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Use of sodium trithiocarbonate for remove of chelated copper ions from industrial wastewater originating from the electroless copper plating process

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Abstract: The possibility of chelated copper ions removal from wastewater from the production of printed circuit boards using Na_2CS_3 as a precipitant agent has been presented. The use of Na_2CS_3 (pH 9–9.5, $FeCl_3$ 1 mL/L, E= +82 mV) enabled successful precipitation of the complexed Cu(II) ions from wastewater (Cu 0.85 mg/L) containing potassium and sodium tartrate ($KNaC_4H_4O_6$) as a complexing agent. The use of higher doses of Na_2CS_3 reduced the copper content to 0.05 mg/L (pH 9–9.5, $FeCl_3$ 1 mL/L, E= -156 mV). Application of Response Surface Methodology (RSM) allowed for the analysis and evaluation of the impact of the various independent parameters (pH, Fe(III) coagulant dose and 44.26% Na_2CS_3 dose) on the concentration of Cu(II) in treated wastewater. The lowest values of copper concentration (0.05, 0.02 and 0.03 mg/L) in the treated wastewater was obtained in the three experiments when an alkaline medium (pH 9.5 and 10) and higher concentration of Na_2CS_3 (0.23 and 0.28 mL/L) were used. The use of Na_2CS_3 solution under optimal process conditions (pH 9–9.5, E< +5 mV, $FeCl_3$ 0.5–1 mL/L, Na_2CS_3 0.28 mL/L), allows for almost complete precipitation of complexed copper ions(II) (Cu≤0.05 mg/L), most probably in the form of a brown solid Na_2CS_3.

Introduction

Intensive development of industry, especially metal industry as well as chemical and electrochemical coating of metals, manufacturing of batteries and accumulators, production of fertilizers, pesticides and dyes, are often associated with the formation of a significant amount of industrial wastes which contain substances harmful to the environment. Due to the content of harmful substances, wastewater from industrial processes must be treated before it is introduced into the sewage system or surface water. Apart from many organic substances of various biodegradability, wastewater may also contain heavy metals which are not biodegradable and can accumulate in the environment leading to irreversible changes. Excessive intake of copper compounds is related to its toxicity, manifested by disorders of the gastrointestinal tract, vomiting, cramps, convulsions, and in the case of large doses also death (Paulino et al. 2006). In addition, tests carried out with the involvement of fish as test organisms (*Oreochromis niloticus* and *Clarias gariepinus*), have shown negative effects of Cu(II) compounds, which caused the occurrence of a change of behaviour (avoidance) after exposure to different concentrations of Cu(II). Research has identified the need for monitoring the concentration of copper because of its toxicity to aquatic organisms, and the performed avoidance tests indicated that they may be an important and sensitive biomarker used in the monitoring and management of aquatic environment pollution. Moreover, the concentration of Cu(II) causing 50% inhibition on the metabolic activity of denitrifiers is only 0.95 mg/L. Copper is also an inhibitor to fermentative bacteria (IC_{50} = 3.5 mg/L), aerobic glucose-degrading heterotrophs (IC_{50} = 4.6 mg/L) and nitrifying bacteria (IC_{50} = 26.5 mg/L) (Ezeonyejiaku et al. 2001, Ochoa-Herrera et al. 2011). Printed circuit boards (PCB) are common thin plates on which microelectronic components are mounted, such as capacitors or semiconductors providing electrical connections between the individual elements. They are used in the production of almost all electronic devices. The production of circuit boards is complex and requires more than 50 stages of production. In the production of printed circuit boards many harmful chemicals are used that are found in more than 170 different chemical products, necessary in making-holes-conductive process (LaDou 2006). Furthermore, PCB's production is difficult also due to hazardous waste disposal which requires a specific recycling processes. (Alireza et al. 2015). Baths for electroless copper plating constitute an important industrial process used for the production of printed circuit boards since they allow metal plating of non-conductive materials, including the inner surface of the holes. The composition of the bath, in addition to Cu(II) compounds in the form of $CuSO_4$ or $CuCl_2$, includes also EDTA and $KNaC_4H_4O_6$ (sodium potassium tartrate) as complexing agents and Na_2CO_3, NaOH, HCHO, stabilizers, wetting agents and others. The very process of applying a layer of copper is often preceded by a dozen processes aimed at proper preparation of the surface to electroless copper plating process taking place in a strongly alkaline bath (Michalski 1992, Coombs and Holden 1996, Keller and Goosey 1999, Electroplating Guide 2002, Cobley et al. 2014). The presence of complexing compounds in baths for electroless copper plating enables, despite using high pH value, the presence of copper compounds in the bath in complexed form and thus it is completely soluble. The complexing agents used in flushing processes are present in the wastewater and limit the quantitative precipitation of copper at the stage of its treatment in wastewater treatment plants. The problem of copper removal from wastewater containing complexing compounds has been the subject of many studies (Keller and Goosey 1999, Chu and Hashim 2000, Dave et al. 2010, Turhanen et al. 2015). Precipitation of Cu(II) is usually carried out by dosing alkaline substances to wastewater in order to precipitate copper in the form of $Cu(OH)_2$, wherein NaOH, CaO or $Ca(OH)_2$ are used as alkalizing compounds (Mirbagheri and Hosseini 2005, Chen et al. 2009). When complexing compounds are present in wastewater, soluble sulfides (Na_2S, NaHS, Na_2S_x) are used wherein the solubility of the precipitated metal sulfides is less than metal hydroxides and therefore metal sulfide precipitation is usually more efficient than precipitation of metal hydroxides. However, it should be noted that in an acidic medium, H_2S gas evolution may take place, and therefore it is preferable to carry out precipitation of metal sulfides at neutral or slightly alkaline reaction (Choi et al. 2006, Ozverdi and Erdem 2006). Alternative methods include the use of sodium salt of trimercapto-s-triazine (TMT), sodium trithiocarbonate (TTC) and sodium diethyl- or diphenyldithiocarbamate (DTC) (Matlock et al. 2002, Fu et al. 2011, Abu-El-Halawa et al. 2017). Research is also being conducted on a laboratory scale using the newly obtained compounds, such as 1,3,5-hexahydrotriazinedithiocarbamate (HTDC) and N,N'-bis-(dithiocarboxy)-piperazine (BDP). These compounds, used for the precipitation of metals, are highly effective. The ions of copper(II) form with HTDC at pH 3–9 sparingly soluble compound $[Cu_3(HTDC)_2]_n$, and final concentration of copper ions(II) in treated wastewater is less than 0.5 mg/L (Fu et al. 2006, Fu et al. 2007). Xanthogenates, which are effective at different concentrations of Cu(II) in the range of 50–1000 mg/L, are also used in the precipitation of copper ions. Potassium ethylxanthate or insoluble starch xanthates (ISX) are used here, wherein 1 g ISX reacts with approx. 120 mg Cu(II) (USEPA 1981, Chang et al. 2002, Chang et al. 2007). In turn, using dipropyl dithiophosphate for precipitation, allows for the removal from wastewater of more than 99.9% of Pb, Cd, Hg and Cu at pH 3–6 (Xu and Zhang 2006). The researchers reported the use of many organic and inorganic compounds for the removal of copper from wastewater but the use of Na_2CS_3 in the presence of tartrate ions has not been investigated. The aim of this study was to verify the possibility of Cu(II) precipitation from wastewater from the process of electroless copper plating, containing $KNaC_4H_4O_6$ as Cu(II) complexing agent with the use of Na_2CS_3. The tests were carried out on a laboratory scale using the statistical planning methods of experiment analysis. The application of Response Surface Methodology (RSM) enabled the analysis and visualization of the obtained results of model tests and determination of the optimum conditions for precipitation process.

