®CW3, consisted of very small size flocs that were not observed while Na_2S and Na_2CS_3 were used.

The smallest, total amount of sediment (45 mL) was obtained using TMT 15 precipitation, while the use of Na_2CS_3 was associated with the formation of a slightly larger amount of sediment (95 mL). Since the use of Na_2CS_3 for precipitation proved to be the most effective, the optimization of metal removal from the examined

Table 4. Analysis of the experiment with the central composite design using Statistica 10. The sheet of estimators effects ANOVA model coefficients for the standardized values of the input values, at the significance level of 0.05 before excluding non-significant interaction of effects (4A) and after excluding non-significant interaction of effects (4B).

4A									
Parameter	Evaluation of the effects, ∑, mg/L, $R^2 = 0.9616$, $R^2_{adj.} = 0.9040$ 3 parameters, 1 block, 16 experiments, MS = 0.0075								
	Effect	Standard error	p-value	-95%, confidence intervals	+95%, confidence intervals	Factor	Standard error of factor	-95%, confidence intervals	+95%, confidence intervals
Constant Value	0.195	0.061	0.0187	0.046	0.344	0.195	0.061	0.046	0.344
pH, (L)	-0.320	0.047	0.0005	-0.435	-0.206	-0.160	0.023	-0.217	-0.103
pH (Q)	0.433	0.057	0.0003	0.294	0.572	0.217	0.028	0.147	0.286
Na_2EDTA, mg/L, (L)	0.165	0.047	0.0126	0.050	0.279	0.082	0.023	0.025	0.140
Na_2EDTA, mg/L, (Q)	0.126	0.057	0.0692	-0.013	0.265	0.063	0.028	-0.007	0.132
Na_2CS_3, mL/L, (L)	-0.175	0.047	0.0096	-0.290	-0.060	-0.088	0.023	-0.145	-0.030
Na_2CS_3, mL/L, (Q)	-0.012	0.057	0.8363	-0.151	0.127	-0.006	0.028	-0.076	0.063
pH/Na_2EDTA, (L)	-0.125	0.061	0.0870	-0.275	0.025	-0.063	0.031	-0.137	0.012
pH/Na_2CS_3 (L)	-0.035	0.061	0.5880	-0.185	0.115	-0.018	0.031	-0.092	0.057
Na_2EDTA/Na_2CS_3,(L)	-0.035	0.061	0.5880	0.185	0.115	-0.017	0.031	-0.092	0.057

Table 4. Continued.

4B									
Parameter	Evaluation of the effects, ∑, mg/L, $R^2 = 0.9307$, $R^2_{adj.} = 0.8845$ 3 parameters, 1 block, 16 experiments, MS = 0.0090								
	Effect	Standard error	p-value	-95%, confidence intervals	+95%, confidence intervals	Factor	Standard error of factor	-95%, confidence intervals	+95%, confidence intervals
Constant Value	0.195	0.067	0.0172	0.044	0.346	0.195	0.067	0.044	0.346
pH, (L)	-0.320	0.051	0.0002	-0.436	-0.204	-0.160	0.026	-0.218	-0.102
pH (Q)	0.433	0.062	0.0001	0.292	0.574	0.217	0.031	0.146	0.287
Na_2EDTA, mg/L, (L)	0.165	0.051	0.0108	0.048	0.281	0.082	0.026	0.024	0.140
Na_2EDTA, mg/L, (Q)	0.126	0.062	0.0748	-0.015	0.267	0.063	0.031	-0.008	0.133
Na_2CS_3, mL/L, (L)	-0.175	0.051	0.0078	-0.291	-0.059	-0.088	0.026	-0.146	-0.029
Na_2CS_3, mL/L, (Q)	-0.012	0.062	0.8484	-0.153	0.129	-0.006	0.031	-0.077	0.064

