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Research on neutralization of wastewater from pickling and electropolishing processes

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Abstract: Process baths used for electropolishing and pickling of stainless steel have become increasingly contaminated with heavy metal ions over time. There is still lack of research on the neutralization of this type of technological wastewater with high concentrations of metal ions and containing complexing compounds, which significantly hinders their effective treatment. The aim of this paper is to study how the selected methods of heavy metals removal will affect the quality of the treated, industrial post-galvanic sewage from pickling and electropolishing of chromium-nickel steel on a laboratory and technical scale. The research used sodium sulphide or a decomplexing agent based on organic sulphur to neutralize wastewater containing triethanolamine or glycerol. Treatment of electropolishing wastewater poses a challenge. Nevertheless, wastewater with glycerol is easier to neutralize than those containing triethanolamine. In the industrial scale the use of a decomplexing agent is necessary to achieve the required nickel values in the wastewater after treatment below 1 ppm. Even in the case of high concentrations of nickel ions in raw wastewater, the neutralization process of the wastewater originating only from pickling alone was effective. The search for effective methods of neutralization of mixed wastewater is especially important in industrial conditions, where it is not always possible to completely separate these two types of sewage. The paper also presents the results of the composition of post-neutralization sludge, which may be useful in planning further management and disposal of this type of waste.

Abbreviations
PI – pickling
EP – electropolishing
WW – wastewater
PIWW – pickling wastewater
EPWW – electropolishing wastewater
IPIWW – industrial pickling wastewater
IEPWW – industrial electropolishing wastewater
WWTP – wastewater treatment plant
n.a. – not analyzed

Introduction

Industrial wastewater from the surface treatment of metals may contain non-biodegradable, carcinogenic and toxic heavy metals, which tend to accumulate in living organisms causing plenty of diseases and disorders. The presence of heavy metals in domestic wastewater disrupts the microbial processes of wastewater treatment and can lead to the deterioration of the natural environment (Bugajski et al. 2017). Thus, the removal of heavy metals from wastewater and sludge is necessary to protect the environment and people's health, and must therefore be conducted before their disposal (Ijagbemi et al. 2009). Even landfill leachate can contain harmful chromium and lead compounds, therefore every effort should be made to prevent their release to the environment (Szymański et al. 2018).

Heavy metals removal from wastewater can be carried out by means of chemical precipitation, ion exchange, adsorption, membrane processes (Bodzek 2013; Bodzek and Konieczny 2011) (reverse osmosis, ultrafiltration, nanofiltration, electrodialysis), coagulation and flocculation, flotation and electrochemical treatment (Fu and Wang 2011; Kurniawan et al. 2006). The performance of conventional treatment methods with respect to this kind of wastewater is often unsatisfactory, which was made evident in an abnormal concentration of substances undesirable in the treated wastewater. This results inter alia from the nonuniform composition of wastewater and specific physicochemical properties of harmful substances present in wastewater (Thomas et al. 2018, 2021).

The surface treatment of chromium-nickel steel through pickling and electropolishing processes generates the post-galvanic sewage containing high concentrations of nickel, chromium, iron, and copper. The treatment of this kind of effluent is usually performed by adjusting pH from 8 to 11 so as to precipitate the metallic cations as the corresponding hydroxide which, as a sludge, is then separated during filtration (Kurama 2009). In the case of a mixture of metals, their hydroxides do not precipitate completely at a single pH and each metal hydroxide has its own favorable to precipitate a range of pH (for nickel 10.0–10.5 pH, for copper 8.5–9.5 pH), beyond which it tends to resolubilize. With an increase in pH the solubility of the precipitated metal hydroxides decreases, while amphoteric hydroxides react with the OH^- anions, causing metals to be retransferred to the wastewater. In addition, organic complexing agents would hinder the precipitation of sparingly soluble metal compounds if they are present in the wastewater. Their negative impact may be eliminated by adjusting pH to the optimal level for the precipitation process (Ain Zainuddin et al. 2019; Kowal and Świderska-Bróż 1981; Thomas et al. 2018).

The complexing agents are applied in the electropolishing process to improve the gloss and smoothening of the surface while reducing bath contamination. The most commonly used complexing agent is glycerol, whose concentration in the bath may reach as much as 35% wt. (Lochynski et al. 2016). Glycerol raises the viscosity and density of the solution, which in turn increases the thickness of the diffusion film and furthers the distance of the anode potential from the thermodynamic value. Glycerol also reduces the relative concentration of water in the near-anode area, and as a substance with active oxygen atoms forms an adsorption film on the surface of the anode (Łyczkowska-Widłak et al. 2020).

After pH adjustment to the basic conditions, the dissolved metals are converted to the insoluble solid phase by the chemical reaction with calcium, which is a good heavy metal precipitant even in concentrations exceeding 1000 mg/dm^3. Sodium hydroxide and sodium sulphide are also applied to the chemical precipitation. Sodium hydroxide is a more expensive chemical than lime but it provides a faster and more efficient neutralization. It is 100 times more soluble than lime in water, so that the precipitation reaction is completed in 5–10 minutes. Lime requires 20–30 minutes of retention time to react when properly mixed. On the other hand, lime gives better sedimentation and dewatering properties of the formed metal hydroxide. Moreover, the risk of hydroxides re-dissolution at higher pH becomes lower, as in the case of chromium (Dahlgren 2010).

Sulphides are less soluble over a broad pH range compared to hydroxides, and the reaction rate between sulphide and metal is much faster than between metal and hydroxide. The sludge generated is smaller compared to hydroxide precipitation. However, sulphide dosing and process control are more difficult due to the sensitivity of the process and odor nuisance resulting from the formation of H_2S (Ain Zainuddin et al. 2019; Thomas et al. 2018). To reduce the risk associated with the formation of toxic H_2S, metal precipitants of similar effectiveness are used. These metal precipitants form insoluble compounds as a result of direct reaction with heavy metals. They may also assist in the formation of metal hydroxides by reducing the "net charge differential" or the zeta potential of the combined wastewater solution being an alternative to hydroxide precipitation (Andrus 2000). The most commonly used metal precipitants are dithiocarbamates, such as sodium dimethyldithiocarbamate and sodium diethyldithiocarbamate, that form insoluble dithio-metal salts with heavy metals. Other reagents which act in a similar way include: trimercapto-s-triazinetrisodium salt, sodium trithiocarbonate, and sodium 1,3,5-hexahydrotriazinedithiocarbamate (Andrus 2000; Fu et al. 2007; Thomas et al. 2018). Nevertheless, overdosing of these reagents may result in environmental degradation and be toxic for bacteria, algae, and aquatic life forms (Andrus 2000).

The drawbacks of chemical precipitation include reagents high consumption to reduce the heavy metal concentration to the normative content, which in Polish regulations amounts to 1 mg/dm^3 and 0.5 mg/dm^3 for total chromium, nickel and copper when discharged to the sewage system and to the environment, respectively. Other disadvantages include: excessive amount of sludge requiring further treatment, high disposal costs of this sludge, and poor settling (Fu and Wang 2011; Kurniawan et al. 2006). This sludge consists of heavy metals from acidic or alkaline solutions and from rinse waters generated by the electroplating processes. The sludge is categorized as hazardous waste, generally disposed in hazardous waste landfills (Li et al. 2010).

