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Removal of copper, nickel and tin from model and real industrial wastewater using sodium trithiocarbonate. The negative impact of complexing compounds

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Abstract: The possibility of Cu(II), Ni(II) and Sn(II) removal from model solutions and real wastewater from the production of PCBs using Na_2CS_3 for precipitation was presented in this paper. The testing was carried out on a laboratory scale using model and real industrial wastewater containing additives in the form of complexing compounds used in the production of PCBs (Na_2EDTA, $NH_{3(aq)}$, thiourea) and recommended by the USEPA (Na_3MGDA, Na_4GLDA). Application of Na_2CS_3 in optimal conditions of conducting precipitation process was connected with obtaining wastewater containing low concentrations of metals (Cu 0.02 mg/L, Sn <0.01 mg/L, Ni <0.005 mg/L at pH 9.39 and Cu 0.07 mg/L, Sn <0.01 mg/L, Ni 0.006 mg/L at pH 7.79). Controlled application of Na_2CS_3 by the use of a platinum redox electrode was also connected with obtaining treated wastewater containing low concentrations of metals (Cu 0.019 mg/L, Sn <0.05 mg/L, Ni <0.0098 mg/L at pH 9–9.5 and E= -142 mV in the laboratory scale and Cu 0.058 mg/L, Sn <0.005 mg/L, Ni 0.011 mg/L at pH 9.14 and E= +10 mV in the industrial scale). Changing the value of redox potential of treated wastewater by dosing Na_2CS_3 made it possible to control the precipitation process on laboratory and industrial scale by the use of a platinum redox electrode. Controlled application of Na_2CS_3 can be used to remove Cu(II), Ni(II) and Sn(II) from industrial effluent containing chelating compounds like Na_2EDTA, $NH_{3(aq)}$, thiourea, Na_3MGDA and Na_4GLDA.

Introduction

Despite many studies and enormous technological progress that has been made in the recent years in the field of wastewater treatment, there are still many problems of a technical or technological nature. These problems are generally connected with unsatisfactory performance of specific treatment methods, expressed as abnormal concentration of substances undesirable in the treated wastewater, which is often the result of non-uniform composition of wastewater, varied concentrations of organic compounds and specific physicochemical properties of harmful substances present in wastewater. Efficient use of water, associated with the use of modern industrial processes, usually results in the increased concentrations of toxic substances in raw wastewater. These conditions lead to the need for using increasingly sophisticated methods of wastewater treatment, and often in order to obtain wastewater whose quality is in accordance with current standard regulations, it is necessary to use a combination of multiple physicochemical and biological processes. Heavy metals such as copper, nickel and tin are present in raw industrial wastewater in different amounts, depending on the type of process from which they come from, the applied technology and the technical solutions as far as using water in the plant is concerned. Nickel, copper and tin content in the industrial effluents from different sources is presented in Table 1. Copper, nickel and tin have a diverse toxicity both in terms of the human body, as well as aquatic organisms, which is related to the type of metal compound, the type of an anion, an oxidation degree and also other factors specific to a given aquatic environment (Seńczuk 2012). Nickel compounds have been recognized as carcinogenous for humans (Das and Buchner 2007, IARC 1990). For this reason, and for the sake of the natural environment, precipitation of metals from wastewater is carried out, which is one of the stages of industrial waste treatment, and can be accomplished by the use of many types of precipitation methods. One of them is the precipitation of metal in the form of hydroxides. The solubility of the precipitated metal hydroxides is pH dependent, and generally decreases with the increase of pH, yet hydroxides with amphoteric properties react with the OH^- ions, which causes the transition of metals to wastewater. In the presence of ammonia, the system becomes complicated due to the formation of complex compounds and therefore the quantitative precipitation of copper is usually impossible. The negative impact of ammonia on the efficiency of Cu(II) precipitation depends on the pH of the effluent, ammonia concentration, the concentration of Cu(II) and the presence of other chemicals in wastewater

(Hartinger 1991, Cywiński et al. 1983). In the case of Sn(II) compounds, precipitation already occurs in acidic medium – above pH 4.3, the concentration of Sn(II), is less than 2 mg/L; however, above pH 9.2, dissolution of the precipitated $Sn(OH)_2$ occurs as well as transition of Sn(II) ions to the solution as a result of the formation of tin tetrahydroxy (II) ion. Sn(II) can be oxidized with oxygen present in the air to Sn(IV), which are less soluble than Sn(II) compounds (Hartinger 1991). Increasing the efficiency of removal of Cu(II) from the wastewater is increased in some cases by the use of Fe(III) ions. In this case, a process of co-precipitation of Cu(II) from Fe(III) takes place, and the addition of Fe(III) (100 mg/L) to a solution containing Cu(II) (10 mg/L) and increasing pH above 7, cause a decrease in the concentration of Cu(II) and Fe(III) to less than 0.05 mg/L (Kang et al., 2003). The preferred results can be accomplished also by the use of limestone containing 95% of $CaCO_3$, 3.5% of $MgCO_3$ and 1.5% of other components. With an initial concentration of Cu(II) of 50 mg/L, the use of limestone caused removal of approx. 90% of Cu(II), whereas the amount of the removed copper did not depend only on pH, but also on adsorption and absorption processes taking place simultaneously (Aziz et al. 2001). Satisfactory results were also obtained when using a synthetic mineral $Mg(HCO)_3(OH)\cdot 2H_2O$, which added to the wastewater in an amount of 459 mg per 1 g of copper, caused a reduction in the concentration of Cu(II) to 0.1 mg/L at the final pH of 6.8, and the precipitated sediments contained $Cu(OH)_2$, $CuCO_3$, $Cu_2(OH)_2CO_3$, $Cu_3(OH)_2(CO_3)_2$ and $Cu_4(OH)_6SO_4\cdot H_2O$ (Shan et al. 2013). Improvement in the efficiency of Cu(II) precipitation can be obtained by the use of a hydrated mixture of Fe_3O_4, in which Fe(II):Fe(III) amounts to (1–2):10. The use of FFH made it possible to reduce the concentrations of Cu and Zn in the treated wastewater to less than 0.01 mg/L (Budilovskis 1998, Budilovskis and Eshchenko 2004). Similar results were obtained by applying the ferrite produced during aeration and alkalizing of wastewater containing the addition of Fe(II). For the initial concentrations of 10 and 23 mg/L, the concentration of Cu(II) after precipitation with ferrite was 0.01 and 0.08 mg/L, respectively (UEPA 1980). In the case when there are complexed heavy metal ions in the treated wastewater, the precipitation of metal hydroxides must be preceded by the breakdown of complexes, due to the treatment of wastewater with e.g. waste acids. Reducing pH to 2 causes the complex breakdown, and increasing pH to 11 causes the precipitation of insoluble metal hydroxides. This method is not always effective, and its additional disadvantage is high salinity of wastewater (Stefanowicz 2001, Thomas et al. 2014). The presence of complexing compounds in wastewater, hindering the effective precipitation of metals, necessitates the use of more effective methods. Therefore, sulphide ions are used and metals are precipitated in the form of sulphides, whereas precipitation of metal sulphides is much more effective than the precipitation of hydroxides or metal carbonates. The source of sulphide ions can be Na_2S, NaHS, and less often CaS and FeS. Precipitation of metal sulphides (Me_nS_m) proceeds at a specific pH, after previous dissociation of precipitants with the formation of sulphide ions. Typically, the quantitative precipitation of heavy metal ions requires the use of an excess of Na_2S which must be removed by use of H_2O_2 or by oxidation with atmospheric oxygen in the final phase of wastewater treatment. The use of this method for Cu(II) precipitation in an acidic medium, involves the risk of H_2S gas separation, since in solutions of pH<5, almost 100% of the sulphide is present in the form of toxic and volatile H_2S (Hartinger 1991, Stefanowicz 2001, USEPA 1980, USEPA 1981). In view of the toxicity of H_2S, the need of reactors ventilation and maintaining far-reaching security measures, currently reagents are frequently used which are similar in efficacy, and their use is not associated with an increased risk. Typically, sodium diethyldithiocarbamate (DTC), trimercapto-s-triazine trisodium salt (TMT), sodium trithiocarbonate (TTC) are used for this purpose as well as their derivatives in the phase of the laboratory tests and laboratory research (Poradnik 2002, Hartinger 1991, Kieszkowski 1992, BLFW 2005). An effective reagent for the precipitation of Cu is HTDC (1,3,5-hexahydrotriazinedithiocarbamate) that can be used to remove Cu(II) in the form of CuEDTA, at pH 3–9 from