wastewater was carried out using this reagent. Table 3 shows the concentrations of copper, nickel, and tin in treated wastewater obtained in each of the 16 experiments conducted according to the generated design. The smallest value of the sum of metals was obtained in the 14th experiment, and the largest in the third experiment (i.e., 0.07 and 0.78 mg/L, respectively). Table 4A shows a sheet of ANOVA estimator effects and model coefficients for normalized input values, which are the result of a preliminary statistical analysis of the experimental data. Although the conducted statistical analysis indicated five statistically significant parameters, all major linear-quadratic effects were adopted for further analysis while the non-significant effects of linear-linear interactions (i.e., pH/EDTA(L), pH /Na_2CS_3(L) and Na_2EDTA/Na_2CS_3(L)), for which p>0.05 were excluded from the model. The results of the re-conducted analysis, excluding non-significant interactions, are presented in Table 4B. As a result of the analysis, coefficients of approximation function shown in the 'effect' column were obtained and the verification of significance was carried out under the assumed significance level of $\alpha = 0.05$. The conducted analysis confirmed the significance of five coefficients while the calculated coefficient of determination (R^2) was 0.9307, and the corrected coefficient of determination ($R^2_{adj.}$) was 0.8845, which means that 88.45% of the dependent variable can be explained by a square model. The values of both coefficients indicated a good adjustment of the model to the experimental data, despite the exclusion of linear-linear interaction of effects. An increased R^2 value can be achieved by adding statistically insignificant variables (Table 4A), thus a better indicator of model adjustment for experimental data is $R^2_{adj.}$[18]. It should also be noted that after excluding statistically insignificant linear-linear interactions from the model, the difference R^2-$R^2_{adj.}$ is smaller (0.0462) than for the model taking into account the presence of these variables (0.0576).

The analysis also yielded a small mean square error (MS), i.e., 0.009. Table 5 shows the adequacy verification

Table 5. Analysis of the experiment with the central composite design using Statistica 10. The verification of the adequacy of the model using ANOVA at the significance level of 0.05 after excluding the non-significant linear-linear interaction of effects.

Parameter	Evaluation of the effects, ∑, mg/L, $R^2 = 0.9307$, $R^2_{adj.} = 0.8845$ 3 parameters, 1 block, 16 experiments, MS = 0.0090			
	SS	MS	F	p-value
pH, (L)	0.350	0.350	38.848	0.0002
pH, (Q)	0.435	0.435	48.262	0.0001
Na_2EDTA, mg/L, (L)	0.092	0.092	10.265	0.0108
Na_2EDTA, mg/L, (Q)	0.037	0.037	4.0580	0.0748
Na_2CS_3, mL/L, (L)	0.105	0.105	11.610	0.0078
Na_2CS_3, mL/L, (Q)	0.001	0.001	0.039	0.8484

SS-predicted residual error sum of squares, MS-mean square, F-statistics

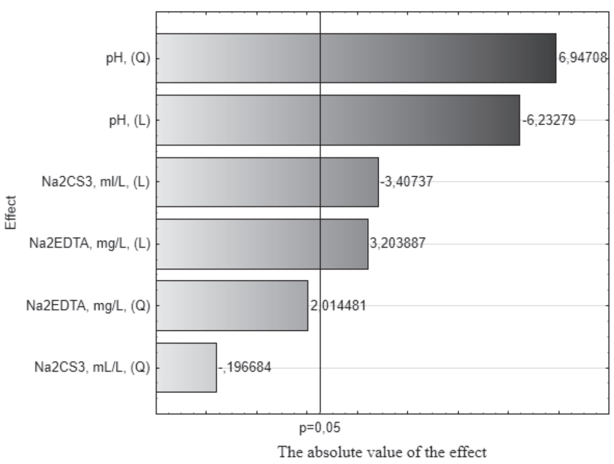

Fig. 2. Pareto chart showing the absolute value of standardized assessment of the effects ($\sum_{\text{of metals}}$, mg/L, 3 values, 1 block, 16 experiments, MS = 0.0090).

with the use of ANOVA. The adequacy verification performed using ANOVA indicated the importance of four main input parameters, i.e., pH(L), pH(Q), Na_2EDTA(L), and Na_2CS_3(L). Fig. 2 shows a Pareto chart showing estimators of standardized effects that were ordered according to their absolute value, while the vertical line shows the minimum values of statistically significant effects at significance level α = 0.05. The data presented in Fig. 2 shows the significance of four main factors, i.e., pH(Q), pH(L), Na_2CS_3(L), and Na_2EDTA(L), and non-significance (or minor significance) of the two main factors, i.e., Na_2EDTA(Q) and Na_2CS_3(Q). In order to visually verify the quality of the adjustment of the experimental data to the created model, a graph of the dependence of the estimated values versus the observed values was presented in Fig. 3.