Materials and methods

Materials and chemical reagents

A basic model solution containing 109 mg/L of Cu(II) was used for the study. For the preparation of the model solution $CuSO_4 \cdot 5H_2O$ (POCH, Poland), and H_2SO_4, ρ=1.84 g/mL (Chempur, Poland), were used. Reagents of analytical purity and double-distilled water were used. A working model solutions were prepared, which in addition to Cu(II) contained appropriate amount of $KNaC_4H_4O_6$ acting as a complexing compound. Potassium and sodium tartrate, is a component of a bath for electroless copper plating. Research on real wastewater was conducted using raw wastewater collected in a sewage treatment plant of PCB production plant located in Poland. Raw wastewater from the process of electroless copper plating was taken from storage tanks located in the on-site wastewater treatment plant. Samples of raw wastewater were collected for 7 consecutive days, then their composition was averaged by mixing. Wastewater samples collected in the plant and averaged sample used for the testing were not fixed, and their physical and chemical composition is shown in Table 1. As the precipitant Na_2CS_3 (sodium trithiocarbonate, KiZChS Siarkopol S.A., Poland) was used in a concentration of 44.26% and 10%. In the study, a coagulant containing $FeCl_3$ (Donau Klar® Smart, Donauchem, Poland) and the anionic flocculant (0.05% w/w, Furoflock CW277, Chemische Fabrik Wocklum GmbH & Co. KG, Germany) were used.

Analytical methods

The value of pH was measured using WTWinolab® pH/Ion/Cond 750 with a combination electrode SenTix® 81 according to PN-EN ISO 10523:2012 and redox potential was measured using Elmetron® CPC411 with a platinum electrode ErPt-11 (Hydromet, Poland). Heavy metals (Cu, Ni, Sn, Fe) were determined by ISP-OES method using Optima 5300DV

Table 1. The physicochemical parameters of industrial wastewater originating from electroless copper plating process

Parameter	Unit	Value
pH	–	3.05
Copper	mg/L	49.5
Tin	mg/L	<0.01
Nickel	mg/L	<0.01
Chelating agents (calculated as Na_2EDTA)	mg/L	128.5

by Perkin Elmer according to PN-EN ISO 11885:2007. Complexing agents were determined by spectrophotometry according to Nanocolor® Complexing Agents 10 (Bi(III)/xylenol orange), in compliance with DIN 38409-26:1989-05, whereas the following calculation from comprehensive index of Bi(III) was used: (I_{BiK}): 1mg/L I_{BiK}=1.4 mg/L EDTA=1.61 mg/L Na_2EDTA. For the determination of Na_2CS_3 content, iodometric method was used in which Na_2CS_3 after decomposition in acidic condition was determined as Na_2S. Then, from the total amount of reducing substances, a correction was subtracted for the content of reducing impurities (sulfates(IV) and thiosulfates(VI)) according to PN-C-84042:1997. The content of determined Na_2S was converted to Na_2CS_3 using the following relationship: $\%_{Na2CS3} = \%_{Na2S} \cdot 1.976$, wherein the ratio 1.976 is the quotient of the molar mass of Na_2CS_3 (154.189 g/mol) and Na_2S (78.046 g/mol). All analytical methods without determination of complexing agents (as Na_2EDTA) and concentration of Na_2CS_3 were accredited.