Table 1. Metal content in the untreated industrial wastewater

Process/Source	Metal	Quantity of metal mg/L	Reference
Untreated industrial wastewater	Cu	500–2800	Seńczuk 2012
Galvanic copper plating	Cu	36 000	Chen et al. 2013
Galvanic copper, nickel, zinc and chromium plating	Cu	283 250	Dermentzis et al. 2011 Dutta and Basu 2014
Post-treatment wastewater from chromium plating	Cu	20–250	Bartkiewicz and Umiejewska 2010
Post-treatment wastewater from alkaline cyanide zinc plating	Cu	0.2–1.8	Bartkiwiecz and Umiejewska 2010
Electroplating industrial wastewater	Ni	285–300	Sivaprakash et al. 2015
Electroplating industrial wastewater	Ni	16.3	Lekhlif et al. 2014
Electroplating industrial wastewater	Ni	10.2	Ali et al. 2014
Ammonia wastewater from syngas scrubber	Ni	2–4	Keranen et al. 2015
Industrial wastewater from the galvanic treatment	Sn	11	Torabian et al 2005
Printed circuit boards production	Sn	6.9	Thomas et al. 2014

synthetic and industrial wastewater. Ions Cu(II) form with HTDC sparingly soluble compound $[Cu_3(HTDC)_2]_n$ and thus the final concentration of Cu(II) in the treated wastewater was less than 0.5 mg/L (Fu et al. 2007). Using DTC for the treatment of galvanic wastewater containing the complexed Cu(II) at a ratio DMDTC:Cu of 0.8:1.2, allowed for their removal with the efficiency of more than 99.6% (Li eta al. 2003). For the removal of metals, xanthates (dithiocarbonates) are also used, e.g.: potassium ethyl xanthate or insoluble starch xanthates (ISX), whereas 1 g of ISX binds approx. 120 mg Cu(II) (USEPA 1981, Chang eta al. 2007, Chang eta al., 2002). By the use of DTC, TMT and TTC, it is possible to remove Cu(II), Ni(II), Sn(II) and other metals from industrial effluents, wherein these reagents have a different efficacy, depending on the composition of wastewater, the initial concentration of metals and the process conditions (Erbsloeh 2007, Evonik 2012, Bobrowska-Krajewska et al. 1994, Bobrowska--Krajewska et al. 1994). Testing of Cu(II) and Ni(II) precipitation using Na_2CS_3, confirmed the possibility of their removal from the model solutions with the efficiency of 94.0–99.9% for Cu (II) and 24.3–94.2% for Ni(II) at pH 1–13. Under the same precipitation conditions, removal efficiency of both metals using Na_2S was 56.3–99.9% for Cu(II) and 14.0–99.9% for Ni(II), respectively (Stechman and Orłowska 2010). The aim of this study was to determine the effectiveness of Na_2CS_3 as the precipitant of Cu(II), Ni(II) and Sn(II) ions from model wastewater containing metal ions as well as metal ions and complexing agents. The tests of removal efficiency of metals from real wastewater were also conducted. Wastewater came from the production of PCBs and their aim was to demonstrate the possibility of using Na_2CS_3 on an industrial scale and to verify its effectiveness in the presence of the substances absent in the model wastewater prepared in the laboratory.

Materials and methods

Materials and chemical reagents

Basic model solutions containing Cu(II), Ni(II) and Sn(II) ions were used for the study. The composition of the basic model solutions is presented in Table 2. For the preparation of model solutions the following were used: $CuSO_4 \cdot 5H_2O$ (POCH, Poland), $NiCl_2 \cdot 2H_2O$ (Chempur, Poland), $SnCl_2 \cdot 2H_2O$ (Chempur, Poland), H_2SO_4, ρ=1,84 (Chempur, Poland) as well as HCl ρ=1,18 (Chempur, Poland). The reagents of analytical purity and double-distilled water were used. Working model solutions were prepared using basic model solutions presented in Table 2, which apart from metal cations contained suitable amounts of the selected complexing compounds: Na_2EDTA (Chempur, Poland), $NH_{3(aq)}$ (Chempur, Poland), Na_3MGDA (alanine, N,N-bis(carboxymethyl)-, sodium salt, (1:3), Trilon® M, BASF AG), Na_4GLDA (tetrasodium N,N-bis(carboxylatomethyl)-L-glutamate, Dissolvine® GL, Akzo Nobel Functional Chemicals B.V.) and $(NH_2)_2{=}CS$ (Chempur, Poland). The selected complexing agents are used in the production of PCBs as components of chemical copper plating bath (Na_2EDTA), alkali etching ($NH_{3(aq)}$) and chemical tinning ($(NH_2)_2{=}CS$). In the next stage of the research, model solutions were used containing a mixture of metal cations, and the additive of Na_2EDTA as a complexing compound. Three model solutions were prepared of the smallest, the largest, and the average concentration of Cu(II), Ni (II), Sn(II) and Na_2EDTA (model solutions $A_{(min.)}$, $B_{(max.)}$, $C_{(aver.)}$, respectively). Types and composition of model solutions $A_{(min.)}$, $B_{(max.)}$, $C_{(aver.)}$ are shown in Table 3. In this case, the assumed values of metal concentrations and Na_2EDTA corresponded to the smallest and the largest values of metal concentrations and complexing compounds which are determined by the authors in the wastewater from the production of PCBs at the stage of preliminary studies. Research on real wastewater was conducted using raw wastewater collected in a wastewater treatment plant of PCB production located in Poland. Raw wastewater flowed through pipelines from the machines into storage tanks located at the wastewater treatment plant, followed by their mixing. Samples of raw wastewater were collected for 5 consecutive days, and then their composition averaged by mixing. The collected samples of wastewater and averaged sample for the study were not fixed and their physical and chemical composition is shown in Table 4. Na_2CS_3 was used (sodium trithiocarbonate, KiZChS Siarkopol S.A., Poland) as the precipitant at various concentrations, as shown in Table 5. In addition, the coagulant was used $FeCl_3$ (Donau Klar® Smart, Donauchem, Poland), polyaluminum chloride (Donau PAC® Activis, Donauchem, Poland), and the anionic flocculant (0.05% Furoflock CW277, Chemische Fabrik Wocklum GmbH & Co. KG, Germany).

Analytical methods

The reaction was measured by means of a device WTWinolab pH/IONCond 750, using a combination electrode by SenTix81 according to PN-EN ISO 10523:2012, and electrical conductivity using the electrode TetraCon325 according to PN-EN 27888:1999. Redox potential was determined by means of a multifunctional device Elmetron CPC411 using a platinum electrode ErPt-11 (Hydromet, Poland). Turbidity was determined by nephelometric method using a turbidimeter

Table 2. Types and compositions of model solutions

The name of the model solution	The quantity of the metal salt	The quantity of the acids	The metal concentration in the model solution
The model solution of Cu(II)	3.923 g of $CuSO_4 \cdot 5H_2O$ per 10 L of water	H_2SO_4, ρ = 1.84 g/mL 10 mL per 10 L of solutions	109.0 mg/L
The model solution of Ni(II)	4.050 g of $NiCl_2 \cdot 2H_2O$ per 10 L of water	HCl, ρ = 1.18 g/mL 10 mL per 10 L of solutions	100.0 mg/L
The model solution of Sn(II)	1.901 g of $SnCl_2 \cdot 2H_2O$ per 10 L of water	HCl, ρ = 1.18 g/mL 20 mL per 10 L of solutions	100.0 mg/L

Cyberscan IR Turbidimeter TB1000 according to PN-ISO 7027:2003, and the colour with a spectrophotometer SPEKOL 1200 according to ISO 7887:2012. COD (Chemical Oxygen Demand) was determined by means of spectrophotometric method using sealed test tubes and spectrophotometer Spekol 1200 according to PN-ISO 15705:2005, and TOC (Total Organic Carbon) by means of high-temperature combustion method at 680ºC with IR detection using the analyzer TOC-L_{CPH} by Shimadzu in compliance with 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) and phosphorus were determined by adopting ISP-OES using Optima 5300DV spectrometer by Perkin Elmer according to PN-EN ISO 11885:2009. Complexing compounds were determined by spectrophotometric method in compliance with Nanocolor® Organische Komplexbildner 10 (Bi(III)/xylenol orange), according to DIN 38409-H26, followed by the calculation from an index of bismuth complex (I_{BiK}): 1 mg/L I_{BiK}=1.4 mg/L EDTA=1.61 mg/L Na_2EDTA. Sulphides were determined by the spectrophotometric method in accordance with Visocolor® Sulphides 0.1–0.8 mg/L (sulphide/N,N-

Table 3. Types and compositions of model solutions ($A_{(min.)}$, $B_{(max.)}$, $C_{(aver.)}$)

The name of the model solution	The composition of the model solution (per 1 L of solution)	The quantity of the acids	The metal concentration in the model solution
The model solution $A_{(min.)}$	15.69 mL of model solution of Cu^{2+} 1.60 mL of model solution of Sn^{2+} 0.24 L of model solution of Ni^{2+}	HCl, ρ = 1.18 g/mL 1 mL per 1 L of solutions	Cu 1.60 mg/L Sn 0.15 mg/L Ni 0.025 mg/L Na_2EDTA < 0.8 mg/L
The model solution $B_{(max.)}$	0.680 g of $CuSO_4{\cdot}5H_2O$ 0.114 g of $SnCl_2{\cdot}2H_2O$ 0.019 g of $NiCl_2{\cdot}2H_2O$ 0.058 g of $Na_2EDTA{\cdot}2H_2O$	HCl, ρ = 1.18 g/mL 10 mL per 1 L of solutions	Cu 173.0 mg/L Sn 59.9 mg/L Ni 4.75 mg/L Na_2EDTA 52.1 mg/L
The model solution $C_{(aver.)}$	0.346 g of $CuSO_4{\cdot}5H_2O$ 0.034 g of $SnCl_2{\cdot}2H_2O$ 7 mL of model solution of Ni^{2+} 0.028 g of $Na_2EDTA{\cdot}2H_2O$	HCl, ρ = 1.18 g/mL 10 mL per 1 L of solutions	Cu 88.1 mg/L Sn 18.4 mg/L Ni 0.70 mg/L Na_2EDTA 25.0 mg/L