The presented relationship shows a good adjustment of the experimental values to the approximated values, which, combined with the values of the calculated

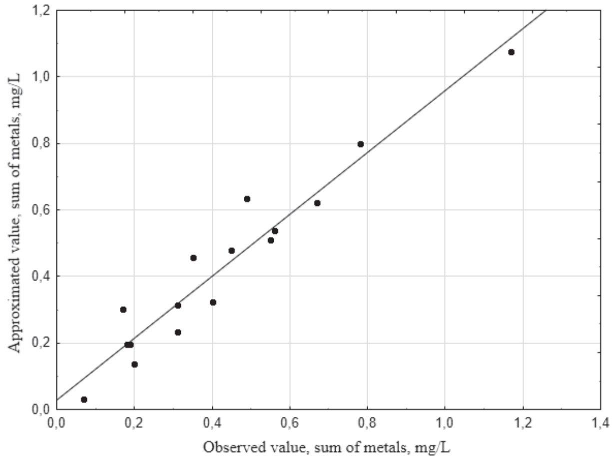

Fig. 3. Estimated vs. observed value plots ($\sum_{\text{of metals}}$, mg/L, 3 values, 1 block, 16 experiments, MS = 0.0090).

determinants for the model, indicates that the created model is suitable for the obtained experimental data. Fig. 4a) presents a change in the sum of metals in relation to Na_2EDTA and pH, assuming constant dose of Na_2CS_3 0.13 mL/L. The conducted model studies indicated that at a fixed dose of Na_2CS_3 of 0.13 mL/L and Na_2EDTA concentration of c.a. 34-53 mg/L, the use of precipitation pH of about 8.9-9.2 resulted in the wastewater having the smallest value of total metal content. Model studies have shown that, as Na_2EDTA concentration increases, the total metal content is also increased, which means that they are difficult to remove with the adopted dose of Na_2CS_3. There is also a slight reversal trend that involves the increase in the sum of metals as Na_2EDTA concentration decreases. This seemingly abnormal relationship may be due to the application of the Na_2EDTA addition just before the start of the precipitation process to achieve the concentrations specified in the experimental plan (raw wastewater contained 20.9 mg/L Na_2EDTA) and disturbance of the balance of complexing reaction in the examined wastewater (presence of Cu^{2+} ions, $Cu(OH)_2$ sediment, Fe^{3+} ions, $Fe(OH)_3$ sediment, and other ions and pH changes). This may also be due to the properties of the response surface method that optimizes the process, indicating the optimum reaction process. The mathematical description of the change in the sum of metals after eliminating the non-significant interaction as a function of Na_2EDTA concentration and pH, assuming the use of constant dose of Na_2CS_3 for precipitation (i.e., 0.13 mL/L, is presented by Equation (1):

$$\sum_{\text{of metals}} = 287.838 - 63.023[\text{pH}] + 3.466[\text{pH}]^2 - 0.055[Na_2EDTA] + 0.001[Na_2EDTA]^2 \quad (1)$$