Methodology of research

The effectiveness of Cu(II) precipitation was tested in the first stage using the model solution (109 mg/L of Cu(II)) and using the model solutions with the addition of 50, 100 and 200 mg/L $KNaC_4H_4O_6$ in the corresponding pH ranges. Higher concentrations of complexing compounds were used than the pre-determined ones in raw wastewater (in Na_2EDTA equivalent) in order to verify the effectiveness of Na_2CS_3 also in non-standard technological conditions. Therefore, the possibility has been assumed of increasing concentrations of Cu(II) and tartrate, e.g. in the case of reducing the amount of rinsing water. Methodology of Cu(II) precipitation consisted in a measurement of an appropriate amount of model solution, adjusting its pH to a predetermined pH by means of HCl or NaOH solution, and addition of an equimolar amount of 10% Na_2CS_3 to the amount of metal, and if necessary the pH was corrected. After 15 min. of mixing, wastewater was filtered through a nylon membrane filter (pore diameter of the filter was 0.45 µm) and the amount of copper was determined in the filtrate. On the basis of the determined amount of copper in the filtrate after the reaction, the amount of precipitated copper was calculated, and it was expressed as percentage (precipitation efficiency). Testing the effectiveness of Cu(II) precipitation was carried out in the pH range from 2–10. In the next stage, the possibility of optimizing the precipitation of Cu(II) from real wastewater has been studied. The tests were carried out in the following stages: (1) precipitation of Cu(II) contained in wastewater using a stoichiometric dose of Na_2CS_3 and the excess relative to the stoichiometric dose amounting to 2.5, 5, 10, 15 and 20% with the addition of a coagulant containing $FeCl_3$ and the final pH of 9–9.5, (2) precipitation of Cu(II) ions contained in the wastewater with the simultaneous measurement of the redox potential using a platinum redox electrode, with Na_2CS_3 doses of: 180, 200, 220, 240, 260 and 280 µL of 44.26% Na_2CS_3 (stoichiometric dose was 196 µL of 44.26% Na_2CS_3/1L wastewater), (3) testing of Cu(II) precipitation on a laboratory scale to develop a model of Cu(II) removal from the examined wastewater and determining the most optimal process conditions, using the platinum redox electrode to control this process, assuming the necessary decrease in the redox potential below 100 mV. Research into precipitation conditions was carried out using real wastewater in beakers containing 1L wastewater, in the position equipped with a tripod, magnetic stirrer, pH meter and redox electrode. The testing was carried out in the temperature of 18ºC, with a constant rate of wastewater stirring (500 RPM) and using $FeCl_3$ additive in an amount of 1 mL/L of wastewater. After the addition of iron coagulant, the pH of wastewater was corrected to 9, followed by the addition of the calculated amount of 44.26% Na_2CS_3 and then pH was corrected again to 9–9.5. Then 2 mL of 0.05% solution of anionic flocculant was added (Furoflock CW277). After 15 min. of sedimentation, a sample was collected for testing to determine copper concentration. Studies into precipitation conditions with simultaneous measurement of the redox potential were carried out by analogy except that the potential was measured after adding a coagulant, pH adjustment, and then after the addition of each subsequent dose of 44.26% Na_2CS_3 and pH adjustment to 9–9.5. The research was performed three times.

Experimental design

Optimizing Cu(II) precipitation process using Na_2CS_3 was carried out using Response Surface Methodology and software Statistica 12 (StatSoft, Poland). In the first stage, on the basis of the carried out tests of Cu(II) precipitation from model solutions and real wastewater, the type of dependent and independent parameters and input values for independent parameters was chosen. The potential impact of the following parameters was analysed: temperature (°C), stirring rate (RPM), reaction time (min.), pH of the reaction, Na_2CS_3 dose (mL/L), and the dose of the coagulant (mL/L). In the next stage the experimental design was established, i.e.: the final values of the independent variables were determined, for which the measurement of the dependent variable was performed (concentration of Cu(II) in the treated wastewater), and a number of experiments was decided on. The required number of experiments for given values of the independent variables was conducted by measuring the value of the dependent variable (concentration of Cu(II) in treated wastewater) according to the experimental design. In the last stage, the significance of the coefficients of the function describing the process and the function adjustment to the object of research were verified. For the purposes of this work, the following designations for the dependent variable and independent variables were adopted: x_1 – pH, x_2 – coagulant dose, mL/L, x_3 – dose of 44.26% Na_2CS_3, mL/L, Z_1 – Cu(II) concentration, mg/L. Therefore, the following values were assumed constant: temperature (18.0±0.5°C), stirring rate (750 RPM) and reaction time (5 min.). On the basis of preliminary tests carried out for the model solutions and real wastewater, it was assumed that the adopted stirring rate (750 RPM) in the case of using wastewater samples with a volume of 1L will ensure immediate mixing after the addition of precipitant. Similarly, a suitable reaction time will be applied (5 min.), as during the preliminary stage of the study immediate precipitation of $CuCS_3$ was observed after adding Na_2CS_3 solution to wastewater at ambient temperature (18.0±0.5°C). Therefore, a constant value of the above independent variables was assumed. On the basis of preliminary tests, taking into account the required pH value for wastewater discharged into the sewage system (6.5–9.5), the type of coagulant (Fe(III)) was determined and the efficiency of the process also at higher pH values for planning the experiment pH was adopted in the range of 8–9.5. Finally, using the denotations listed above, the following were adopted:

$x_1 \in$ ‹8.00; 9.50›,
$x_2 \in$ ‹0.25; 1.75›,
$x_3 \in$ ‹0.18; 0.28›

It was assumed that these ranges will be subjected to regulation within ‹-1, +1›:

$x_{1(-1)} = 8.00$ $x_{1(0)} = 8.75$ $x_{1(+1)} = 9.50$,
$x_{2(-1)} = 0.50$ $x_{2(0)} = 1.00$ $x_{2(+1)} = 1.50$,
$x_{3(-1)} = 0.18$ $x_{3(0)} = 0.23$ $x_{1(+1)} = 0.28$.

The accepted ranges of independent factors were expanded, which resulted from the standardization in the range of <-α, α>, instead of the initially adopted standardization in the range <-1.1>, for which α = 1. After adopting α = 1.6818 (according to the experimental design), the parameters ranges (x_1, x_2, x_3) were as follows:

$x_{1(-\alpha)} = 7.49$ $x_{1(0)} = 8.75$ $x_{1(+\alpha)} = 10.01$;
$x_{2(-\alpha)} = 0.16$ $x_{2(0)} = 1.00$ $x_{2(+\alpha)} = 1.84$;
$x_{3(-\alpha)} = 0.15$ $x_{3(0)} = 0.23$ $x_{3(+\alpha)} = 0.31$

The central composite design was used for the experiment planning, as a result of which 16 experiments were obtained for the three independent factors (pH, the amount of iron coagulant and the amount of Na_2CS_3). The experimental design and the obtained results are shown in Table 2. The results of the model research are presented in a graphical form using response surface plots.