Table 4. Physicochemical parameters of wastewater from production of PCB

Parameter	Unit	Value
pH	–	1.80
Electrical conductivity in 20ºC	μS/cm	6570
Turbidity	NTU	26
Colour	mg Pt/L	20
Chemical Oxygen Demand (COD)	mg O_2/L	150
Total Organic Carbon (TOC)	mg/L	48
Total phosphorus	mg/L	0.90
Chlorides	mg/L	460
Sulphates	mg/L	200
Copper	mg/L	70.80
Tin	mg/L	3.36
Nickel	mg/L	1.10
Complexing agents (Na_2EDTA)	mg/L	20.9

Table 5. Physicochemical parameters of sodium trithiocarbonate solutions

Parameter	Unit	The stock solution	The solution No. 1	The solution No. 2
Density in 18°C	g/L	1.388	1.083	1.009
Sodium trithiocarbonate	%	44.26	10.00	1.01
Sum of sulphites and thiosulphates	%	0.77	0.12	< 0.1
Iron	%	0.01	< 0.01	< 0.01

dimethyl-1,4-phenylenediamine/Fe(III)). For the determination of Na_2CS_3 content in the used solutions, the iodometry was used in which Na_2CS_3, after decomposition in acidic medium was determined as Na_2S. Then, from the total amount of reducing substances, the correction for the content of reducing additives (sulphates(IV) and thiosulphates(VI)) was subtracted according to PN-C-84042. The following conversion of the determined content of Na_2S to Na_2CS_3 was adopted: $\%_{Na2CS3} = \%_{Na2S} \cdot 1.976$, whereas the coefficient 1.976 is the quotient of the molar mass Na_2CS_3 (154.189 g/mol) and Na_2S (78.046 g/mol). Na_2CS_3 density in temperature of 18ºC was determined by pycnometric method according to PN-C-04504:1992 (Method B), and the content of Fe in Na_2CS_3, was determined by spectrophotometry after oxidation of Fe(II) to Fe(III) with HNO_3 in accordance with PN-C-04521-3:1981. All analytical methods without determination of complexing agents and parameters of sodium trithiocarbonate were accredited.

Methodology of research

Examination of the effectiveness of metal precipitation on laboratory scale

The adopted methodology consisted of an exact measurement in a beaker of 50 mL of model solution of a given metal or metal mixture, by immersing the pH electrode and adjusting the reaction of a specified pH by means of HCl or NaOH solutions. To a model solution with a determined pH, equimolar amount of Na_2CS_3 to metal was added, followed by the corrected pH, where necessary. After 15 min. of mixing, it was filtered through a syringe membrane filter with a pore size 0.45 μm and metal content determined. The standard fixation of samples using HNO_3 or HCl was not used since this would lead to a change in pH and would cause the precipitation of additional amount of metal. In the case of changes in pH decomposition of Na_2CO_3 would follow with H_2S separation and precipitation of metal sulphides. Based on the determined amount of the metal after the reaction, the amount of precipitated metal was calculated and expressed in percentage (percentage precipitation). The type and concentration of complexing compounds were selected based on the analysis of the composition of technological baths used in the production and concentration of the complex compounds in wastewater with the assumption that their concentration can be increased several times. The effectiveness of metal cations precipitation using Na_2CS_3 was therefore analysed in less favourable conditions, since it was accomplished at higher concentrations of complexing compounds in raw wastewater than indicated by the authors at the stage of preliminary studies. Efficiency testing was carried out in the pH range of 2–10 for copper, pH of 4–12 for nickel (to precipitate Ni(II) ions, generally a higher pH is required) and pH of 2–8 for tin (due to the rapid hydrolysis of Sn(II) compounds even at acidic pH). The above research methodology was also used for model solutions containing metal mixture and the addition of Na_2EDTA as the model complexing compound (model solution $A_{(min.)}$, $B_{(max.)}$, $C_{(aver.)}$). In the next stage of the study, the issue of optimizing metal precipitation from wastewater is discussed. The studies were carried out in the following stages: (i) precipitation of metals contained in wastewater by using a stoichiometric dose of Na_2CS_3 and excess in relation to the stoichiometric dose of 2.5, 5, 10, 15, and 20% for the two types of coagulant ($FeCl_3$ and PAC). Therefore, different final pH values were applied (respective ranges of 9.0–9.5 for $FeCl_3$ and 7.5–8.0 for PAC), (ii) precipitation of metals contained in wastewater, with simultaneous measurement of the redox potential using a platinum redox electrode – these studies were also carried out for the two types of coagulants, at different doses of Na_2CS_3: 80, 160, 240, 320, 400, 480 and 560 μL 44.26% Na_2CS_3 (stoichiometric dose was 290 μL 44,26% Na_2CS_3/1 L of wastewater), (iii) testing the precipitation of metals on an industrial scale by using this process to control the platinum redox electrode, assuming the necessary decrease in the redox potential of below 100 mV. Research into precipitation conditions was carried out using real wastewater in beakers containing 0.5 L and 1 L of wastewater in the test stand equipped with a tripod, a magnetic stirrer and a pH meter. The studies were carried out in the temperature of 18ºC, with a constant stirring rate of 500 rpm and the addition of two coagulants ($FeCl_3$ and PAC) in an amount of 0.5 mL for 0.5 L of wastewater. The reaction of the wastewater was pre-corrected with 30% NaOH to the value of 9.0 or 7.5. Then the calculated amount of 44.26% of Na_2CS_3 was added and pH adjusted to a final value in the range of 9.0–9.5 (when $FeCl_3$ is used) and 7.5–8.0 (when PAC is used) with 30% NaOH or 10% HCl. After approx. 10 min., 1 mL of 0.05% solution of Furoflock CW277 was added. After 15 min. of sedimentation, a test sample was taken for the assessment of pH, turbidity, colour, chlorides, sulphates(VI), COD, phosphorus, TOC, Cu, Ni, Sn, Fe and Al. Studies into precipitation conditions with simultaneous measurement of the redox potential were carried out analogously, except that the potential was measured after the addition of coagulants, pH adjustment, and then after the addition of subsequent each dose of the calculated amount of 44.26% of Na_2CS_3 and pH adjustment to 9.0–9.5 (in the case of using $FeCl_3$) or 7.5–8.0 (when using PAC). Research into precipitation conditions was carried out on a test stand equipped with a tripod, magnetic stirrer, pH meter equipped with a pH electrode and a temperature sensor, plus a platinum electrode redox ErPt-11X. The research was performed twice and the presented results are arithmetic mean.

Examination of the effectiveness of metal precipitation on industrial scale

Tests were carried out on industrial scale in wastewater treatment plant shown in Fig. 1. The wastewater treatment process was implemented in the following stages: (i) filling the reactor with raw wastewater to the working volume and a start of the mixer, (ii) dosing Furofloc® F3 in the amount of 0.5 L/1 m^3 of wastewater, (iii) adjusting pH to 8.5–9.0 with 30% of NaOH, (iv) dosing a solution of 44.26% of Na_2CS_3 to a complete precipitation of metals, whereas the dosing control was carried out using a platinum redox electrode ErPt-11X (v) adding a solution of 0.05% anionic flocculant in an amount of 2 L/1 m^3 of waste water, (vi) after the formation of large flocs, turning the stirring off. After 15 min. of sedimentation, the treated wastewater sample was taken for the assessment of pH, turbidity, colour, phosphorus, COD, TOC, Al, Fe, Cu, Ni, Sn, and sulphides. According to the described methodology, six attempts of wastewater treatment were made, and the dosing process of Na_2CS_3 was monitored by a platinum redox electrode ErPt-11X. Dosing 44.26% of Na_2CS_3 was terminated at the moment of the decrease in the redox potential to a value in the range of 0–50 mV.

Results and discussion

Precipitation of copper from model solutions

Fig. 2 shows the precipitation of Cu(II) expressed as a percentage, after application of the stoichiometric amount of Na_2CS_3 solution. Precipitation of Cu(II) was carried out with the model solution containing only Cu(II) ions and solutions containing the additive of Na_2EDTA in an amount of 50, 100 and 200 mg/L. After the addition of the stoichiometric amount of Na_2CS_3 to model solutions containing Cu(II) ions, the precipitation of a brown sediment of $CuCS_3$ was observed. The efficacy of copper removal (the amount of precipitated copper in relation to the initial amount) varied within 90.0–99.7%, which corresponded to a concentration of Cu(II) in solution in the range of 10.9–0.38 mg/L. The largest efficiency (over 99%) was observed at pH of 4–9, whereas the concentration of Cu(II) in post-reaction solution was always <1.0 mg/L. Carried out determination of the concentration of Cu(II) in model solutions after the precipitation showed that the addition of Na_2EDTA has a significant effect on the concentration of copper, and thus the effectiveness of its removal which decreases with the increase in the concentration of the Na_2EDTA (Fig. 2). For subsequent concentrations of Na_2EDTA used in the amount of 50, 100 and 200 mg/L, the effectiveness of Cu(II) removal varied depending on pH, in the ranges: 84.3–89.9% and 77.1–88.7% as well as 55.6–88.0%, respectively. In these