Fig. 4b) depicts a change in the sum of metals depending on the dose of Na_2CS_3 and pH, assuming a constant concentration of Na_2EDTA 50 mg/L. The model study indicated that the smallest values of total metal content in treated wastewater were obtained in the pH range of 9-9.15 using c.a. 0.21 mL/L of Na_2CS_3 solution for precipitation and a fixed dose of Na_2EDTA 50 mg/L. The obtained results again pointed to the need to conduct the process at the optimum pH range, since as pH increases or decreases, the total metal content increases. In addition, as the dose of the precipitant increases, the total metal content is reduced, but it is the largest in the optimum pH range, where the efficiency of the precipitant is the greatest. The mathematical description of the change in total metal content, after elimination from the model of non-significant interaction as a function of Na_2CS_3 dose and pH (assuming constant Na_2EDTA concentration, i.e., 50 mg/L), as presented by Equation (2):

$$\sum_{\text{of metals}} = 286.971 - 63.023[\text{pH}] + 3.466[\text{pH}]^2 - 0.736[Na_2CS_3] - 6.814[Na_2CS_3]^2 \quad (2)$$

Fig. 4c) depicts a change in total metal content depending on the dose of Na_2CS_3 and Na_2EDTA concentrations assuming a constant value of pH 9. The lowest total metal values were obtained with a Na_2CS_3 dose of 0.21 mL/L and EDTA concentration within 36-50 mg/L and constant value of pH 9. Model studies have shown that as Na_2CS_3 dose increases, a decrease in total metal content is observed, and a similar correlation is observed when the concentration of the complexing compound decreases (i.e., Na_2EDTA). The reasons for a slight increase in total metal content due to the reduction in Na_2EDTA concentration shown in Fig. 4c) may be similar to those discussing the similar relationship shown in Fig. 4a). The mathematical description of the change in total metal content, after eliminating non-significant interactions as a function of Na_2CS_3 dose and Na_2EDTA concentration from the model (assuming a constant pH value of 9), is shown by Equation (3):

$$\sum_{\text{of metals}} = 1.646 - 0.055[Na_2EDTA] + 0.001[Na_2EDTA]^2 - 0.736[Na_2CS_3] - 6.814[Na_2CS_3]^2 \quad (3)$$