Results and discussion

Precipitation of copper from model solutions

Fig. 1 shows the test results of copper precipitation efficiency from model solutions containing the additive of $KNaC_4H_4O_6$ which changed within the ranges 92.1–99.4% (for 50 mg/L of $KNaC_4H_4O_6$), 91.7–99.2% (for 100 mg/L of $KNaC_4H_4O_6$) and 83.8–99.1% (for 200 mg/L of $KNaC_4H_4O_6$). The carried out studies have shown the possibility of removing Cu(II) with

Table 2. Experimental conditions and results of central composite design

The number of the experiment	Variables			Response
	Faktor 1	Faktor 2	Faktor 3	
	pH	Fe(III) as coagulant, mL/L	Na_2CS_3, mL/L	Cu, mg/L
1	8.00	0.50	0.18	3.98
2	8.00	0.50	0.28	3.65
3	8.00	1.50	0.18	3.75
4	8.00	1.50	0.28	3.55
5	9.50	0.50	0.18	1.56
6	9.50	0.50	0.28	0.05
7	9.50	1.50	0.18	1.80
8	9.50	1.50	0.28	0.02
9	7.49	1.00	0.23	6.97
10	10.01	1.00	0.23	0.03
11	8.75	0.16	0.23	1.23
12	8.75	1.84	0.23	1.19
13	8.75	1.00	0.15	4.86
14	8.75	1.00	0.31	2.20
15	8.75	1.00	0.23	2.33
16	8.75	1.00	0.23	2.36

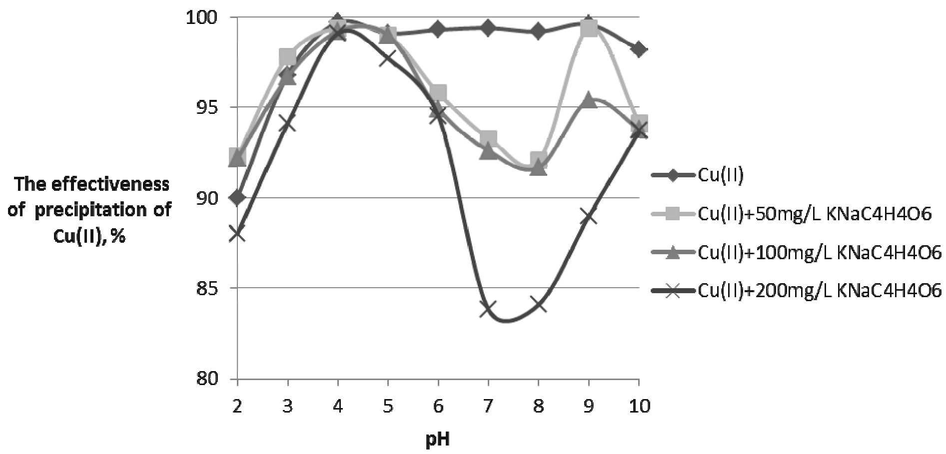

Fig. 1. Removal of copper using Na_2CS_3 in the presence of $KNaC_4H_4O_6$ (50, 100, 200 mg/L)

the efficiency greater than 95% at pH of approx. 3.25–5.75. Increasing the efficiency of copper removal for all doses of $KNaC_4H_4O_6$, was also observed at pH of approx. 8–9. The comparable effectiveness of copper removal (>90%) from wastewater using sulfides was reported in previous studies (Choi et al. 2006). The use of dithiocarbamates at pH 3–11 caused also the removal of copper over 90% (95.42–98.42% for diethyldithiocarbamate and 96–99.98% for dibenzyldithiocarbamate in laboratory scale) (Abu-El-Halawa, Zabin 2017). The carried out research has shown probably lower stability of the Cu(II) complex with tartrate ions in an environment similar to neutral rather than in acid one, wherein the reduced effectiveness of precipitation in a strongly acidic pH of approx. 2–3 should be interpreted as the lack of effectiveness due to the properties of Na_2CS_3 with respect to Cu(II), not as a result of tartrate complex formation. In the case of Cu(II) precipitation from the solution without the addition of complexing agents, also reduced Na_2CS_3 efficacy was shown in a strongly acidic pH.

Precipitation of copper from industrial wastewater

Table 3 shows the results of copper precipitation from real wastewater with the composition shown in Table 1 using a stoichiometric, in relation to the amount of copper, dose of Na_2CS_3 and doses higher than the stoichiometric dose of 2.5, 5, 10, 15 and 20%. Using stoichiometric dose of Na_2CS_3 (196 µL of 44.26% Na_2CS_3) at pH 9–9.5, and coagulant dose of 1 mL/L, copper concentration in treated wastewater was 1.35 mg/L. Reducing copper concentration to values lower than 1 mg/L in the given conditions of the process, required the use of higher doses of Na_2CS_3 than the calculated stoichiometric dose. Similar effects (possibility of reducing copper concentration to less than 0.5 mg) were reported in previous studies using HTDC for removal of copper from both synthetic and industrial wastewater containing EDTA at pH 3–9 (Fu et al. 2007). The inability to quantify the result of copper precipitation resulted from the presence of complexing compounds in wastewater, mainly sodium and potassium tartrate, derived from a bath for electroless copper plating. However, one cannot exclude the presence of other complexing compounds used as additives to the process baths, which are used to prepare the surface of the plates before the process of electroless copper plating. Low concentrations of iron in the range of 0.22–0.52 mg/L, which originated from the used coagulant containing Fe(III), was also found in the treated wastewater (Table 3). In the next stage of the study, the impact of the dose of 44.26% Na_2CS_3 on the value of the redox potential (E) of treated wastewater and the concentration of copper in the treated wastewater were analysed. The results of the carried out tests are shown in Table 4 and Fig. 2. The tests carried out on a laboratory scale