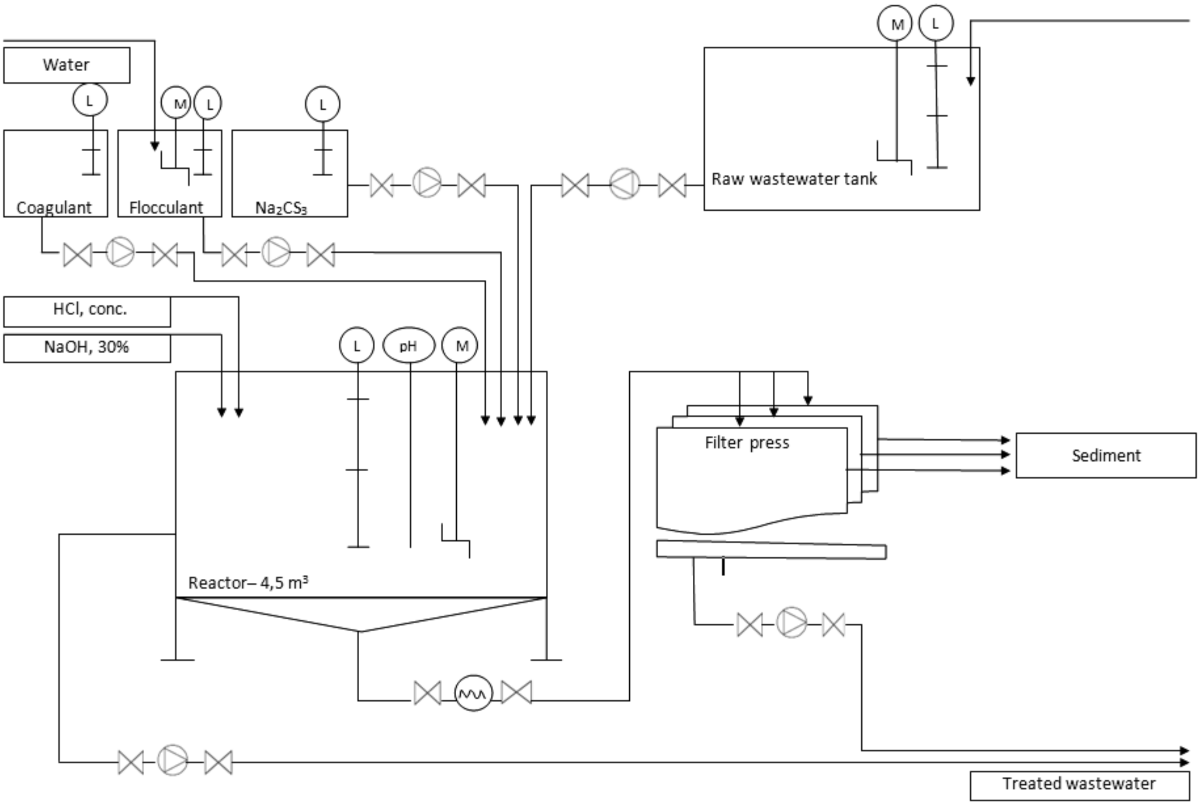

Fig. 1. Schematic diagram of the wastewater treatment plant (L-level sensor, M-stirrer, pH-pH electrode)

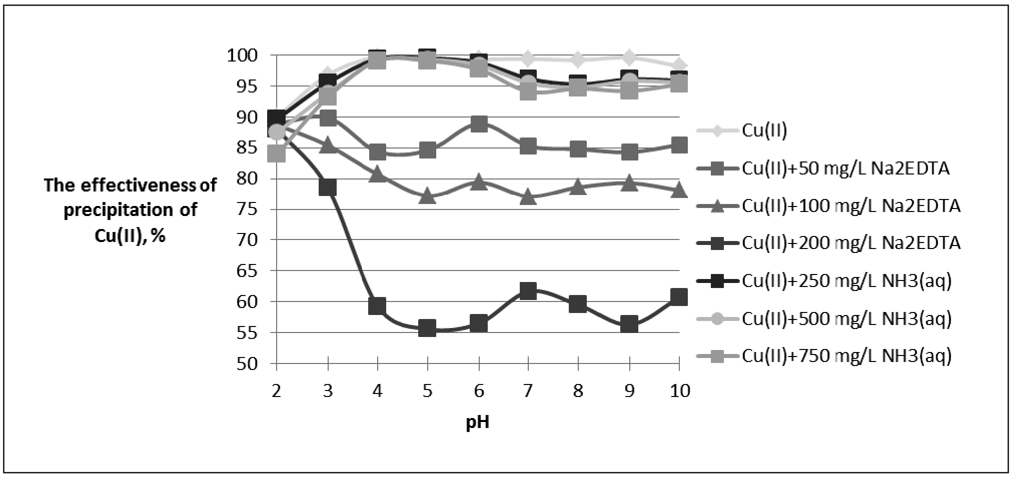

Fig. 2. Removal of copper using sodium trithiocarbonate in the presence of Na_2EDTA and $NH_{3(aq)}$ (250, 500, 750 mg/L)

cases, the most effective removal of copper was observed usually at pH of 2–3, which indicated a greater stability of CuEDTA complex in alkaline medium. Fig. 2 shows also the efficiency of Cu(II) removal from model solutions containing $NH_{3(aq)}$, which, depending on the pH and applied amount of $NH_{3(aq)}$, varied within the ranges of 89.7–99.5% (250 mg/L), 87.5–99.3% (500 mg/L) and 84.0–99.1% (for 750 mg/L). The increased efficiency of Cu(II) removal (above 95% for all doses $NH_{3(aq)}$) was observed at pH of approx. 3.25–6.75. A lower efficiency was observed at a strongly acidic pH, similarly as in the case of a solution containing no added $NH_{3(aq)}$ and for pH of 5.0–5.25, wherein in the pH range of approx. 7–10, a stabilization of the performance of Cu(II) removal was observed for all model solutions. Slight (1–5%) reduction in the efficiency of Cu(II) precipitation in alkaline conditions was probably caused by the formation of $NH_{3(aq)}$ with Cu^{2+} ions of soluble complex cation $[Cu(NH_3)_4]^{2+}$. On the basis of the carried out studies it has been shown that increasing the doses of $NH_{3(aq)}$ in the range of 250–750 mg/L, would not cause a significant change in the effectiveness of Cu(II) precipitation as when using Na_2EDTA. Fig. 3 shows the percentage of Cu(II) precipitation from model solutions containing Na_3MGDA additive which decreased with the increase of Na_3MGDA concentration. For the applied doses in the amount of 50, 100 and 200 mg/L, the effectiveness of precipitation varied in the ranges 86.8–98.6%, 81.2–98.1% and 81.7–97.4%. The conducted studies showed that the increased effectiveness of Cu(II) precipitation in the presence of Na_3MGDA can be achieved when pH of precipitation process is about 3 and at pH> 8. In the pH range from slightly acidic to slightly alkaline, the deterioration in the efficiency of Cu(II) removal was observed. Fig. 3 shows also the results of research which demonstrate greater efficacy (pH 6–8, 200 mg/L Na_4GLDA) of removing Cu(II) using the stoichiometric dose of Na_2CS_3 from model solutions containing the additive of Na_4GLDA, rather than from model solutions containing the same Na_3MGDA doses. For 50, 100 and 200 mg/L of Na_4GLDA, the efficiency of copper precipitation varied in the ranges of 80.8–96.7%, 80.3–94.9% and 78.5–96.8%, respectively. The highest efficiency of Cu(II) removal was observed at pH equal to about 3 and at pH>9. The studies have shown that Na_2CS_3, used for the precipitation of Cu(II) ions was more effective in the presence of Na_4GLDA than Na_3MGDA, with the application of identical doses of both complexing compounds. The carried out research into the precipitation of Cu(II) in the presence of tested complexing compounds (Na_2EDTA, $NH_{3(aq)}$, Na_3MGDA, Na_4GLDA), using a stoichiometric amount of Na_2CS_3 have pointed out the possibility of its use as a precipitation reagent in various pH ranges. However, depending on the type and concentration of the complexing compound and pH, it displays differentiated efficacy, which is associated with the value of the constant stability of the complex compounds formed by Cu(II) ions with individual complexing compounds. Durability of complex compounds in which the central atom is Cu(II) ion, also depends on the reaction of the solution, thus probably causes the varied effectiveness of using Na_2CS_3, compared to its effectiveness of Cu(II) precipitation from model solutions without the additives of complexing compounds. Testing of Cu(II) precipitation using Na_2CS_3, confirmed the possibility of their removal from the model solutions with the efficiency of 94.0–99.9% at pH of 1–13. (Stechman and Orłowska 2010).

Precipitation of nickel from model solutions

Fig. 4 shows the results of Ni(II) removal efficiency. When adding Na_2CS_3 to the model solutions, the formation of red sediment of $NiCS_3$ was observed. Studies have shown that the efficiency of removing Ni(II) ions, depending on pH of the model solution containing only Ni(II) ions, is small for a strongly acid reaction (pH increases in the range 2–3), and therefore further studies with the addition of Na_2EDTA were carried out in the pH range of 4–12. Testing of Ni(II) precipitation using Na_2CS_3, confirmed the possibility of their removal from the model solutions with the efficiency of 24.3–94.2% for Ni(II) at pH of 1–13 (Stechman and Orłowska 2010). The removal efficiency of Ni(II) ions from the solution containing no Na_2EDTA added varied within 75.2–93.4%, and was the highest at pH of approx. 3.5–7.0. In the pH range of 6–7, a slight deterioration in the effectiveness of precipitation for the model solution containing the additive of 200 mg/L Na_2EDTA, was observed. Starting with pH of around 7, a decrease in the efficiency of Ni(II) ions removal from all model solutions was observed. In addition, it was observed that increasing the concentration of Na_2EDTA