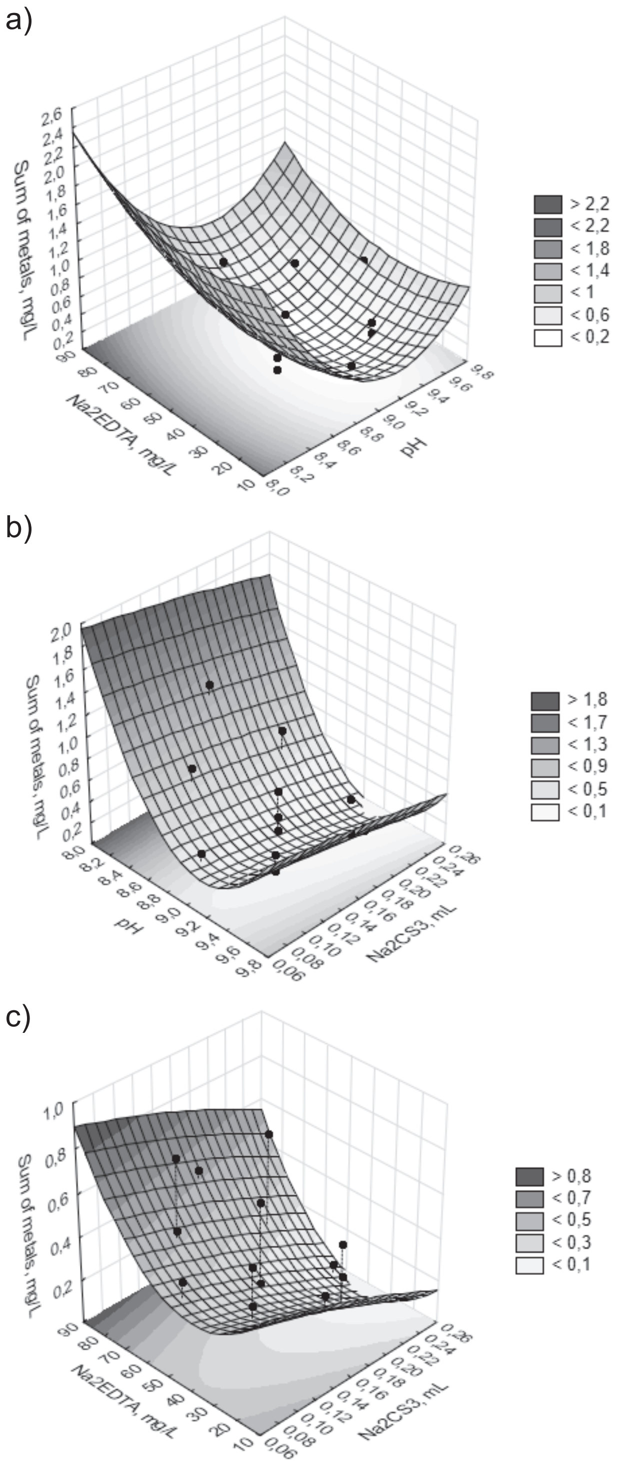

Fig. 4. Response surface plots for $\sum_{\text{of metals}}$ (mg/L) with respect to Na_2EDTA and pH a), Na_2CS_3 and pH b), and Na_2CS_3 and Na_2EDTA c).

Table 6 shows the determination coefficients for the full model, taking into account all major linear-quadratic effects and linear-linear interaction effects (i.e., pH/EDTA(L), pH/Na_2CS_3(L), and Na_2EDTA/ Na_2CS_3(L)). To determine the approximation polynomial for the experimental data presented in Table 3, the general linear model (GLM) was adopted, using effects adjusted to the intergroup system, assuming that the grade II polynomial would be appropriate to describe precipitation of heavy metals from wastewater using Na_2CS_3 in the presence of Na_2EDTA. An approximation polynomial was obtained in the form of a 'forecast equation,' which describes the change in values of $\sum_{\text{of metals}}$ as a function of all independent factors, i.e., pH, Na_2EDTA concentration, and Na_2CS_3:

$$\sum_{\text{ofmetals}} = 273.100 - 61.400[pH] + 3.466[pH]^2 + 0.180[Na_2EDTA] + 0.001[Na_2EDTA]^2 + 23.180[Na_2CS_3] - 6.810[Na_2CS_3]^2 - 0.025[pH][Na_2EDTA] - 2.330[pH][Na_2CS_3] - 0.058[Na_2EDTA][Na_2CS_3] \quad (4)$$

The determinant for the full model (R^2 = 0.962) indicates a very good adjustment of the model to the experimental data, as well as the corrected coefficient of determination ($R^2_{adj.}$ = 0.904). When all variables are included together with statistically non-significant ones, the difference R^2-$R^2_{adj.}$ is 0.058 and is it is slightly higher than for the model that does not take into account statistically non-significant linear-linear interactions (0.046). According to the authors, in the case of such small differences in determination coefficient values, a full model can also be applied to the mathematical description of the process of heavy metals removal from the examined wastewater. At the same time, the high value of the obtained adjusted coefficient of determination indicates a very good adjustment of the model approximating the equation to a set of other experimental data derived from precipitation processes of heavy metals from wastewater of a similar composition, derived from the processes of PCBs with Na_2CS_3 in the presence of Na_2EDTA and

Table 6. Value of the determination coefficient (R) for the full model – a general linear model method.

Parameter	Test SS for the full model relative to the SS for the rest							
	R^2	$R^2_{adj.}$	SS Model	MS Model	SS Rest	MS Rest	F	p-value
$\sum_{\text{of metals}}$, mg/L	0.962	0.904	1.124	0.125	0.045	0.007	16.692	0.001