Table 3. The physicochemical parameters of wastewater treated using stoichiometric and excess dose of 44.26% Na_2CS_3

Parameter	Unit	Results
196 µL 44.26% Na_2CS_3 – the stoichiometric dose		
pH	–	9.23
Copper $_{\text{(after add. NaOH to pH 9)}}$	mg/L	3.40
Copper $_{\text{(after add. Na2CS3)}}$	mg/L	1.35
Iron	mg/L	0.52
201 µL 44.26% Na_2CS_3 – excess 2.5%		
pH	–	9.36
Copper	mg/L	0.80
Iron	mg/L	0.36
206 µL 44.26% Na_2CS_3 – excess 5%		
pH	–	9.45
Copper	mg/L	0.22
Iron	mg/L	0.41
216 µL 44.26% Na_2CS_3 – excess 10%		
pH	–	9.40
Copper	mg/L	0.20
Iron	mg/L	0.22
225 µL 44.26% Na_2CS_3 – excess 15%		
pH	–	9.39
Copper	mg/L	0.05
Iron	mg/L	0.35
235 µL 44.26% Na_2CS_3 – excess 20%		
pH	–	9.47
Copper	mg/L	0.05
Iron	mg/L	0.36

have shown that dosing of NaOH solution to wastewater in order to adjust pH to 9, and precipitation of certain amount of copper as $Cu(OH)_2$ is associated with a decrease in the redox potential measured using a platinum redox electrode (from +652.9 mV to +189.5 mV). Further decrease in the value of the redox potential in the direction of negative values was observed during dispensing of 44.26% Na_2CS_3 (from +189.5 mV to -156.0 mV). Copper concentration in the treated wastewater less than 1 mg/L (0.85 mg/L) was obtained by using 200 µL of 44.26% Na_2CS_3 for 1L of the wastewater and was associated with a decrease in the redox potential to +82.0 mV. The lowest value of copper concentration of 0.05 mg/L was obtained after using 240, 260 and 280 µL of 44.26% Na_2CS_3.

The change of the redox potential indicates a change of oxidizing environment on reducing environment. Such situation is typical for the environments where the metals with low degrees of valence and also hydrogen sulfide are present (Goncharuk et al 2009). On the basis of the conducted studies and the relation between copper concentration and redox potential and the dose of Na_2CS_3 as shown in Fig. 2, it can

Table 4. Physicochemical parameters of wastewater treated using 44.26% Na_2CS_3 – the effect of dose on the redox potential (E)

Parameter	Unit	Results
180 µL 44.26% Na_2CS_3 per 1L of wastewater		
pH	–	3.05
E	mV	+652.9
pH (after add. of 1 mL of FeCl3)	–	2.06
E after add. of 1 mL of FeCl3)	mV	+684.6
E pH */**	mV	+189.5
E (after add. of Na2CS3)	mV	+106.4
Copper	mg/L	1.86
200 µL 44.26% Na_2CS_3 per 1L of wastewater		
E(after add. of Na2CS3)	mV	+82.0
Copper	mg/L	0.85
220 µL 44.26% Na_2CS_3 per 1L of wastewater		
E(after add. of Na2CS3)	mV	+34.2
Copper	mg/L	0.2
240 µL 44.26% Na_2CS_3 per 1L of wastewater		
E(after add. of Na2CS3)	mV	+5.0
Copper	mg/L	0.05
260 µL 44.26% Na_2CS_3 per 1L of wastewater		
E(after add. of Na2CS3)	mV	-98.5
Copper	mg/L	0.05
280 µL 44.26% Na_2CS_3 per 1L of wastewater		
E(after add. of Na2CS3)	mV	-156.0
Copper	mg/L	0.05

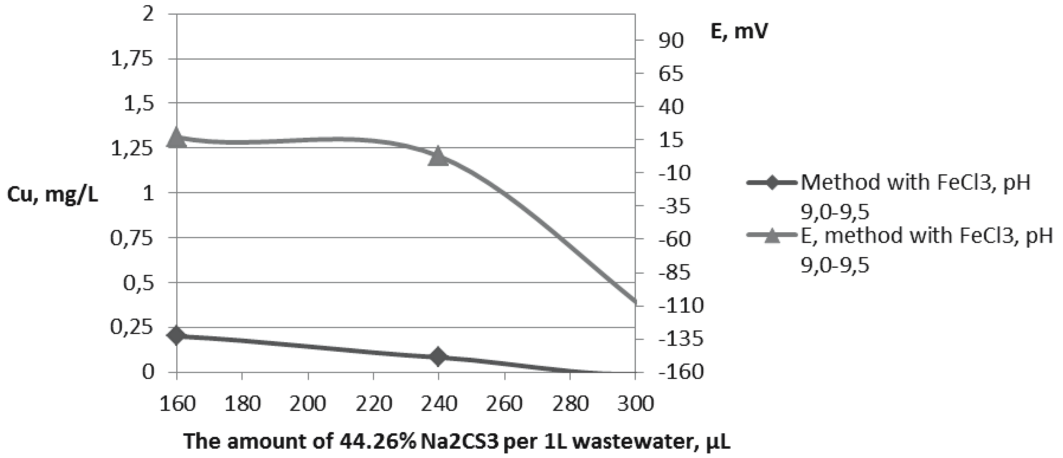

Fig. 2. Removal of copper from industrial wastewater using Na_2CS_3 in the presence of $FeCl_3$ as coagulant and platinium redox electrode at pH 9–9.5