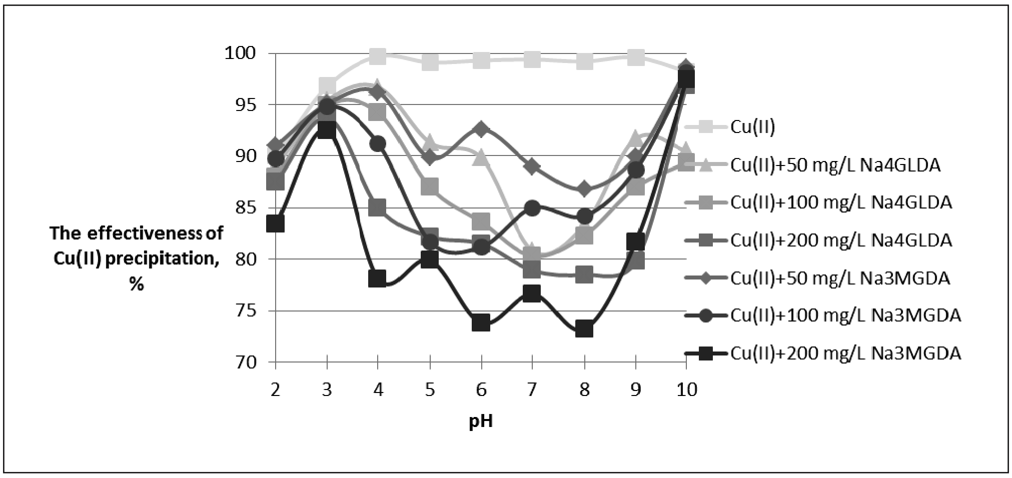

Fig. 3. Removal of copper using sodium trithiocarbonate in the presence of Na_3MGDA and Na_4GLDA (50, 100, 200 mg/L)

in model solution from 100 to 200 mg/L, resulted in a greater reduction in the precipitation efficiency of Ni(II) ions than in the case of increasing concentrations from 50 to 100 mg/L (in both cases, doubling the concentration of Na_2EDTA). In the next stage of the study (Fig. 4), the effectiveness of Ni(II) ions removal from the model solutions with added $NH_{3(aq)}$ of 250, 500 and 750 mg/L, was verified. Having conducted the studies, varied Ni(II) ions removal efficiency was observed, depending on pH and $NH_{3(aq)}$ concentration, whereas the optimal conditions for precipitation by means of Na_2CS_3 occurred at pH of 10–12, similarly to precipitation of Ni(II) in the form of $Ni(OH)_2$. For all the subsequently used concentrations of $NH_{3(aq)}$, the corresponding Ni(II) precipitation was observed in the ranges of 45.1–86.1%, 40.9–83.9% and 11.0–81.3%. The determination of Ni(II) ions in model solutions after the completion of precipitation process indicated that the ranges of pH within 8.5–12 (for the dose 250 mg/L), pH about 9.2–12 (for the dose of 500 mg/L) and pH of about 9.7–12 (for the dose of 750 mg/L), a higher Ni(II) removal efficiency from the solutions with the addition of $NH_{3(aq)}$ were obtained than for the model solution containing no $NH_{3(aq)}$ Added. This phenomenon may seem problematic and needs clarification. The addition of $NH_{3(aq)}$ contained in the model solutions causes the initial precipitation of a green Ni(OH)Cl sediment, which is soluble in an excess of $NH_{3(aq)}$ with formation of a complex ion $Ni(NH_3)_6^{2+}$, of a sapphire-violet colour. During the research, there was no discolouration of the solution evident, and hence the dissolution of Ni(OH)Cl, probably due to an insufficient concentration of $NH_{3(aq)}$. Moreover, in the model solution, due to the addition of Na_2CS_3, simultaneous precipitation of $NiCS_3$ and probably of Ni(OH)Cl and $Ni(OH)_2$ occurred. There may also be a certain amount of Ni(II) ions adsorption on the surface of precipitated sediments or the effect of systematic error caused by the negligence regarding the volume of the added reactants during the determination of Ni(II) ion content in solutions after the reaction completion. It is therefore likely that in the case under consideration, Ni(II) ions precipitation efficiency in the presence of additive $NH_{3(aq)}$, and thus the efficiency of the precipitation agent is due to a decrease in Ni(II) ion concentration resulting from conducting of several chemical reactions simultaneously, the formation of other compounds or stabilization of a specific ion balance in the model solution. The exact explanation of the course of these reactions requires further studies, which were not the subject of this paper. Fig. 5 shows the results of performance of Ni(II) precipitation in the presence of Na_3MGDA. For individual

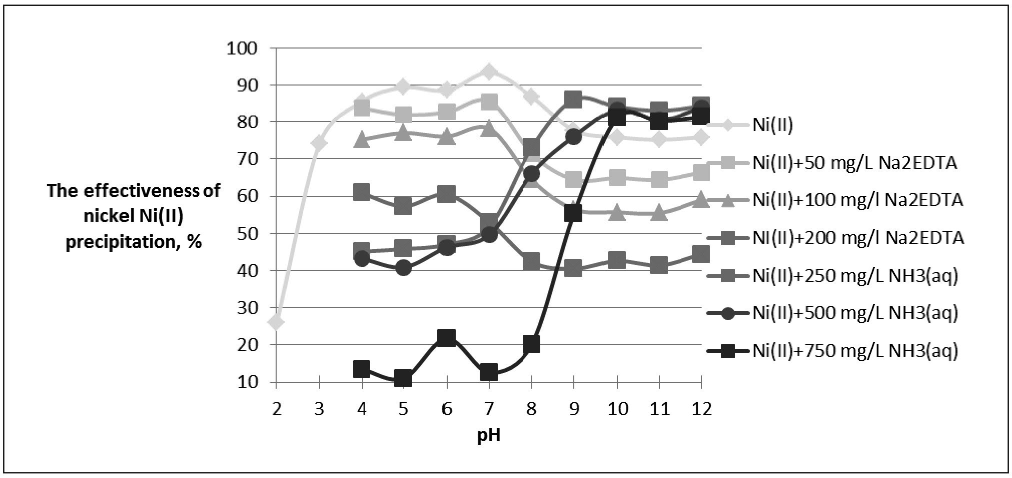

Fig. 4. Removal of nickel using sodium trithiocarbonate in the presence of Na_2EDTA (50, 100, 200 mg/L) and $NH_{3(aq)}$ (250, 500, 750 mg/L)

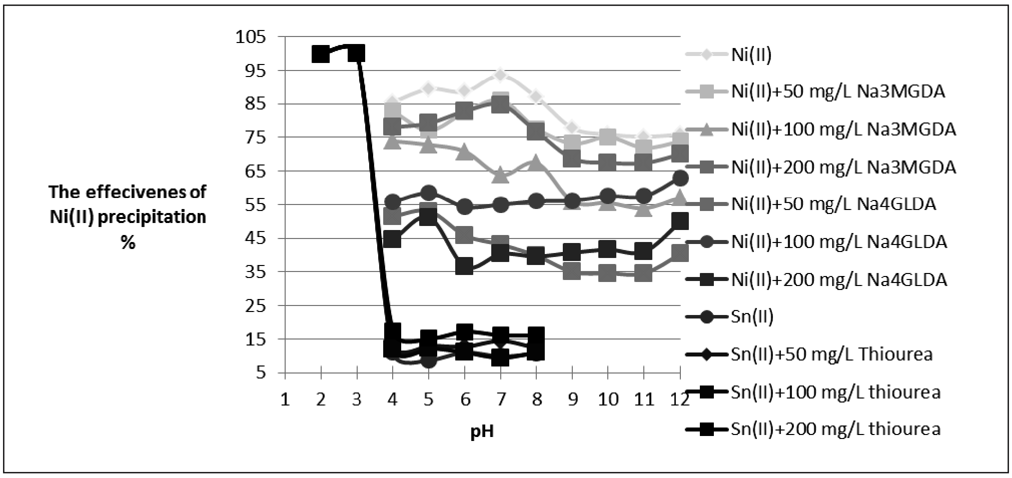

Fig. 5. Removal of nickel and tin using sodium trithiocarbonate in the presence of Na_3MGDA, Na_4GLDA and thiourea (50, 100, 200 mg/L)

doses of Na_3MGDA of 50, 100 and 200 mg/L, nickel removal efficiency varied in the ranges of 71.9–86.0%, 53.9–73.9% and 34.6–53.0%, respectively. The greater efficiency of the process and, therefore, lower concentrations of Ni(II) ions in solutions after the reaction completion were obtained by carrying out the precipitation reaction in slightly acid medium rather than in alkaline medium. Attempts were also made of Ni(II) ions removal from model solutions containing Na_4GLDA at 50, 100 and 200 mg/L, the results of which are shown in Fig. 5. Similarly as for the model solutions with the addition of Na_3MGDA, also in the case of application of Na_4GLDA, the efficiency of Ni(II) ions removal decreases with the increase in the concentration of Na_4GLDA, and it is not a linear relationship. For the applied doses of Na_4GLDA of 50, 100 and 200 mg/L, the effectiveness of Ni(II) removal varied in the ranges of 67.4–84.7%, 54.3–63.1% and 36.6–51.2%, respectively. The optimal pH for Ni(II) precipitation varies slightly depending on the applied dose of Na_4GLDA. For a pure model solution and the model solution containing the addition of 50 mg/L of Na_4GLDA, the optimal pH of precipitation is about 7, while for the solutions containing 100 and 200 mg/L Na_4GLDA, the optimal pH ranges are of about 5 and 12. The carried out studies of Ni(II) ions removal from model solutions containing the selected complexing agents showed moderate usefulness of stoichiometric doses of Na_2CS_3 used for this purpose and confirmed the expected negative effect of the additive of the complexing compounds of nickel removed from the respective solutions. Following the carried out studies, generally lower ion removal efficiency of Ni(II) than the Cu(II) was observed.