In the neutralization process of the post-galvanic sewage, special attention is paid to the presence of Cr(VI), which is a very toxic and carcinogenic strong oxidizing agent. Its removal requires reduction to Cr(III), which is not toxic and immobile in the environment. The reduction is conducted by the addition of sulphuric acid(VI) and soluble iron(II) salt or sodium bisulphate ($NaHCO_3$), with a final adjustment of pH at up to about 9.0 to form the precipitate (Lugo-Lugo et al. 2010).

In the composition of wastewater from pickling and electropolishing of chromium-nickel steel, Cr(III) occurs (Łyczkowska-Widłak et al. 2020). If Cr(VI) occurs in the raw wastewater from the surface treatment of chromium-nickel steel, it can be reduced to Cr(III) with the aid of sodium metabisulphite ($Na_2S_2O_5$) prior to the neutralization process.

Industries consuming large volumes of water generally pay more attention to reused wastewater, thus membrane processes can be an alternative to conventional physicochemical processes of wastewater treatment in the electropolishing industry, as they save up on operational costs and water consumption through water recycling. Membrane processes are highly effective, easy to operate, and compatible with other treatment processes (Petrinic et al. 2015). On the other hand, fluctuations in raw post-galvanic sewage quality and susceptibility of membranes to fouling may necessitate additional pretreatment of sewage, which leads to extra investment costs. Micro- and ultra-filtration are very effective pretreatments for reverse osmosis since reverse osmosis membranes are sensitive to fouling; however, high costs, process complexity, membrane fouling and low permeate flux have limited their use to heavy metals removal (Clever et al. 2000; Fu and Wang 2011; Petrinic et al. 2015).

The ion exchange process is another approach to heavy metals removal from wastewater. Weakly or strongly acidic synthetic resins are typically used for this purpose. The ion exchange process has many advantages such as high treatment capacity, high removal efficiency, and fast kinetics. Wastewater, however, should be treated for the removal of suspended solids prior to ion exchange. Additionally, suitable ion exchange resins are not available for all heavy metals, while the capital and operational cost is high. In the literature on the subject, there have been plenty of investigations on the removal of heavy metals on the natural zeolites (e.g. clinoptylolite), but these were conducted mainly in a laboratory and not on an industrial scale (Alyüz and Veli 2009; Fu and Wang 2011; Keane 1998; Kurniawan et al. 2006; Papadopoulos et al. 2004; Rodríguez-Iznaga et al. 2002).

Adsorption is characterized by high effectiveness, easy handling, wide availability of different adsorbents, and cost-effectiveness (Bhattacharya et al. 2006). The main disadvantage of this process is the high cost of conventional adsorbents (e.g. activated carbons) and their regeneration. Therefore, the substitutes from natural materials (e.g. clay materials), which are cheaper and may have high ion exchange capacity, are commonly applied. In order to enhance the adsorption capacity, the natural exchangeable cations can be replaced with the organic molecules forming the so-called "organoclays" (Ijagbemi et al. 2009). The natural materials used to adsorb heavy metals include natural clay minerals (e.g. montmorillonite), zeolites, bentonites, as well as biosorbents. Typical biosorbents can be derived from non-living biomass (such as bark, lignin, shrimp, etc.), algal biomass, and microbial biomass (e.g. bacteria, fungi, and yeast) (Cooper et al. 2002; Fu and Wang 2011; Khan et al. 1995; Liu et al. 2004; Panayotova and Velikov 2002; Taha et al. 2017).

Nevertheless, the research on adsorption and biosorption is conducted chiefly on a laboratory scale. In addition, there is plenty of research in the literature concerning the removal of heavy metals from synthetically prepared solutions, not from real wastewater. Moreover, these metals are introduced to the solution by adding the appropriate salts (Chaudhari and Murthy 2010; Juang and Shiau 2000; Khan et al. 1995; Lin and Kiang 2003). Some of the investigations only concern solutions containing one metal, not mixtures of them (De Pablo et al. 2011; Priya et al. 2009). Taking this into account, it is difficult to anticipate how the presence of different heavy metals, occurring at changeable concentrations, would affect heavy metals removal from wastewater. To the authors' knowledge, there is also little research on the removal of heavy metals from post-galvanic sewage coming from the electropolishing industry concerning chemical precipitation or application of metal precipitants. On the contrary, there is plenty of research on biosorption, ion exchange or membrane processes. Those researchers often pay much attention to the reduction of Cr(VI), which clearly results from its toxicity (Agrawal et al. 2006; Lugo-Lugo et al. 2010; Malaviya and Singh 2011), but to a lesser extent on the removal of nickel from real post-galvanic sewage coming from the electropolishing industry in the chemical precipitation process.

The main goal of the presented research is to study how the selected methods of heavy metals removal will affect the quality of the treated, industrial post-galvanic sewage from pickling and electropolishing of chromium-nickel steel on a laboratory and technical scale. In industrial conditions, wastewater of various compositions, characterized by a wide range of initial concentrations, was tested. In order to investigate the impact of the treatment process on the composition of sewage, the content of nickel, chromium, copper and iron in concentrated and diluted post-galvanic sewage as well as in the sludge (with the aid of ICP-OES) was analyzed.

In this paper, the application of calcium hydroxide, sodium hydroxide, sodium sulphide as well as metal precipitant and agents containing organic sulphur was studied for treating different types of post-galvanic sewage (containing triethanolamine or glycerol) from pickling and electropolishing processes. The issue of neutralization of mixed wastewater containing both electropolishing and etching wastewater is an important one but upon which the literature is non-existent. The search for effective methods of neutralization of mixed sewage is especially important in industrial conditions, where it is not always possible to completely separate these two types of sewage. The original research results from the analysis of the physicochemical composition of industrial post-galvanic sewage and sludge are also presented.

Materials and methods

In order to perform laboratory tests, model wastewaters (PIWW and EPWW) were prepared by diluting concentrated process baths which were intensively exploited in an industrial scale. The pickling solution based on HNO_3 and HF as well as an electropolishing solution composed of H_3PO_4, H_2SO_4, and triethanolamine or glycerol were mixed with deionized water in various proportions in order to create wastewaters (PIWW and EPWW) with different initial concentrations of iron, chromium, nickel, and copper ions. In order to maintain the conditions that enable repeated neutralization attempts while striving to best reflect the characteristics of the process, the selected variants were referred to the range of wastewater contamination in an industrial scale. The pH level was adjusted by adding NaOH or $Ca(OH)_2$ suspension to the wastewater until the desired pH value, measured with a pH meter, was attained. During the neutralization process, the solution was continuously stirred by a magnetic stirrer. After completion of the neutralization process, the resulting solution was filtered through a Munktell Filter Paper Disc Grade 390 to separate the precipitate.

The tests on a technical scale included neutralization of wastewater with $Ca(OH)_2$ in a neutralization chamber with simultaneous pH control, flocculation and pumping of the sludge to the settling tank, and separation of the sludge from the filtrate on a filter press (Figure 1). The filtrate was mineralized with concentrated HNO_3 before the concentration of metals was examined using an ICP-OES optical spectrometer.