SS-predicted residual error sum of squares, MS-mean square, F-statistics

using the optimum PH range. Industrial tests were also carried out in a continuous treatment plant using Na_2CS_3 solution proportionally to the wastewater flow rate and heavy metals content, so as to obtain treated wastewater in which the maximum concentrations of the individual metals and sulphides would meet the requirements to which a wastewater treatment plant introducing treated wastewater to sewerage facilities is obliged (Cu 1 mg/L, Ni 0.5 mg/L, Sn 2 mg/L, and S^{2-} 1.0 mg/L). Table 7 shows the results of raw and treated wastewater with the use of Na_2CS_3 solution for precipitation. Due to the heterogeneous composition of wastewater – despite using storage tanks in a wastewater treatment plant which also fulfilled the function of averaging tanks – an increased dose of Na_2CS_3 solution was used, which enabled us to obtain treated wastewater containing very small amounts of metals and some excess precipitant causing an increase in S^{2-} ions in treated wastewater (0.2-0.4 mg/L). In none of these cases did values exceed the maximum possible sulphide concentrations in treated wastewater (1 mg/l). It is likely that in addition to the changes in metal concentrations in wastewater entering the treatment plant, there were also periodic changes in the concentration of complexing agents, which affected the effectiveness of the precipitant and was related to its temporary lower or higher demand. As a result of the adjustment of the dose of Na_2CS_3 solution, the wastewater was obtained in which the concentration of Cu^{2+} ions ranged between <0.005-0.014 mg/L and for Ni^{2+} and Sn^{2+} ions amounting to <0.01 and <0.005 mg/L, respectively. In none of these cases was the permissible value specified in the water-law permit for the plant for each metal that has not been exceeded. As a result of the adopted method of metal precipitation, almost transparent and colourless wastewater with a low content of heavy metals was obtained, and the presented dosing method, consisting of adjusting the dose of Na_2CS_3 solution to the flow rate and metal content in wastewater, only requires the installation of the metering pump and the initial metal concentration control and a precipitant in treated wastewater at the dose adjustment phase, provided that an inflow of raw wastewater of uniform composition to the wastewater treatment plant is ensured.

Conclusions

Industrial wastewater from PCB production contains, in addition to heavy metal ions, complexing compounds that impede the quantitative removal of metals from wastewater. The laboratory scale tests allowed the choice of the precipitant (Na_2CS_3) which, when used in the treatment of examined wastewater, guaranteed the effective removal of heavy metals. Optimization studies using the surface response method have allowed us to analyse the influence of particular parameters on the wastewater treatment efficiency expressed by the concentration of individual metals in the treated

Table 7. Physicochemical parameters of raw wastewater and wastewater treated using Na_2CS_3 (*1 – raw wastewater, 1A – treated wastewater, etc.).

Parameter	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
	1*	1A*	2	2A	3	3A	4	4A	5	5A	6	6A
pH	2.5	8.0	5.9	9.1	6.4	9.5	6.3	9.5	6.9	9.4	6.0	9.6
Turbidity, NTU-IR	8.6	7.5	17	7.6	27	4.4	31	5.4	12	2.9	7.8	5.4
Colour, mg Pt/L	12	21	10	20	8	18	16	18	19	19	11	19
Al, mg/L	-	<0.03	-	<0.03	-	<0.03	-	<0.03	-	<0.03	-	<0.03
Fe, mg/L	-	0.3	-	0.5	-	0.5	-	0.4	-	0.3	-	0.2
Cu, mg/L	26.9	0.008	19.1	0.011	18.1	0.012	14.6	<0.005	7.10	0.014	85.0	<0.005
Sn, mg/L	2.69	<0.005	1.13	<0.005	5.05	<0.005	2.51	<0.005	0.71	<0.005	4.3	<0.005
Ni, mg/L	0.031	<0.01	0.068	<0.005	0.034	<0.005	0.045	<0.01	0.041	0.008	0.76	<0.005
S^{2-}, mg/L	<0.1	0.4	<0.1	0.4	<0.1	0.3	<0.1	0.20	<0.1	0.1	<0.1	0.3

wastewater. According to the authors, the use of methods for planning experiments to optimize wastewater treatment processes is very useful and fully justified, but the interpretation of the obtained results always requires critical analysis in the context of knowledge of the technological process and the chemical reactions taking place. The use of Na_2CS_3 on an industrial scale enabled the efficient precipitation of metals from wastewater and, consequently, the production of treated wastewater with parameters complying with the requirements of the relevant legal norms issued for wastewater treatment plants introducing wastewater to wastewater facilities.

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