Precipitation of tin from model solutions

Fig. 5 demonstrates the results of Sn(II) precipitation, which showed that the content of Sn(II) in model solutions after the precipitation reaction, displays a close dependence on pH at which the precipitation process was carried out. The lowest concentration of Sn(II), and therefore the greatest efficiency of the process carried out by using a stoichiometric amount of Na_2CS_3 may be achieved in the pH range of 2–3. Starting from pH 3, a decrease in the efficiency of Sn(II) precipitation from about 99% to about 9–17%, was observed. Changes indicating lower efficiency at pH>3 were visually observed in the course of research. While dosing Na_2CS_3 to model solutions with pH of 2–3, precipitation of a pale yellow sediment was observed ($SnCS_3$ most probably), then while dosing Na_2CS_3 to model solutions of pH>3, initial precipitation of sediment was observed which gradually dissolved, and the colour of the solution changed to slightly yellow. The observed reaction process was most likely due to the formation of a soluble complex anion $[Sn(CS_3)_2]^{2-}$. At the same time, a small amount of sediment floc was visible, suspended throughout the whole volume of the model solution. At pH of 2–3, complete decomposition of Na_2CS_3 (into Na_2S and CS_2) does not take place, because if such decomposition was possible then the precipitate would be of a brown colour, derived from SnS. It can therefore be concluded that under the reaction conditions, $SnCS_3$ precipitates, and the calculated removal efficiency of Sn(II) is the result of the effectiveness of the precipitation reagent. Therefore, the carried out studies show the limited usefulness of Na_2CS_3 for Sn(II) ions precipitation with the exception of situations where it is possible to conduct precipitation in the pH range of 2–3. On the one hand, the observed efficiency of Cu(II), Ni(II) and Sn(II) removal is related to the stability of the complex metal compounds concerned at a given pH value. On the other hand, the precipitation of metals can occur as a result of several reactions at the same time and cause the metals to be removed in the form of trithiocarbonates, hydrated hydroxides or metal oxides.

Precipitation of a mixture of metals from model solutions

The effectiveness of metal removal from model solutions (Fig. 6) changed to a wide extent and for the solution $A_{(min.)}$ it was 36.6–87.4%, for the solution $B_{(max.)}$ 40.9–97.5% and for the solution $C_{(aver.)}$ 71.1–94.4%. The removal of metals for the model solution $A_{(min.)}$, containing small amounts of metals (Table 2, $\sum_{of\ metals}$=1.775 mg/L) proceeded with the highest efficiency (over 80%) in the pH range of about 4.2–7.2 and about 7.5–9. The removal of metals for the model solution $C_{(aver.)}$ proceeded with the efficiency of over 90% in the pH range of 3–5 and at pH 10. In the case of the model solution $B_{(max.)}$, the largest efficiency (over 90%) was observed in the pH range of about 2.0–6.25. In the case of the removal of metals

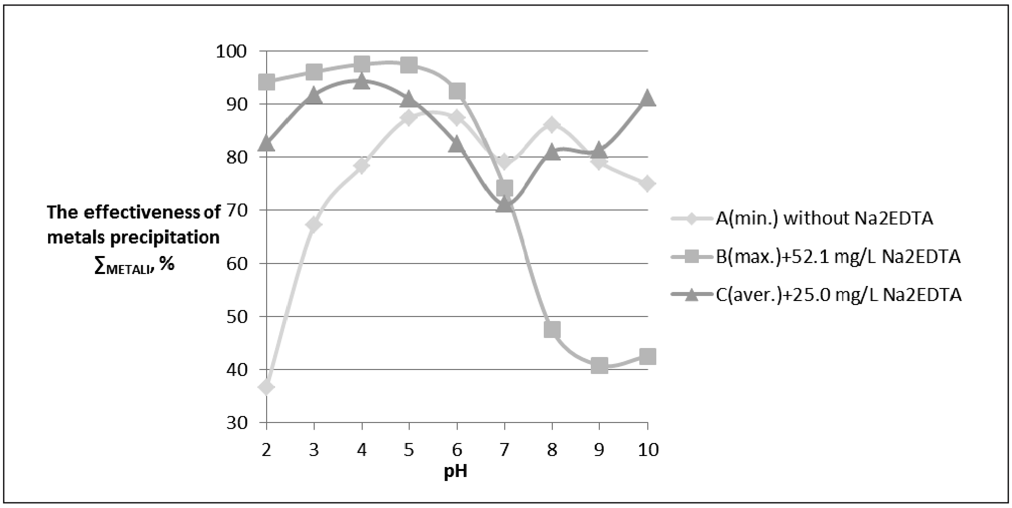

Fig. 6. Removal of copper, nickel and tin using sodium trithiocarbonate

from the model solution $B_{(max.)}$, a decrease in effectiveness was observed from a pH of about 7.2. The discussed model solution contained 59.9 mg/L of Sn(II) ions, and in the case of tin precipitation, using an alkaline pH is not advantageous, as it forms a complex soluble compound of tin, which causes tin transformation from the sediment into solution. This process was partly influenced by the total efficiency of metal removal. The model solution contained the largest addition of Na_2EDTA, which, as demonstrated by earlier studies, had a negative impact on the effectiveness of Cu(II) and Ni(II) precipitation, and ultimately on the total removal efficiency of metals. The carried out precipitation experiments for a solution $B_{(max.)}$ indicate that in the case of wastewater containing high concentrations of metals and complexing agents, it is favourable to use Na_2CS_3 at pH of 3–5 (efficiency over 96%). In the case of the model solution $C_{(aver.)}$, the carried out studies have indicated the potential use of Na_2CS_3 at pH of 3–5 (more than 90% of the removed metals). Above pH 5 a reduced efficiency was observed, and then its slight increase in the alkaline medium. What needs to be explained is more efficient removal of metals from the model solution $B_{(max.)}$, rather than from the solution $C_{(aver.)}$ in an acid medium, although solution $B_{(max.)}$ contained a higher amount of metals and Na_2EDTA than $C_{(aver.)}$ solution. Shown in Fig. 6, the shape of the two curves indicates a more efficient removal of metals from a model solution containing their larger concentrations than from a solution containing lower concentration of metals. An important role in the process play most likely large amounts of precipitated sediments of a certain active surface, on which metal ions absorption can take place and thereby result in an increased performance of metal removal from the model solution. In the case of solutions with less metal concentration, the adsorption process may take place at a lower intensity, which is caused by the precipitation of small amounts of colloidal sediments.

Removal of Cu(II), Ni(II) and Sn(II) from industrial wastewater on laboratory scale

During the alkalization of industrial wastewater from the manufacture of PCBs (Table 4) with NaOH at 7.5 or 9, precipitation of spongy sediments of metal hydroxide was observed. After adding the calculated amount of Na_2CS_3, previously precipitated sediments changed their colour to intensely brown-black, which probably came mainly from precipitating $CuCS_3$. After addition of 0.05% flocculant solution, a formation of large flocs was observed that after switching off the stirring, immediately underwent sedimentation, whereas sediments precipitated in the samples in which $FeCl_3$ solution was used as a coagulant, sedimented more quickly. As a result of the carried out studies, in each case, wastewater was produced (Table 6) of low ion content of Sn(II) and Ni(II) amounting to <0.01 mg/L, and in the range of <0.005-0.009 mg/L. The iron content in the purified wastewater varied in the range of 0.54–0.67 mg/L, in cases where $FeCl_3$ was applied and in the range of 0.35–0.5 mg/L in cases in which PAC was used. Much higher concentrations of aluminum (4.22–4.52 mg/L) were determined in the cases in which PAC was used as a coagulant. For comparison, in the samples where $FeCl_3$ was used, much lower concentrations of aluminum (0.48–0.73 mg/L) were determined. The carried out studies clearly showed a faster decrease in copper concentration in the method in which $FeCl_3$ was used as a coagulant and pH was neutralized to 9.0. The decrease in copper content to the order of hundredths of mg/L had already been observed when 2.5% excess of Na_2CS_3 solution was used at a final pH of 9.25. Similar reduction of the concentration of copper in the case of using PAC solution was observed after the application of 10% of Na_2CS_3 solution at a final pH of 7.71. In the next stages of research, i.e. at doses of 15 and 20% higher than the stoichiometric dose, copper concentration was maintained in the range of 0.02–0.07 mg/L, with very low concentrations of tin and nickel. The carried study showed that in the case of wastewater from the production of PCBs containing complexing compounds, it may be necessary to use a slight excess of Na_2CS_3 solution for a complete precipitation of copper. Furthermore, the application of $FeCl_3$ and pH precipitation of about 9 instead of PAC solution and pH precipitation of about 7, allows for more extensive removal of Cu(II) from the wastewater and lower use of Na_2CS_3. It is likely to be connected with the precipitation of larger amounts of Cu(II) (present in the wastewater in the form of uncomplexed ions) in the form of $Cu(OH)_2$ due to the use of a more alkaline medium, and consequently the consumption of the dosed amount of Na_2CS_3 on the precipitation of the remaining complexed amount of copper. What cannot be ruled out is the reaction of the precipitated $Cu(OH)_2$ from Na_2CS_3 and formation of $CuCS_3$, due to the decreased solubility of $CuCS_3$ or precipitation of a certain amount of copper sulphide(II). In the next phase of experiments, research was conducted to determine the change in the value of the redox potential, depending on the amount of Na_2CS_3 solution dispensed into the reaction system and changes in metal concentrations associated with it. The stoichiometric dose corresponded to the 290 µL 44.26% of Na_2CS_3 solution, which means that when using 560 µL of 44.26% Na_2CS_3, the dose was used representing 193% of the stoichiometric dose. In the course of research it was observed that when using 560 µL of 44.26% Na_2CS_3 for precipitation, after the sedimentation process, the treated wastewater was characterized by a dark red colour derived from the excess of precipitation reagent. Coloration that was not removed by means of the applied coagulants ($FeCl_3$ and PAC), although in comparison to the research whose results are presented in Table 6, two times higher doses of coagulants (1 mL/L) were applied. Table 7 shows the test results of treated wastewater. Due to the fact that the marked concentrations of metals in some cases were smaller than the detection limit of the adopted analytical method, the sum of metal was adopted as a criterion of the process efficiency. In cases where the metal concentrations were lower than the detection limit, the value of 0 mg/L was adopted to the sum. The results of the conducted tests showed that when using Na_2CS_3 solution for removing metals from wastewater, it is more preferable to carry out metal precipitation reaction in the range of pH 9–9.5 rather than in the pH range of 7.5–8. In the conditions of the experiment, at an increased dose of $FeCl_3$ (1 mL/L) and after the application of 240 µL of 44.26% Na_2CS_3 (stoichiometric dose was 290 µL) the sum of metals in the treated wastewater was 0.082 mg/L. For comparison, using the same dose of 44.26% Na_2CS_3 for wastewater containing an increased dose of PAC solution (1 L/L), at pH precipitation of 7.5–8, the wastewater with a sum of metal 0.52 mg/L was obtained. Therefore, using $FeCl_3$ for solution coagulation made it possible to carry out the precipitation reaction at elevated pH, which caused that the