ICP-OES (inductively coupled plasma – optical emission spectroscopy) tests were conducted using the Thermo Scientific iCAP 7000 Series ICP-OES apparatus with an automated sample feeder and software manufactured by Qtegra Intelligent Scientific Data Solution. In the case of the industrial post-neutralization sludge samples, the ICP-OES measurements were made using the Thermo Scientific iCAP 7400 Duo.

Results and discussion

In plants for the surface treatment of chromium-nickel steels, the following types of process wastewater can be distinguished: wastewater from flow scrubbers that results from washing elements with wastewater from stationary scrubbers with a relatively low concentration of contaminants; wastewater with a very high concentration of used technological solutions; and wastewater from washing technological surfaces. The wastewater may contain several to several dozen mg/dm^3 of heavy metal ions in the case of less concentrated solutions, and in the case of concentrated sewage, usually from several dozen to several hundred mg/dm^3, and in some cases even up to several or tens of thousands. It is good practice to store wastewater at high concentrations and then dose it in small amounts to the diluted wastewater. "The best way is to treat sewage at the place where it is generated, in the absence of an on-site treatment plant, solutions resulting from metal surface treatment processes should be entrusted to a specialized company" (Rubel et al. 2009). Before discharging wastewater into the sewage system, the sewage required a series of tests, both on a laboratory and industrial scale.

Comparison of neutralization methods

Taking into account the economic, technical and environmental aspects, the measures often used to neutralize acidic technological wastewater are sodium hydroxide or calcium hydroxide. In the first series of tests, 10 experiments were carried out in which the influence of NaOH or $Ca(OH)_2$ in reducing the content of iron, chromium, nickel, and copper ions after the neutralization process was verified.

The model wastewater was produced by mixing distilled water with solutions of concentrated process baths after electropolishing and pickling of stainless steel. Laboratory tests were carried out for PIWW, EPWW, and PIWW + EPWW of various compositions, correcting the pH level to the lowest possible value (pH = 8.5), and then separating the resulting sediment on the filter; the filtrate was subjected to ICP-OES tests.

In wastewater before neutralization, the contaminants concentration was respectively: 166–542 mg Fe/dm^3, 47–115 mg Cr/dm^3, 6–66 mg Ni/dm^3, and 2–8 mg Cu/dm^3 (Table 1). For PIWW with an initial concentration of 542 mg Fe/dm^3, 132 mg Cr/dm^3, and 66 mg Ni/dm^3, it was possible to reduce the concentrations of the analyzed pollutants to 0–1 mg/dm^3 after the neutralization process. For EPWW with an initial content of 47 mg Cr/dm^3, 6 mg Ni/dm^3, and 4 mg Cu/dm^3 with the use of $Ca(OH)_2$, values below 1 mg/dm^3 were obtained for chromium and copper, while much higher values were observed with the use of NaOH. Regardless of the type of hydroxide used, significant exceedances of nickel concentration after neutralization, ranging from 2.2–2.9 mg/dm^3, were observed. When neutralizing EPWW with a twice higher initial concentration, it was also observed that the results for chromium and copper after neutralization were lower with $Ca(OH)_2$ than with NaOH, and regardless of the hydroxide used, the content of mg Ni/dm^3 after neutralization was 3.4–4.6 (Table 1).

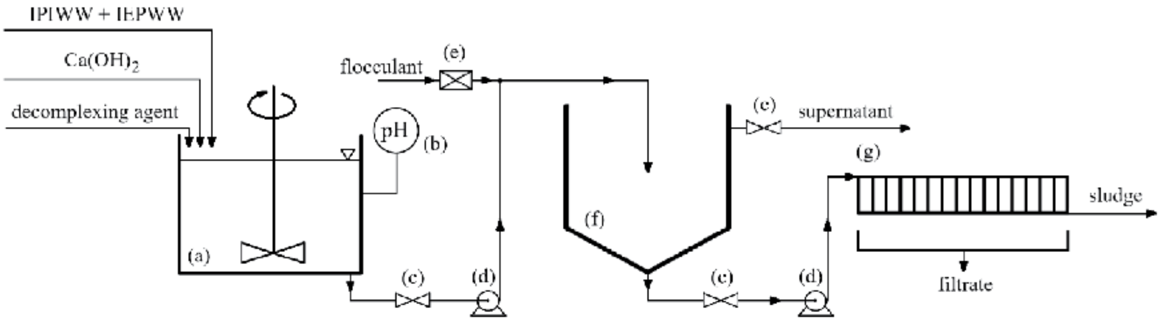

Fig. 1. Simplified diagram of the installation for treatment and neutralization of wastewater from steel pickling and electropolishing processes a) neutralization chamber, b) pH-meter, c) valve, d) pump, e) non-return valve, f) settling tank, g) filter press

Table 1. Composition of model wastewater and its contamination with iron, chromium, nickel, and copper ions after the neutralization process with NaOH and $Ca(OH)_2$

Type of WW	Fe [mg/dm^3]			Cr [mg/dm^3]			Ni [mg/dm^3]			Cu [mg/dm^3]		
	before treatment	treated $Ca(OH)_2$	treated NaOH	before treatment	treated $Ca(OH)_2$	treated NaOH	before treatment	treated $Ca(OH)_2$	treated NaOH	before treatment	treated $Ca(OH)_2$	treated NaOH
PIWW + EPWW	**445**	0.1	0.7	**115**	0.0	0.3	**40**	4.1	3.8	**7**	0.2	0.1
PIWW + EPWW	**445**	0.1	1.2	**115**	0.0	0.5	**40**	3.8	3.9	**7**	0.1	0.2
PIWW	**271**	0.0	0.0	**66**	0.0	0.0	**33**	0.6	0.1	**2**	0.0	0.0
PIWW	**271**	0.0	0.0	**66**	0.0	0.0	**33**	0.1	0.0	**2**	0.0	0.0
PIWW	**542**	0.0	0.1	**132**	0.0	0.0	**66**	0.1	0.0	**4**	0.0	0.0
PIWW	**542**	0.0	0.0	**132**	0.0	0.0	**66**	1.0	0.1	**4**	0.0	0.0
EPWW	**166**	0.1	37.3	**47**	0.0	14.2	**6**	2.2	2.9	**4**	0.5	1.4
EPWW	**166**	0.0	4.7	**47**	0.0	2.4	**6**	2.6	2.4	**4**	0.3	0.8
EPWW	**332**	0.9	10.5	**94**	0.3	4.9	**12**	4.6	4.1	**8**	1.2	1.4
EPWW	**332**	4.6	7.0	**94**	1.4	3.9	**12**	3.4	3.8	**8**	0.7	1.4

In the case of the neutralization of mixed PIWW + EPWW, very good results were obtained for iron, chromium, and copper, but in the case of nickel, the neutralization was insufficiently effective and the obtained concentrations ranged from 3.8–4.1 mg Ni/dm^3. The content of nickel ions before and after the neutralization process for PIWW, EPWW, and PIWW + EPWW with the use of either $Ca(OH)_2$ or NaOH is here presented in graphical form for better illustration (Figure 2).