be assumed that for the tested wastewater the condition that must be met to reduce copper concentration to less than 1 m/L is dosage of Na_2CS_3 until a reduction in the value of the redox potential of less than +90 mV is obtained. Table 2 shows the concentration of copper (dependent factor) for 16 experiments carried out on a laboratory scale at different pH values and different amounts of iron coagulant and 44.26% of Na_2CS_3. Two experiments (15 and 16) were carried out in the design centre and similar copper concentrations were obtained for them (2.33 and 2.36 mg/L, respectively). The lowest values of copper concentration in the treated wastewater was obtained in the experiments 6, 8 and 10 of 0.05, 0.02 and 0.03 mg/L respectively, and the largest in experiments 9 and 13 of 6.97 and 4.86 mg/L, respectively. Different values for copper were associated with different experimental conditions resulting from the generated plan of experiment. Table 5 shows a sheet of estimators effects ANOVA for the standardized values of the input values, while only the important parameters were taken into consideration and verification of significance was carried out at a given standard significance level of α = 0.05. Such a procedure indicated three statistically significant input parameters, i.e.: pH (L), the amount of iron coagulate (Q) and the amount of Na_2CS_3(L). The values of calculated correlation coefficients (R^2=0,9169, R^2_{adj}=0,8961) indicated a very good adjustment of the created model to the obtained experimental data, despite the exclusion from the model of all non-significant linear-linear and linear-square interactions. The carried out analysis of the adequacy of the model using ANOVA, presented in Table 6, also point to the importance of the three input parameters at low values of mean square error (MS=0.3795). Fig. 3 shows the Pareto chart on which the estimators of standardized results are ordered according to their absolute value, whereas the vertical line indicates the minimum values of statistically significant effects at a given standard significance level of α = 0.05. The biggest impact on the concentration of copper in the treated wastewater should be attributed therefore to the pH value at which copper precipitation is conducted using Na_2CS_3. This conclusion

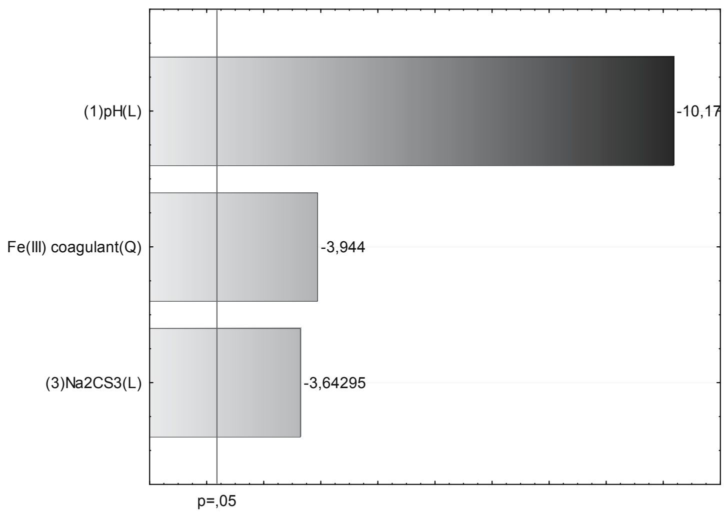

Fig. 3. Pareto chart – (Cu, mg/L, 3 value, 1 block, 16 experiments, MS=0.3795)

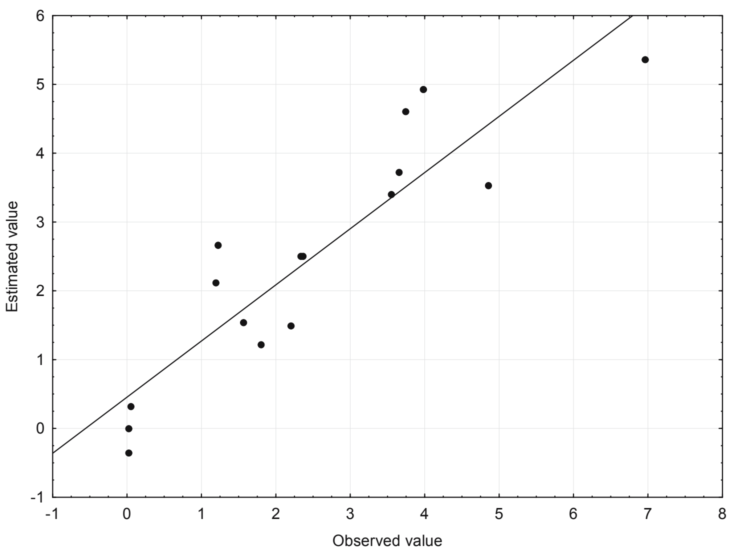

Fig. 4. Estimated vs. observed values plot (Cu, mg/L, 3 value, 1 block, 16 experiments, MS=0.3795)

is confirmed by the results of preliminary tests in which approx. 93% of the initial amount of copper contained in raw wastewater was precipitated at the stage of alkalizing wastewater with NaOH solution to pH 9 (Table 3). This effect can also be increased by the adopted precipitant, which has an alkaline reaction. Despite this, for the quantitative copper precipitation it is necessary to use dosages 44.26% Na_2CS_3 excessing stoichiometric doses, which indicates the possibility of a reaction of the certain amount of precipitated $Cu(OH)_2$ with added Na_2CS_3 and the formation of brown $CuCS_3$. Such a probable course of the reaction indicates that $CuCS_3$ has a lower solubility product than $Cu(OH)_2$. Fig. 4 presents a graph of the estimated values with respect to the observed values, which is indicative of proper adjustment of predicted values to the experimental values. The developed model of copper precipitation using response surface method is therefore suitable for the obtained experimental data. Figs 5, 6 and 7 present response surface plots which are an image of a three-dimensional response surface projected on a two-dimensional plane, which allowed for the assessment and analysis of the shape of the surface in terms of the impact of various parameters on the course of the discussed process. Fig. 5 shows the change in copper concentration in the treated wastewater, depending on the pH value and the amount of iron coagulant assuming a constant value of the precipitant (0.23 ml/L of 44.26% Na_2CS_3). With increasing pH, a decrease in the concentration of Cu was observed in the wastewater for regular doses of 44.26% Na_2CS_3 and iron coagulant. A similar trend of low intensity was observed with the increase in the dose of iron coagulant, which means that the quantity of the used coagulant also has an impact on the amount of the precipitated copper. The probable cause of this phenomenon is Cu(II) adsorption by precipitating $Fe(OH)_3$ in a large amount (in particular at the coagulant dose of 2 mL/L). The mathematical description of the changes in the concentrations of copper, depending on the pH value and the amount of iron coagulant assuming a constant value of precipitant is represented by the equation (1):