Table 6. The physicochemical parameters of wastewater treated using stoichiometric and excess dose of Na_2CS_3 (2.5, 5, 10, 15 and 20%)

Parameter	Unit	Method with $FeCl_3$ – 0,5 mL/0,5 L of wastewater, pH 9–9.5	Method with PAC – 0,5 mL/0,5 L of wastewater, pH 7.5–8
The stoichiometric dose – 145 µL 44.26% Na_2CS_3			
pH	–	9.43	7.82
Copper	mg/L	0.15	0.22
Tin	mg/L	< 0.01	< 0.01
Nickel	mg/L	< 0.005	< 0.005
Iron	mg/L	0.67	0.5
Aluminum	mg/L	0.73	4.48
2.5% excess relative to the stoichiometric value – 149 µL 44.26% Na_2CS_3			
pH	–	9.25	7.79
Copper	mg/L	0.04	0.22
Tin	mg/L	< 0.01	< 0.01
Nickel	mg/L	< 0.005	< 0.005
Iron	mg/L	0.56	0.5
Aluminum	mg/L	0.48	4.22
5% excess relative to the stoichiometric value – 152 µL 44.26% Na_2CS_3			
pH	–	9.41	7.81
Copper	mg/L	0.05	0.24
Tin	mg/L	< 0.01	< 0.01
Nickel	mg/L	< 0.005	< 0.005
Iron	mg/L	0.58	0.45
Aluminum	mg/L	0.59	4.27
10% excess relative to the stoichiometric value – 160 µL 44.26% Na_2CS_3			
pH	–	9.42	7.71
Copper	mg/L	0.05	0.09
Tin	mg/L	< 0.01	< 0.01
Nickel	mg/L	< 0.005	0.009
Iron	mg/L	0.62	0.36
Aluminum	mg/L	0.6	4.52
15% excess relative to the stoichiometric value – 160 µL 44.26% Na_2CS_3			
pH	–	9.39	7.79
Copper	mg/L	0.02	0.05
Tin	mg/L	< 0.01	< 0.01
Nickel	mg/L	< 0.005	0.006
Iron	mg/L	0.57	0.41
Aluminum	mg/L	0.52	4.34
20% excess relative to the stoichiometric value – 174 µL 44.26% Na_2CS_3			
pH	–	9.21	7.69
Copper	mg/L	0.03	0.07
Tin	mg/L	< 0.01	< 0.01
Nickel	mg/L	< 0.005	0.007
Iron	mg/L	0.54	0.35
Aluminum	mg/L	0.59	4.26

Table 7. Physicochemical parameters of wastewater treated using 80, 160, 240, 320, 400, 480, 560 μL of 44.26% Na_2CS_3 per 1 L – the effect of dose on the redox potential (E)

Parameter	Unit	Method with $FeCl_3$ – 1 mL/1 L of wastewater, pH 9–9.5*	Method with PAC– 1 mL/1 L of wastewater pH 7.5–8**
80 μL 44.26% Na_2CS_3 per 1 L of wastewater			
pH	–	1.75	1.75
E	mV	+509.2	+509.2
$\mathrm{pH}_{\text{(after add. of 1 mL of FeCl3/PAC}}$	–	1.70	1.75
$E_{\text{after add. of 1 mL of FeCl3/PAC}}$	mV	+600.9	+509.8
$E_{\text{pH */**}}$	mV	+121.2	+200.5
$E_{\text{(after add. of Na2CS3)}}$	mV	+78.5	+123.1
Copper	mg/L	0.22	4.70
Tin	mg/L	<0.05	<0.05
Nickel	mg/L	<0.005	0.046
$\sum_{\text{of metals}}$	mg/L	0.22	4.75
160 μL 44.26% Na_2CS_3 per 1 L of wastewater			
$E_{\text{(after add. of Na2CS3)}}$	mV	+17.0	+105.2
Copper	mg/L	0.20	4.50
Tin	mg/L	< 0.05	< 0.01
Nickel	mg/L	< 0.005	0.015
$\sum_{\text{of metals}}$	mg/L	0.20	4.52
240 μL 44.26% Na_2CS_3 per 1 L of wastewater			
$E_{\text{(after add. of Na2CS3)}}$	mV	+2.7	+95.5
Copper	mg/L	0.082	0.50
Tin	mg/L	< 0.05	< 0.01
Nickel	mg/L	< 0.005	0.017
$\sum_{\text{of metals}}$	mg/L	0.082	0.52
320 μL 44.26% Na_2CS_3 per 1 L of wastewater			
$E_{\text{(after add. of Na2CS3)}}$	mV	-142.0	-52.8
Copper	mg/L	0.019	0.19
Tin	mg/L	< 0.05	< 0.05
Nickel	mg/L	0.0098	0.0094
$\sum_{\text{of metals}}$	mg/L	0.029	0.20
400 μL 44.26% Na_2CS_3 per 1 L of wastewater			
$E_{\text{(after add. of Na2CS3)}}$	mV	-226.8	-218.8
Copper	mg/L	0.70	0.50
Tin	mg/L	< 0.05	< 0.05
Nickel	mg/L	0.02	0.022
$\sum_{\text{of metals}}$	mg/L	0.72	0.52
480 μL 44.26% Na_2CS_3 per 1 L of wastewater			
$E_{\text{(after add. of Na2CS3)}}$	mV	-345.4	-285.8
Copper	mg/L	0.74	0.84
Tin	mg/L	< 0.05	< 0.05
Nickel	mg/L	0.027	0.032
$\sum_{\text{of metals}}$	mg/L	0.77	0.87
560 μL 44.26% Na_2CS_3 per 1 L of wastewater			
$E_{\text{(after add. of Na2CS3)}}$	mV	-401.7	-355.0
Copper	mg/L	0.79	1.15
Tin	mg/L	< 0.05	< 0.05
Nickel	mg/L	0.038	0.035
$\sum_{\text{of metals}}$	mg/L	0.83	1.19

treated wastewater was obtained with lower concentration of precipitating metals than in the case of using PAC. In both cases, the lowest metal concentrations were obtained after application of 320 µL of 44.26% Na_2CS_3; however, in the case of precipitation at higher pH, metal concentration was approx. seven times smaller than in the case of pH precipitation in the slightly alkaline pH (0.029 and 0.199 mg/L, respectively). Moreover, in both cases when using the following doses of 44.26% Na_2CS_3 (400, 480, 560 µL), significantly exceeding the stoichiometric dose, an increase in the sum of metal concentrations in treated wastewater was observed in the range of 0.72–0.83 mg/L (pH 9–9.5) and 0.52–1.19 mg/L (pH 7.5–8), which was mainly caused by increasing concentrations of copper and, to a small extent, of nickel. When using a large excess of precipitation reagent, the formation of soluble complex compounds took place, which was related to the passing of copper and nickel from the sediment to wastewater. The test results clearly showed that it is undesirable to use a large excess of precipitation reagent, as this can lead to deterioration of metal removal efficiency. Fig. 7 shows the relationship between the sum of metals and the redox potential (E) on the amount of the applied 44.26% of Na_2CS_3. During the research course, it was observed that after adding further doses of Na_2CS_3, reducing the value E from positive values in the direction of negative values, was observed. In the case of the method using $FeCl_3$ with a decrease in the potential to a +78.5 mV and +17.0 mV, wastewater was obtained with a metal sum of 0.22 and 0.20 mg/L, respectively. In the case of PAC method, the reduction in the potential to +95.5 mV and -52.8 mV was associated with the concentrations of metals in wastewater, 0.52 and 0.20 mg/L, respectively. Therefore, if the maximum concentration value of the sum of metals 1 mg/L is adopted as the criterion to meet the requirements for treated wastewater, then in the case of Na_2CS_3 applied to the precipitation (while complying with other conditions) to receive treated wastewater meeting this condition, Na_2CS_3 should be dosed until a decrease moment in a potential to less than +100 mV or for enhancement of the precipitation effectiveness 0–50 mV. Further dosing of Na_2CS_3 in the light of the study is not justified. The possibility of measuring the redox potential using a platinum redox electrode may be used to control the process of metal precipitation using Na_2CS_3 solution. In the first part of this paper the greater efficiency of metal precipitation using sodium trithiocarbonate was demonstrated in alkaline medium than in acid medium. Similar trends were observed during treatment of wastewater originating from industrial processes. Also in this case, the effect of complexing compounds on the efficiency of metal removal was noticeable. The reduction of copper concentration to less than 1 mg/L was possible only after the addition of 80 µL 44.26% Na_2CS_3 per 1 L of wastewater at pH 9–9.50 (Table 7). At this pH copper ions should be quantitatively precipitated without the use of additional chemical reagents.