Despite a much higher initial concentration of nickel ions before neutralization in PIWW (33 mg/dm^3) than in EPWW (6 mg/dm^3), the solution containing only the pickling wastewater obtained the expected content of nickel ions after the neutralization process, i.e., below the permissible value of 1 mg/dm^3 (Figure 2). In the case of this type of wastewater, the nickel removal efficiency was over 90%. Ain Zainuddin et al. (Ain Zainuddin et al. 2019) added NaOH to precipitate heavy metals from acid and nickel rinse wastewater from the electroless copper plating industry, which contained nickel at a concentration level of 12.32 mg/dm^3 and 1.06 mg/dm^3, respectively, and obtained 76.66% and 65.79% removal of this metal, respectively. Papadopoulos et al. (Papadopoulos et al. 2004) applied chemical precipitation to remove nickel from rinse bath in the anodizing process of a metal surface treatment industry. At pH 7.5 and 10.5 they obtained the removal of Ni(II) at the level of 71% and 85%, respectively, with an initial nickel concentration of 51.6 mg/dm^3. Brbooti et al. (Brbooti et al. 2011) compared the efficiency of different precipitants to remove heavy metals from single and multicomponent aqueous solutions. They found that for solutions treated by CaO or NaOH, pH values greater than 10.0 were required to achieve the least solubility values of heavy metals. They managed to achieve a very high Ni removal (more than 90%) from the mixture of metals containing 500 mg/dm^3 of each metal at high pH values (pH>11) with the use of lime.

The wastewater from the electropolishing process, which contained triethanolamine in its composition as well as mixed wastewater from pickling and electropolishing after the neutralization process, differed from 2.3 to 4.0 mg/dm^3 of nickel which proves the significant influence of the EPWW presence on the final value of nickel ions after the neutralization process. Due to the complexing properties of triethanolamine, its influence on wastewater treatment after electropolishing is the greatest with nickel ions compared to chromium and copper ions. Triethanolamine is a versatile ligand having three hydroxyethyl groups and one nitrogen donor atom. Complexes of $N(CH_2CH_2OH)_3$ can have diverse structures. Among metal-triethanolamine complexes are known mononuclear cationic complexes of metals such as, e.g., nickel, cobalt or copper and also others in which triethanolamine may coordinate as a triple and/or tetradentate ligand (Deeloed et al. 2020; Kondratenko et al. 2017, 2020). In combination with nickel ions, one possible complex is $[Ni(N(CH_2CH_2OH)_3)_2]^{2+}$. This shows that except for the adjustment of pH, the type of treated wastewater, especially from the electropolishing process, has also a significant impact on the final nickel concentration after the neutralization process.

Based on the conducted experiments, it was decided to use $Ca(OH)_2$ in a further stage of the research and to monitor the content of nickel ions in the wastewater after treatment. The greatest difficulties were observed with reducing the nickel concentration in the wastewater to the required values below 1 mg Ni/dm^3, as meeting this requirement would also be accompanied by the low contents of chromium and copper ions.

Neutralization of wastewater from the pickling process

The next stage of the research was to carry out 16 trials of neutralization and treatment of PIWW with an initial content of 5–650 mg Ni/dm^3. pH was corrected using $Ca(OH)_2$, adjusting it to the lowest possible pH = 8.5. Then, the precipitate on the filter was separated, with the filtrate after mineralization being subjected to ICP analysis. In the treated wastewater, only two of the results obtained exceeded the value of 1 mg/dm^3 (Figure 3). The exceedances were small, in one case by 0.03 mg/dm^3 and in another by 0.05 mg/dm^3. Based on the conducted analyses, it should be concluded that the nickel removal process is effective for pickling wastewater in a wide range of concentrations. It seems that chemical precipitation of metals contained in PIWW is very effective not only in

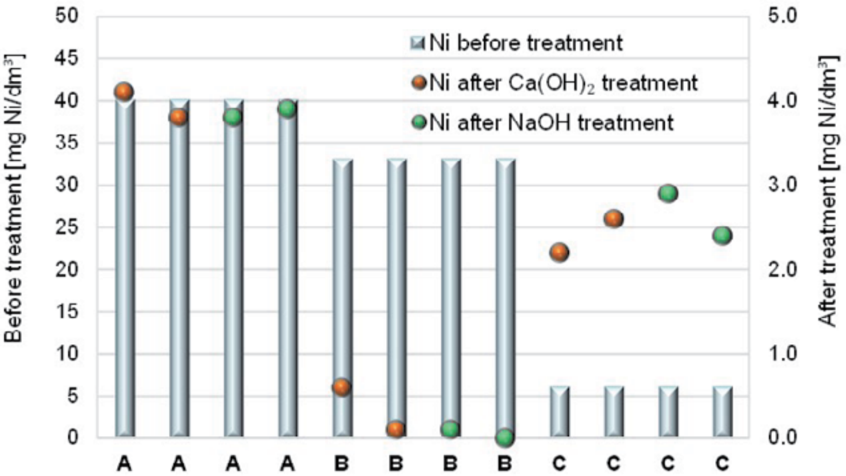

Fig. 2. The content of nickel ions before and after the neutralization process with the use of either calcium hydroxide or sodium hydroxide for model wastewater: A) PIWW + EPWW, B) PIWW, C) EPWW.

a laboratory scale, but also in an industrial scale, as for example in the Old Fonye Steel mill (the stainless steel producer in Shanghai, China) where a similar effectiveness of the neutralisation of pickling wastewater with lime was achieved. Nickel concentrations of the in- and out-going wastewater from the neutralization facility amounted to 1000 mg/dm^3 and 0.15 mg/dm^3, respectively (Dahlgren 2010).

Neutralization of wastewater from the electropolishing process

In the EPWW neutralization trials, the influence of the additives used in the process baths on the effectiveness of neutralization was taken into account (Figure 4). For this purpose, the neutralization process with the use of $Ca(OH)_2$ was applied to wastewater with various initial concentrations containing triethanolamine and glycerol. On the basis of the tests performed, it should be stated that in the case of wastewater containing an electropolishing bath with the addition of triethanolamine, it is much more difficult to remove nickel in the neutralization process compared to wastewater from the bath with the addition of glycerol. For the bath with glycerol, it was possible to lower the nickel concentration below the required level for the initial concentrations of up to 14 mg Ni/dm^3. In the case of baths with the addition of triethanolamine, the required concentration reduction was achieved only in the case of very low initial concentrations. The nickel content in the untreated wastewater above 4 mg/dm^3 before neutralization did not guarantee an acceptable nickel content after neutralization.

The authors are yet to come across any research that compares how complexing agents such as triethanolamine or glycerol affect the neutralization process of post-galvanic sewage from the chromium-nickel steel surface treatment industry. Moreover, the sewage subjected to the neutralization process in plenty of studies does not contain the complexing agent. Often there is also a lack of information whether such complexing agent even exists in the treated sewage. Additionally, if some researchers examine the impact of complexing agents on the treatment of electropolishing wastewater, they generally use compounds other than triethanolamine or glycerol, e.g., ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citric acid or Na_2EDTA (Juang et al. 2006; Thomas et al. 2018; Wang et al. 2019).