$$[Cu,\ mg/L] = 22.461 - 2.262[pH] - 0.161[Fe(III)]^2 \quad (1)$$

Fig. 6 shows the change in the copper concentration depending on the pH and the dose of 44.26% Na_2CS_3 with the assumption that the dose of iron coagulant was fixed at 1 mL/L. The results of model research showed in this case that copper concentration in the treated wastewater was pH-dependent and decreases significantly with increasing pH and the dose of 44.26% Na_2CS_3. The impact of the amount of 44.26% Na_2CS_3 dose on copper concentration is much greater than the impact of iron coagulant dose shown in Fig. 5. The lowest concentration of Cu in the treated wastewater can be achieved by conducting the precipitation process in an alkaline environment in the excess of 44.26% Na_2CS_3. The mathematical description of the changes in the concentrations of copper, depending on the pH value and the amount of 44.26% Na_2CS_3 assuming a constant dose of iron coagulant is represented by the equation (2):

$$[Cu,\ mg/L] = 25.093 - 2.262[pH] - 12.146[Na_2CS_3] \quad (2)$$

Fig. 7 shows the change in the concentration of Cu depending on the dose of 44.26% Na_2CS_3 and iron coagulant dose. The conducted model research with the assumed constant value of pH 8.75 showed a significant impact of 44.26% Na_2CS_3 dose and iron coagulant on copper concentration in wastewater after completion of precipitation. At a constant pH value, definitely greater effect on copper concentration has the dose of 44.26% Na_2CS_3 than the dose of the iron coagulant. At the same time, the lowest concentration of copper in wastewater

Table 5. Analysis of the experiment with the central composite design using Statistica 12. The sheet of estimators effects ANOVA model coefficients for the standardized values of the input values, at the significance level of 0.05 after excluding non-significant interaction of effects

Parameter	The evaluation of the effects, Cu, mg/L, R^2=0.9169, R^2_{adj}=0.8961, MS=0.3795								
	Effect	Standard error	p-value	-95% confidence intervals	+95% confidence intervals	Factor	Standard error of factor	-95% confidence intervals	+95% confidence intervals
Constant Value	3.061	0.215	$1\cdot10^{-8}$	2.593	3.529	3.061	0.215	2.593	3.529
pH, (L)	-3.393	0.333	$1\cdot10^{-7}$	-4.119	-2.667	-1.697	0.167	-2.059	-1.333
Fe(III), as coagulant mL/L, (Q)	-1.383	0.351	0.00194	-2.147	-2.147	-0.692	0.175	-1.074	-0.309
Na_2CS_3 mL/L, (L)	-1.215	0.333	0.00337	-1.941	-1.941	-0.607	0.167	-0.970	-0.244

Table 6. Analysis of the experiment with the central composite design using Statistica 12. Verification of the adequacy of the model using ANOVA at the significance level of 0.05, excluding the non-significant linear–linear interaction of effects

Parameter	The evaluation of the effects, Cu, mg/L, R^2=0.9169, R^2_{adj}=0.8961, MS=0.3795			
	SS	MS	F	p-value
pH, (L)	33.315	39.315	103.594	0.000000296
Fe(III) as coagulant, (Q)	5.903	5.903	15.555	0.001948779
Na_2CS_3, (L)	5.037	5.037	13.271	0.003369815

SS-predicted residual error sum of squares, MS-mean square, F-statistics can be achieved by carrying out precipitation process using a certain excess of 44.26% Na_2CS_3, and increased doses of iron coagulant. The mathematical description of the change in copper concentration, depending on the amount of 44.26% Na_2CS_3 and the amount of iron coagulant, assuming a constant pH value is represented by the equation (3):

$$[Cu, mg/L] = 5.459 - 0.161[Fe(III)]^2 - 12.146[Na_2CS_3] \quad (3)$$

The results of model research shown in Figs 5, 6 and 7 indicate the possibility of precipitation of copper from wastewater containing copper ions in the form of complexes with tartrate after the prior addition of iron coagulant and alkalizing to pH 9–9.5. Generally, this observation is in agreement with earlier results, which pointed to a good efficiency of copper removal also in alkali medium (Bobrowska-Krajewska et al. 1994). Obtaining wastewater with a low content of copper ions required in the case of the tested wastewater the use of an excess of 44.26% Na_2CS_3 in relation to the calculated stoichiometric dose. The need to use a certain amount of 44.26% Na_2CS_3 excess was probably associated with the course of secondary reaction (between $Cu(OH)_2$ and Na_2CS_3) and the complexing reaction of Cu(II) by sodium and potassium tartrate.