Removal of Cu(II), Ni(II) and Sn(II) from industrial wastewater on industrial scale

As a result of the carried out industrial tests (Table 8), treated wastewater was obtained containing minor amounts of Cu(II), Ni(II) and Sn(II), wherein the concentration of Sn(II) in each case was <0.005 mg/L, which was probably also conditioned by small concentrations of Sn(II) in raw wastewater and the result of low susceptibility of tin to form complex compounds. In the case of Ni(II), even despite low concentrations in the raw wastewater, low concentrations in treated wastewater were determined, which varied in the range <0.005–0.017 mg/L. In the case of Cu(II), in all cases, the concentrations of <1.0 mg/L (0.058–0.77 mg/L) were determined. Na_2CS_3 solution was dosed until the decrease in the redox value potential in the range of 0–50 mV, which was sufficient to be achieved in the treated wastewater with low metal concentrations. In the purification process, wastewater small amounts of metals were obtained as compared to local requirements (Cu<1 mg/L, Ni<1 mg/L, Sn<2 mg/L). In none of the examined cases, there were elevated concentrations of sulphide ions, which could indicate overdosing of Na_2CS_3. During the process of wastewater treatment sediment formation was observed, which after the addition of flocculant solution formed bulky flocs, which quickly sedimented, and the treated effluent was transparent. The precipitate was dewatered on a filter press. During this process, no problems with dewatering of the sediment, clogging of the pores of the filter cloth or other signs of improper operation of the press were noted.

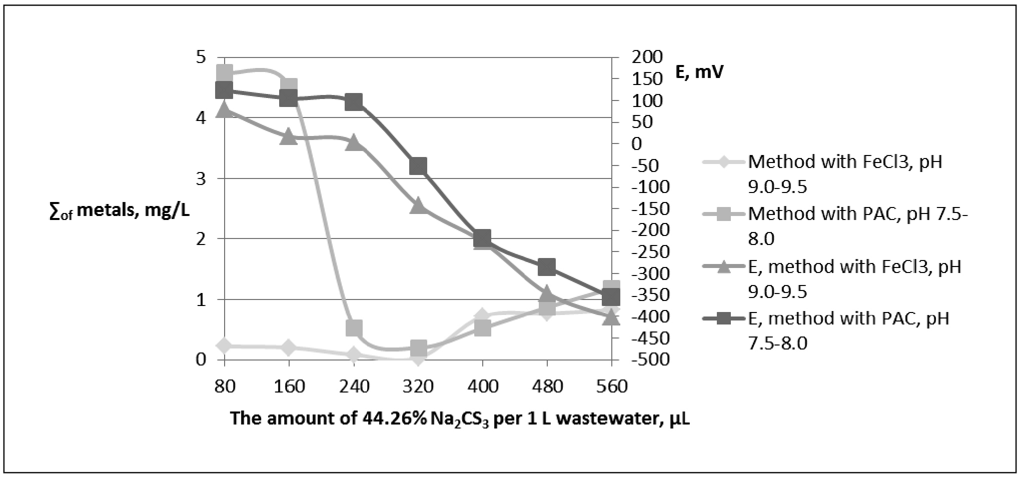

Fig. 7. Removal of copper, nickel and tin from wastewater using sodium trithiocarbonate in the presence of $FeCl_3$, PAC and platinium redox electrode

Table 8. Physicochemical parameters of wastewater treated using Na_2CS_3 under the control of the platinium redox electrode

Parameter	Unit	Sample No. 1		Sample No. 2		Sample No. 3		Sample No. 4		Sample No. 5		Sample No. 6	
		raw	treated	raw	treated	raw	treated	raw	treated	raw	treated	raw	treated
pH	–	6.0	9.10	3.8	9.32	6.9	9.14	3.2	9.38	3.6	9.38	5.6	9.41
Turbidity	NTU	88	<10	77	<10	31	<10	24	<10	14	<10	8.4	<10
Colour	mg Pt/L	14	<10	41	<10	19	<10	26	<10	28	<10	14	<10
Aluminum	mg/L	–	<0.03	–	<0.03	–	<0.03	–	<0.03	–	<0.03	–	<0.03
Iron	mg/L	–	0.56	–	0.24	–	0.71	–	0.33	–	0.54	–	0.30
Copper	mg/L	31.9	0.16	22.0	0.20	11.3	0.058	72.0	0.77	58.0	0.66	200	0.70
Tin	mg/L	3.84	<0.005	5.37	<0.005	3.23	<0.005	2.73	<0.005	1.73	<0.005	0.77	<0.005
Nickel	mg/L	0.027	<0.005	0.024	<0.005	0.022	0.011	0.42	<0.005	0.3	0.017	0.065	<0.005
Redox potential	mV	–	+29.9	–	+10.0	–	+2.1	–	+11.5	–	+17.0	–	+20.3
Sulphides	mg/L	<0,1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Conclusion

The reason for the difficulties in quantitative precipitation of metals from wastewater associated with the PCBs production is the presence of a number of complexing agents in them which can form compounds with metal cations of high durability. In the course of the study, it was found that the type and concentration of the complexing compound and pH of metal precipitation process have a significant impact on the final concentrations of metals in the treated wastewater. The carried out research into precipitation of Cu(II), Ni(II) and Sn(II) from model solutions and the actual wastewater, using Na_2CS_3 solution, indicated the possibility of its use for the removal of the complexed metals from industrial wastewater. The use of Na_2CS_3 in the precipitation process was connected with obtaining wastewater containing low concentrations of metals (Cu 0.02 mg/L, Sn <0.01 mg/L, Ni <0.005 mg/L at pH 9.39 and Cu 0.07 mg/L, Sn <0.01 mg/L, Ni 0.006 mg/L at pH 7.79). It has been shown that it is preferable to use $FeCl_3$ coagulant solution and conducting metal precipitation at alkaline pH (9–9.5) under the control of a platinum redox electrode (E<50 mV). For these conditions, wastewater containing small amounts of heavy metals (Cu 0.019 mg/L, Sn <0.05 mg/L, Ni <0.0098 mg/L on an laboratory scale and Cu 0.058 mg/L, Sn <0.005 mg/L, Ni 0.011 mg/L at pH 9.14 on an industrial scale) was obtained. However, in each of the analysed cases, regardless of the adopted coagulant ($FeCl_3$ or PAC) and the pH of the precipitation (9–9.5 and 7.5–8), there is a significant reduction in the concentration of metals in wastewater. The possibility to conduct the process in a more alkaline medium than it is possible in the case of using PAC, involves the use of a smaller amount of precipitation reagent. Due to it, a fulfillment of local requirements for purified wastewater (Cu<1 mg/L, Ni<1 mg/L, Sn<2 mg/L) was possible. Furthermore, it was found that a significant decrease in the redox potential, relating to the presence of a large excess of Na_2CS_3 in wastewater, has a detrimental effect on purification performance, resulting in re-increase of metal concentration in the treated wastewater and wastewater colour change, which is due to the excess of precipitation reagent. This procedure is uneconomical and impractical. Based on the obtained results, controlled application of Na_2CS_3 can be used to remove Cu(II), Ni(II) and Sn(II) from industrial effluent containing chelating compounds like Na_2EDTA, $NH_{3(aq)}$, tiourhea, Na_3MGDA and Na_4GLDA. The carried out studies confirmed the usefulness of Na_2CS_3 for the treatment of wastewater from the production of PCBs in industrial conditions; however, the application of Na_2CS_3 should be preceded by preliminary optimization of the studies to determine the favourable conditions of the process.

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Usuwania miedzi, niklu i cyny z syntetycznych i rzeczywistych ścieków przemysłowych przy zastosowaniu tritiowęglanu sodu.

Negatywny wpływ związków kompleksujących

Streszczenie: Przedstawiono możliwość usuwania jonów Cu(II), Ni(II) oraz Sn(II) z roztworów modelowych oraz ścieków rzeczywistych pochodzących z produkcji PCB przy zastosowaniu do strącania roztworu Na_2CS_3. Badania prowadzono w skali laboratoryjnej z zastosowaniem roztworów modelowych zwierających dodatki związków kompleksujących stosowanych w produkcji PCB (Na_2EDTA, $NH_{3(aq)}$, tiomocznik) oraz rekomendowanych przez USEPA (Na_3MGDA, Na_4GLDA). Zastosowanie Na_2CS_3 w optymalnych warunkach prowadzenia procesu strącania, związane było z otrzymaniem ścieków zawierających niskie stężenia metali. Zmiana wartości potencjału redoks oczyszczanych ścieków wskutek dozowania Na_2CS_3 umożliwiła kontrolowanie procesu strącania w skali przemysłowej przez zastosowanie platynowej elektrody redoks.