The results show that regardless of nickel concentration in the raw sewage after the electropolishing process, reduction

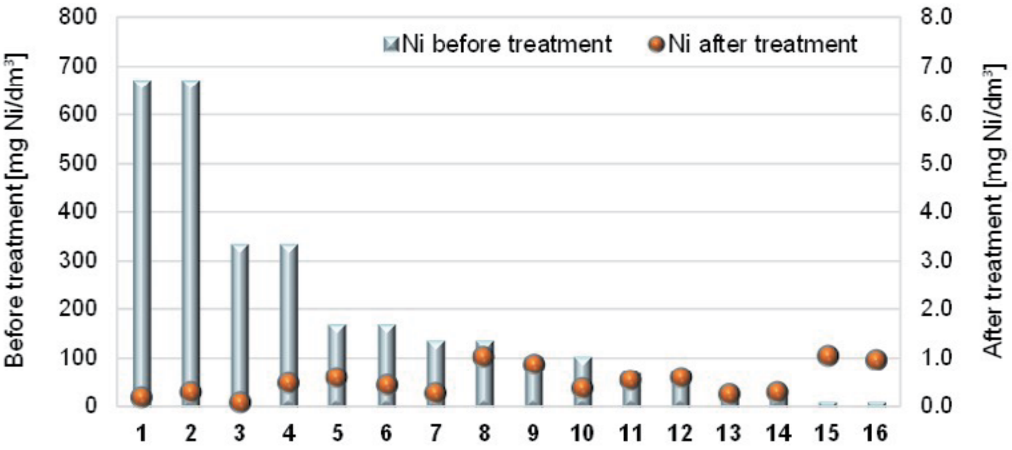

Fig. 3. Nickel content in the model PIWW before and after neutralization for different initial concentrations

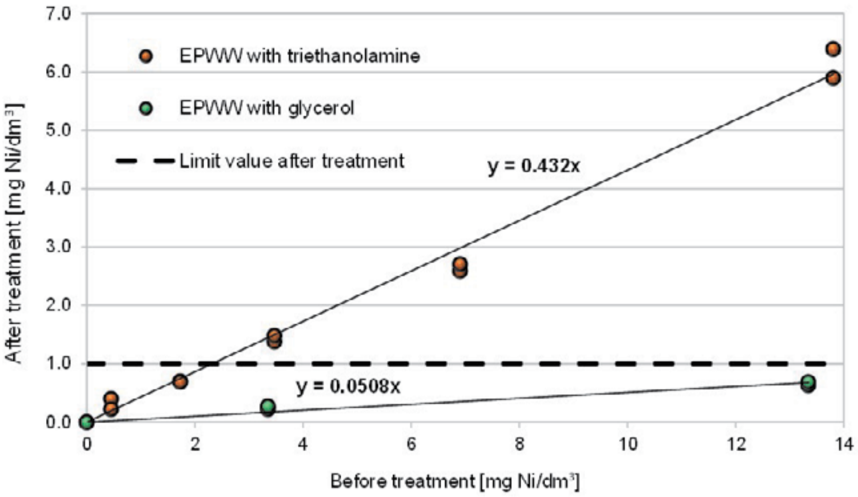

Fig. 4. Nickel content before and after neutralization for the model EPWW with both either triethanolamine or glycerol

in its concentration through chemical precipitation below 1 mg/dm^3 is not possible without the addition of a decomplexing agent.

The use of 5 cm^3 $Na_2S \cdot 9H_2O$ with a concentration of 12 g/dm^3 as an additive in the neutralization process of wastewater from electropolishing allowed for a significant reduction in the content of nickel ions, even in the case of high initial concentrations. For the raw wastewater with a nickel content of 800 mg/dm^3, a concentration reduction of about 96–99% was achieved, and for the raw wastewater with a concentration of 280 mg/dm^3, 93–99% (Figure 5). Despite such a high degree of reduction of the nickel content in the neutralization process with the addition of Na_2S, the obtained final concentration values were in the range of 6.3–30 mg Ni/dm^3 for the series with a higher initial concentration and 2.6–18.4 mg Ni/dm^3 for series with a lower concentration, while significantly exceeding the permissible value of 1 mg Ni/dm^3.

Ain Zainuddin et al. (Ain Zainuddin et al. 2019) added Na_2S to precipitate heavy metals from acid and nickel rinse wastewater from electroless copper plating industry containing nickel at a concentration level of 12.32 mg/dm^3 and 1.06 mg/dm^3, respectively, and obtained 95.32% and 65.79% removal of the metal, respectively.

The presented results from galvanic wastewater studies have clarified the difficulties associated with the neutralization of specific types of wastewater. The use of additives in industrial electropolishing baths can cause problems with the effective reduction of concentrations, especially when using triethanolamine. In case of insufficient effectiveness in the process and exceeding the permissible standards, it is necessary to direct the sewage for re-neutralization or to look for other methods that can achieve the expected results.

Technical trials

Tests on a technical scale were carried out on a technological installation adapted to neutralize wastewater from electropolishing and pickling processes, equipped with a reaction chamber having a working volume of 1.5 to 2.4 m^3. The key elements of the installation comprise a sedimentation tank and a filter press, on which the sludge is separated from treated wastewater and only after this process can it be discharged into the municipal sewage system. Wastewater from the pickling and electropolishing processes was dosed to the neutralization chamber, where the neutralization reaction occurred under the influence of the added $Ca(OH)_2$ suspension. The wastewater was then directed to the settling tank where sedimentation took place, before going to the filter press.

Two series of technical tests were performed. The first with the use of Na_2S, and the second with the use of an organic sulphur-based decomplexing agent. The use of sodium sulphide may pose the risk of H_2S formation at a low pH of the solution, although appropriate pH control and the addition of Na_2S at pH above 8.0 can prevent this. Wastewater neutralization (IPIWW + IEPWW) on a technical scale has made it possible to reduce the concentration of iron ions from 1043 mg/dm^3 to 0.7 mg/dm^3, chromium from 242 mg/dm^3 to a value below 0.05 mg/dm^3, nickel from 338 mg/dm^3 to 0.85 mg/dm^3, and copper from 77 mg/dm^3 to 0.03 mg/dm^3 (Table 2). During the technical tests, sodium sulphide was added to the reaction mixture at pH of 9.5. The pH increase of 0.5–1.0 resulted from the hydrolysis of weak acid and strong base salts. It is worth noting that increasing pH to 10.5 during the next series of neutralization negatively influenced the effect of the process in which a decrease was obtained with chromium from 1043 mg/dm^3 to 1.0 mg/dm^3, and for nickel ions from 338 mg/dm^3 to 1.4 mg/dm^3, hence a value exceeding the acceptable standard. After the sludge was separated on the filter press, the pH of the treated wastewater was within the expected range (pH = 7.5–9.0) each time.