Conclusion

The problems with quantitative precipitation of copper from the wastewater originated from the production of printed circuit boards are due to the presence in wastewater of complexing compounds which are the components of the electroless copper plating baths. The presence of complexing compounds in industrial wastewater leads to complexing of Cu(II) and the difficulty of its quantitative removal at the stage of metal precipitation. The presented test results indicate the potential use for this purpose of 44.26% Na_2CS_3 in the presence of Fe(III) coagulant at pH 9–9.5. The use of Na_2CS_3 solution under optimal process conditions (pH 9–9.5, $FeCl_3$ 1 mL/L, E=+82mV), allows for precipitation of complexed copper ions(II) (Cu(II) 0,85 mg/L). The use of higher doses of Na_2CS_3 (pH 9–9.5, $FeCl_3$ 1 mL/L, E= -156 mV) reduced the copper content to 0.05 mg/L. Model studies using RSM

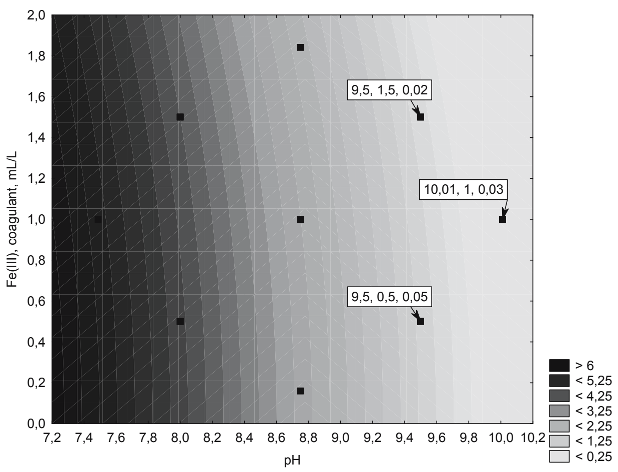

Fig. 5. Response surface plot for Cu removal (mg/L) with respect to pH and Fe(III) as coagulant

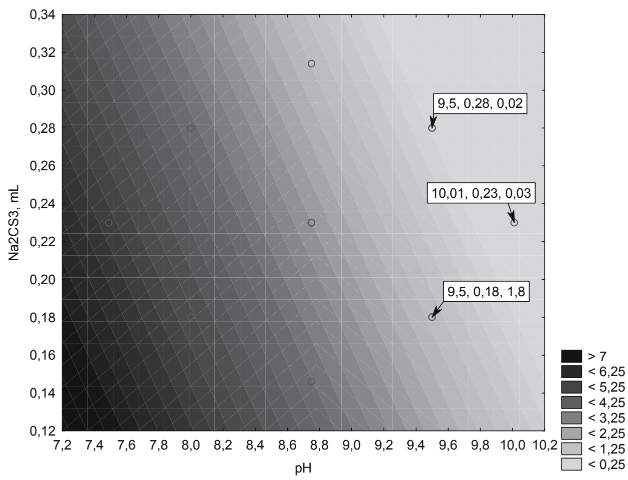

Fig. 6. Response surface plot for Cu removal (mg/L) with respect to pH and 44.26% Na_2CS_3 as precipitating agent

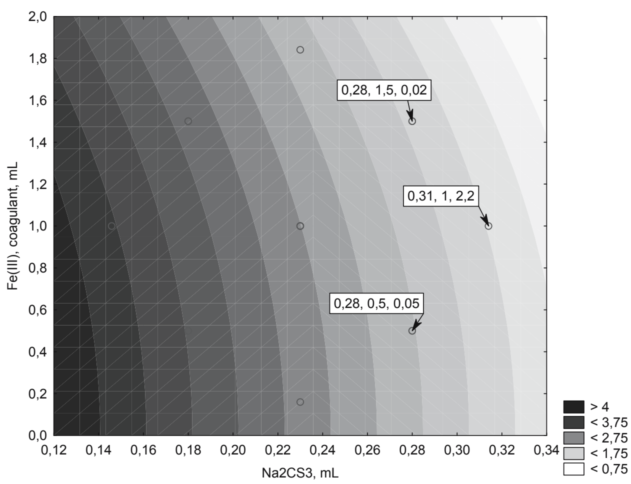

Fig. 7. Response surface plot for Cu removal (mg/L) with respect to 44.26% Na_2CS_3 as precipitating and Fe(III) as coagulant

made it possible to optimize the precipitation process and calculate the critical values of pH, concentrations of Fe(III) and Na_2CS_3. The lowest values of Cu(II) concentration (0.05, 0.02 and 0.03 mg/L) in the treated wastewater were obtained in the three experiments when an alkaline medium (pH 9.5 and 10) and higher concentration of Na_2CS_3 (0.23 and 0.28 mL/L) were used. At the implementation stage of the presented process on an industrial scale, attention should be paid to local requirements for the quality of wastewater introduced into the municipal sewage, industrial sewage system or surface water. On the one hand, this will enable the optimal effective dose of reagents, and, on the other hand, the appropriate cost optimization of the carried out wastewater treatment processes.

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Zastosowaniu tritiowęglanu sodu do usuwania chelatowanych jonów miedzi ze ścieków przemysłowych pochodzących z procesu bezprądowego miedziowania

Streszczenie: Celem przedstawionych badań było zweryfikowanie możliwości strącania Cu(II) ze ścieków pochodzących z procesu bezprądowego miedziowania, zawierających $KNaC_4H_4O_6$ jako związek kompleksujący Cu(II), przy zastosowaniu Na_2CS_3. Przedstawiono możliwość usuwania Cu(II) ze ścieków pochodzących z produkcji obwodów drukowanych przy zastosowaniu Na_2CS_3 jako odczynnika strącającego. Zastosowanie Na_2CS_3 przy pH 9–9,5 w obecności koagulantu żelazowego (Fe(III)), umożliwiło skuteczne strącenie skompleksowanych jonów Cu(II) ze ścieków zawierających winian sodu i potasu ($KNaC_4H_4O_6$), jako związek kompleksujący. Zastosowanie metody powierzchni odpowiedzi (Response Surface Methodology, RSM) pozwoliło na analizę i ocenę wpływu poszczególnych parametrów niezależnych (pH, dawka koagulantu żelazowego, dawka 44,26% Na_2CS_3) na stężenie miedzi w ściekach oczyszczonych.