Laboratory studies have shown that electropolishing wastewater with a high initial concentration of nickel cannot be effectively neutralized with only $Ca(OH)_2$ and Na_2S. On the basis of laboratory tests and the results of technical tests obtained so far, for which the concentrations obtained were close to the limits set by Polish regulations, no attempt was made to neutralize the wastewater as part of the planned series of technical tests using Na_2S with a relatively high content of nickel ions above 350 mg/dm^3 for raw IPIWW + IEPWW. In the case of wastewater with an increased share of IEPWW and, at the same time, a greater share of H_3PO_4, H_2SO_4 and organic additives, even lower nickel ions well below 350 mg/dm^3

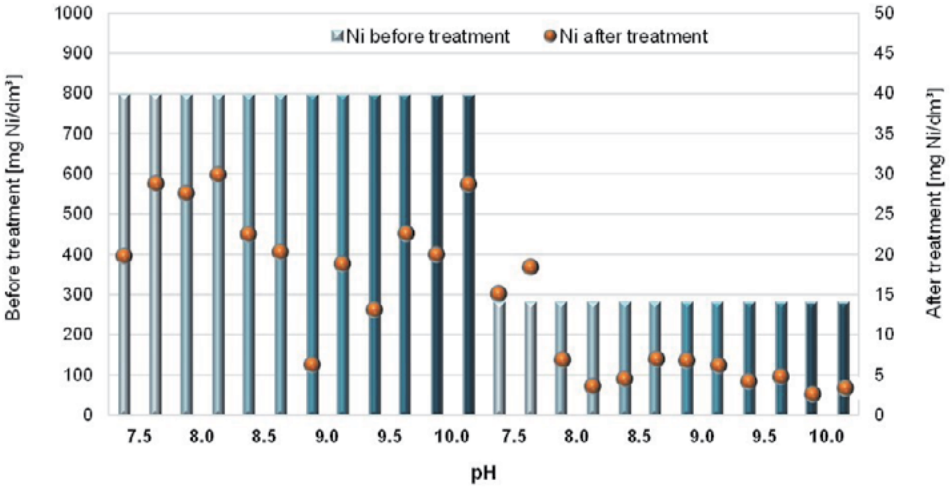

Fig. 5. Nickel content in the PIWW + EPWW before and after neutralization for different initial concentrations

may pose a significant challenge. Triethanolamine or glycerol contained in electropolishing process baths form complexes with metal ions, which, especially in the case of nickel ions, make it difficult to precipitate them in the form of insoluble sediments (metal hydroxides and metal sulphides) and to treat wastewater to a level below 1 mg/dm^3.

Subsequent technical tests were performed at the installation by adding a decomplexing agent based on organic sulphur to the reaction mixture. Figure 6 compares the content of iron (A), chromium (B), nickel (C), and copper (D) ions in industrial wastewater from the pickling and electropolishing process for a series of 10 technical tests before and after neutralization. The vast majority of the conducted studies have made it possible to obtain the results of Cr, Ni, Cu content below 1.00 mg/dm^3 even at very high concentrations of raw wastewater, respectively: 200–7000 mg Cr/dm^3, 60–3200 mg Ni/dm^3, and 30–2200 mg Cu/dm^3. Only for the sixth sample, which did not have outstanding parameters, were fully satisfactory results not obtained after neutralization; instead, 1.5 mg Cr/dm^3 and 1.5 mg Ni/dm^3 were obtained, which may have resulted from an improperly conducted wastewater neutralization process. Even at very high concentrations of nickel ions in raw wastewater reaching 2400–3200 mg Ni/dm^3 (IPIWW> IEPWW), the values below 0.7 mg Ni/dm^3 were obtained after neutralization. The wastewater with a composition characterized by a higher share of IEPWW (IPIWW <IEPWW) was also treated to a level of 0.5 mg Ni/dm^3 and 0.5 mg Cr/dm^3. The very high initial content of copper ions above 2000 mg Cu/dm^3 was not a problem in the neutralization process and the result was less than 0.3 mg Cu/dm^3, and in the case of lower concentrations, even below 0.1 mg Cu/dm^3.

An important aspect in the context of describing the obtained results of neutralization studies, although often marginalized, is the assessment of the composition of the sludge formed as a result of the process. The resulting sediments are hazardous materials and their collection is possible only by specialized companies dealing with the collection of hazardous substances. These wastes can potentially be a source of valuable raw materials, but further treatment of these sludges plus the relatively high hydration and variability of composition directly related to the varying concentration of raw wastewater remain a challenge. Table 3 presents the composition of the content of pollutants in industrial wastewater in g/dm^3 (iron, chromium, nickel, copper, phosphorus, sulphur) and the corresponding pollutants in the filter cake per g/kg of dry matter (iron, chromium, nickel, copper, phosphorus, sulphur, calcium). It is worth paying attention to some dependencies that in the future may help in designing solutions for the management of waste from the pickling and electropolishing processes of chromium-nickel steels. The Fe/Cr content ratio in the sediments ranged from 4.0–4.4; the P/S content, regardless of the type of neutralized sewage, from 0.6–2.0. The calcium content was from 262 to 313 g Ca/kg DM, and the iron, chromium, and nickel content was respectively: 31–126, 8–30, and 1–15 g/kg DM. The content of phosphorus and sulphur in the sludge after neutralization ranged respectively from 13–131 g P/kg DM and 30–74 g S/kg DM. The percentage of sludge hydration was also similar regardless of the performed test and the initial composition of the sewage, ranging from 61.7% to 71.4%. The compiled results of technical tests should be assessed holistically, by analyzing the whole series of obtained results. Due to the fact that the research was conducted under industrial conditions, it cannot be ruled out that the sludge is partially contaminated by a previously carried out neutralization batch. Efforts were made to minimize the potential negative impact described above, and in most experiments on a technical scale the raw wastewater was neutralized, which was preceded by batch neutralization with a similar level of impurities.

The obtained results may form the basis for further research in the quest for ways to manage waste or reduce its negative impact on the environment. The increase in prices of hazardous waste collection may contribute to the search for ways to reduce the water content in filter cake and for solutions towards reducing the formation of pollutants at the source, better monitoring of the electrochemical treatment process, looking for methods of recovery or management of already partially used technological solutions, and rationing the use of rinsing water.

Conclusions

1. The results of laboratory tests indicate the possibility of neutralization with the use of $Ca(OH)_2$ in the case of wastewater from the steel pickling process alone. Even at very high initial concentrations, up to 650 mg Ni/dm^3, it was possible to reduce the nickel concentration afterwards to a value below 1 mg/dm^3.
2. It was not possible to lower the concentration below 1 mg Ni/dm^3 in the case of mixed wastewater containing wastewater from the electropolishing process or from electropolishing itself. Due to the use of organic additives hindering the precipitation of metal ions in the electropolishing baths, it is advisable to use decomplexing agents to obtain the expected wastewater treatment efficiency.

Table 2. Iron, chromium, nickel and copper content before and after treatment for IPIWW + IEPWW on a technical scale

pH*	Fe		Cr		Ni		Cu	
	Before treatment	treated $Ca(OH)_2$ + Na_2S	Before treatment	treated $Ca(OH)_2$ + Na_2S	Befor etreatment	treated $Ca(OH)_2$ + Na_2S	Before treatment	treated $Ca(OH)_2$ + Na_2S
	[mg/dm^3]	[mg/dm^3]	[mg/dm^3]	[mg/dm^3]	[mg/dm^3]	[mg/dm^3]	[mg/dm^3]	[mg/dm^3]
10.5	1043	1.0	242	< 0.05	338	1.4	77	< 0.1
9.5	1043	0.7	242	0.1	338	0.8	77	< 0.1

* pH value before Na_2S addition

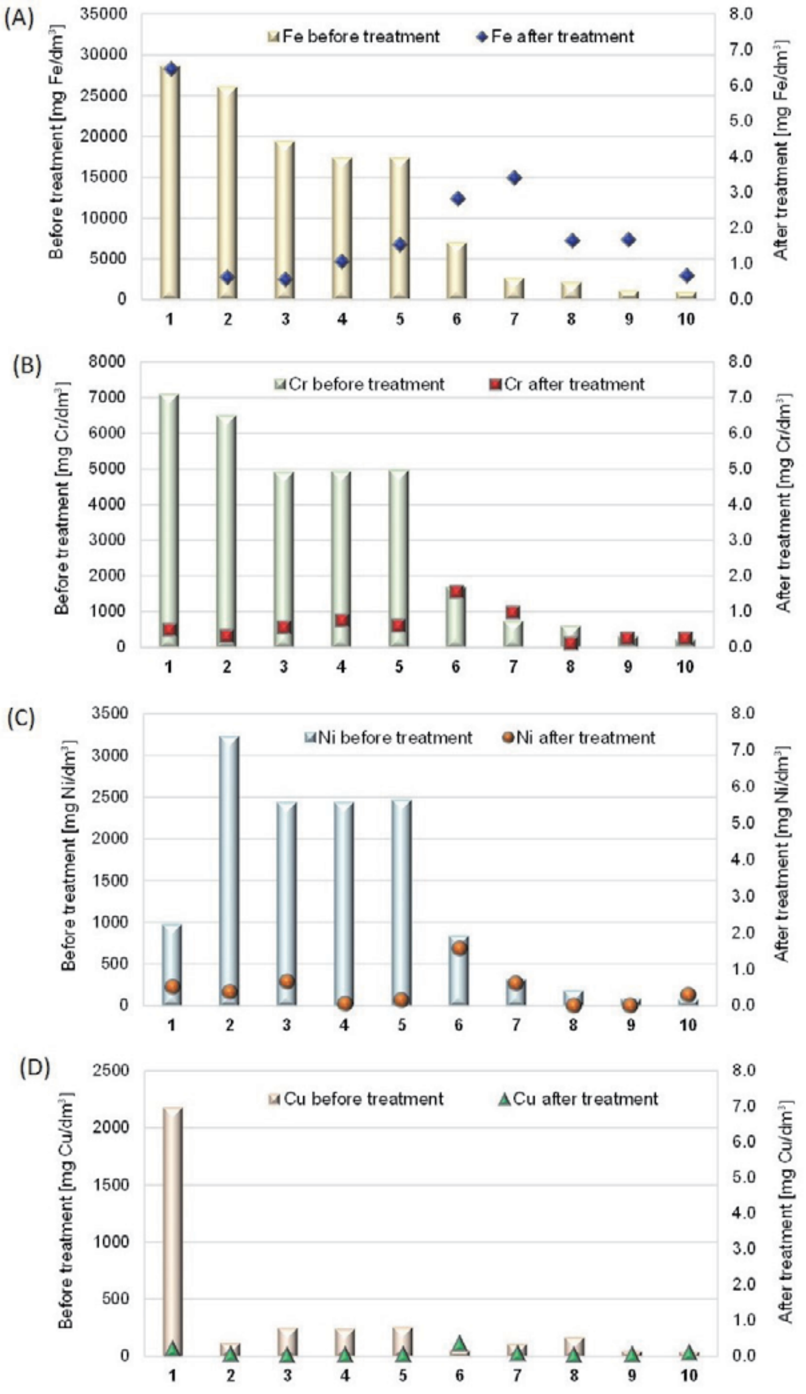

Fig. 6. Comparison of iron (A), chromium (B), nickel (C), copper (D) ions in industrial wastewater from pickling and electropolishing for a series of 10 technical tests before and after neutralization

3. The use of organic additives in the electropolishing bath makes it difficult to neutralize the resulting wastewater. In the case of a bath containing glycerol, it is possible to achieve final concentrations below 1 mg Ni/dm^3 for an initial concentration of up to 14 mg Ni/dm^3, while for a bath with triethanolamine it was only possible at very low initial concentrations of up to 4 mg/dm^3.
4. The use of Na_2S as an additive to the neutralization process, even in the case of high initial concentrations at the level of 280 mg/dm^3 and 800 mg/dm^3, makes it possible to achieve a high efficiency in nickel concentration reduction, amounting to 93–99% and 96–99%, respectively, despite the fact that the results achieved exceeded the limit values.
5. The possibility of separating wastewater streams from pickling and electropolishing and monitoring the level of their contamination, the possibility of storing wastewater, the volume of the neutralization chamber, the amount of water used, and the methods of rinsing details can have an impact on the effective management of the wastewater neutralization process.
6. The presented characteristics of sludge composition after the neutralization process may be useful in planning for the management and neutralization of wastes such as post-galvanic sludge.

Table 3. Composition of the of pollutants in industrial wastewater in g/dm^3 (iron, chromium, nickel, copper, phosphorus, sulphur) and the corresponding pollutants in the filter cake per g/kg of dry matter (iron, chromium, nickel, copper, phosphorus, sulphur, calcium

No	Description	Sludge hydration	Type of sample	Fe	Cr	Ni	Cu	P	S	Ca	Fe/Cr	P/S	Ca/Fe
1	IPIWW < IEPWW	68%	wastewater [g/dm^3]	28.6	7.1	1.0	2.2	119.0	76.2	n.a.	4.0	1.6	n.a.
			filter cake [g/kg d.m.]	31	8	1	2	115	74	305	4.1	1.5	9.7
2	IPIWW > IEPWW	65%	wastewater [g/dm^3]	26.0	6.5	3.2	0.1	<0.1	0.4	n.a.	4.0	0.1	n.a.
			filter cake [g/kg d.m.]	126	31	15	1	13	20	275	4.1	0.6	2.2
3	IPIWW > IEPWW	68%	wastewater [g/dm^3]	19.3	4.9	2.4	0.2	0.2	0.6	n.a.	3.9	0.4	n.a.
			filter cake [g/kg d.m.]	81	19	7	3	100	55	292	4.2	1.8	3.6
4	IPIWW > IEPWW	62%	wastewater [g/dm^3]	17.3	4.9	2.4	0.2	0.2	0.6	n.a.	3.5	0.4	n.a.
			filter cake [g/kg d.m.]	122	29	13	6	35	58	277	4.3	0.6	2.3
5	IPIWW > IEPWW	64%	wastewater [g/dm^3]	17.3	4.9	2.5	0.2	0.2	0.7	n.a.	3.5	0.4	n.a.
			filter cake [g/kg d.m.]	123	30	12	2	61	55	302	4.1	1.1	2.5
6	IPIWW > IEPWW	62%	wastewater [g/dm^3]	6.9	1.7	0.8	<0.1	<0.1	0.2	n.a.	4.1	0.1	n.a.
			filter cake [g/kg d.m.]	69	17	7	4	100	61	289	4.0	1.6	4.2
7	IPIWW + IEPWW	64%	wastewater [g/dm^3]	2.6	0.7	0.3	0.1	3.3	2.6	n.a.	3.6	1.3	n.a.
			filter cake [g/kg d.m.]	98	23	10	2	81	49	297	4.3	1.6	3.0
8	IPIWW + IEPWW	71%	wastewater [g/dm^3]	2.0	0.6	0.2	0.2	8.2	5.7	n.a.	3.5	1.4	n.a.
			filter cake [g/kg d.m.]	54	12	4	3	131	66	313	4.4	2.0	5.8
9	IPIWW + IEPWW	63%	wastewater [g/dm^3]	0.9	0.3	0.1	<0.1	3.0	2.3	n.a.	3.2	1.3	n.a.
			filter cake [g/kg d.m.]	51	13	4	2	99	73	262	4.0	1.3	5.1
10	IPIWW + IEPWW	71%	wastewater [g/dm^3]	0.8	0.2	0.1	<0.1	2.0	1.7	n.a.	4.0	1.2	n.a.
			filter cake [g/kg d.m.]	66	16	6	4	106	46	272	4.1	2.3	4.1

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References

Agrawal, A., Kumar, V. & Pandey, B.D. (2006). Remediation options for the treatment of electroplating and leather tanning effluent containing chromium – A review, *Mineral Processing and Extractive Metallurgy Review*, 27, 2, pp. 99–130. DOI: 10.1080/08827500600563319

Ain, Z.N., Azwan, R.M.T., Imam, M.H., Wahidah, P.S. & Rohana, M.Y.S. (2019). Removal of Nickel, Zinc and Copper from Plating Process Industrial Raw Effluent Via Hydroxide Precipitation Versus Sulphide Precipitation, *IOP Conference Series: Materials Science and Engineering*, 551, 1. DOI: 10.1088/1757-899X/551/1/012122

Alyüz, B. & Veli, S. (2009). Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, *Journal of Hazardous Materials*, 167, 1–3, pp. 482–488. DOI: 10.1016/j.jhazmat.2009.01.006

Andrus, M.E. (2000). A review of metal precipitation chemicals for metal-finishing applications, *Metal Finishing*, 98, 11, pp. 20–23. DOI: 10.1016/S0026-0576(00)83532-1

Bhattacharya, A.K., Mandal, S.N. & Das, S.K. (2006). Adsorption of Zn(II) from aqueous solution by using different adsorbents, *Chemical Engineering Journal*, 123, 1–2, pp. 43–51. DOI: 10.1016/j.cej.2006.06.012

Bodzek, M. (2013). Inorganic micropollutants removal by means of membrane processes – State of the art, *Ecological Chemistry and Engineering S*, 20, 4, pp. 633–658. DOI: 10.2478/eces-2013-0044

Bodzek, M. & Konieczny, K. (2011). Membrane techniques in the removal of inorganic anionic micropollutants from water environment state of the art, *Archives of Environmental Protection*, 37, 2, pp. 15–19.

Brbooti, M.M., Abid, B. & Al-shuwaiki, N.M. (2011). Removal of Heavy Metals Using Chemicals Precipitation, *Enginering and Technology Journal*, 29, August 2017,

Bugajski, P.M., Nowobilska-Majewska, E. & Kurek, K. (2017). The variability of pollution load of organic, biogenic and chromium ions in wastewater inflow to the treatment plant in Nowy Targ, *Journal of Water and Land Development*, 35, 1, pp. 11–17. DOI: 10.1515/jwld-2017-0063

Chaudhari, L. B. & Murthy, Z. V. P. (2010). Separation of Cd and Ni from multicomponent aqueous solutions by nanofiltration and characterization of membrane using IT model, *Journal of Hazardous Materials*, 180, 1–3, pp. 309–315. DOI: 10.1016/j.jhazmat.2010.04.032

Clever, M., Jordt, F., Knauf, R., Räbiger, N., Ruedebusch, M. & Hilker-Scheibel, R. (2000). Process water production from river water by ultrafiltration and reverse osmosis, *Desalination*, 131, 1–3, pp. 325–336. DOI: 10.1016/S0011-9164(00)90031-6

Cooper, C., Jiang, J. Q. & Ouki, S. (2002). Preliminary evaluation of polymeric Fe- and Al-modified clays as adsorbents for heavy metal removal in water treatment, *Journal of Chemical Technology and Biotechnology*, 77, 5, pp. 546–551. DOI: 10.1002/jctb.614

Dahlgren, L. (2010). Treatment of Spent Pickling Acid from Stainless Steel Production, Master of Science Thesis, ???

De Pablo, L., Chávez, M. L. & Abatal, M. (2011). Adsorption of heavy metals in acid to alkaline environments by montmorillonite and Ca-montmorillonite, *Chemical Engineering Journal*, 171, 3, pp. 1276–1286. DOI: 10.1016/j.cej.2011.05.055

Deeloed, W., Wannapaiboon, S., Pansiri, P., Kumpeerakij, P., Phomphrai, K., Laobuthee, A., et al. (2020). Crystal Structure and Hirshfeld Surface Analysis of Bis(Triethanolamine)Nickel(II) Dinitrate Complex and a Revelation of Its Characteristics via Spectroscopic, Electrochemical and DFT Studies Towards a Promising Precursor for Metal Oxides Synthesis, *Crystals*, 10, 474.

Fu, F. & Wang, Q. (2011). Removal of heavy metal ions from wastewaters : A review, *Journal of Environmental Management*, 92, 3, pp. 407–418. DOI: 10.1016/j.jenvman.2010.11.011

Fu, F., Zeng, H., Cai, Q., Qiu, R., Yu, J. & Xiong, Y. (2007). Effective removal of coordinated copper from wastewater using a new dithiocarbamate-type supramolecular heavy metal precipitant, *Chemosphere,* 69, 11, pp. 1783–1789. DOI: 10.1016/j.chemosphere.2007.05.063

Ijagbemi, C.O., Baek, M.H. & Kim, D.S. (2009). Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions, *Journal of Hazardous Materials*, 166, 1, pp. 538–546. DOI: 10.1016/j.jhazmat.2008.11.085

Juang, R.S., Kao, H.C. & Chen, W. (2006). Column removal of Ni(II) from synthetic electroplating waste water using a strong-acid resin, *Separation and Purification Technology*, 49, 1, pp. 36–42. DOI: 10.1016/j.seppur.2005.08.003

Juang, R.S. & Shiau, R.C. (2000). Metal removal from aqueous solutions using chitosan-enhanced membrane filtration, *Journal of Membrane Science*, 165, 2, pp. 159–167. DOI: 10.1016/S0376-7388(99)00235-5

Keane, M.A. (1998). The removal of copper and nickel from aqueous solution using Y zeolite ion exchangers, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 138, 1, pp. 11–20. DOI: 10.1016/S0927-7757(97)00078-2

Khan, S.A., Riaz-ur-Rehman, & Khan, M.A. (1995). Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite, *Waste Management*, 15, 4, pp. 271–282. DOI: 10.1016/0956-053X(95)00025-U

Kondratenko, Y., Fundamensky, V., Ignatyev, I., Zolotarev, A., Kochina, T. & Ugolkov, V. (2017). Synthesis and crystal structure of two zinc-containing complexes of triethanolamine, *Polyhedron*, 130, pp. 176–183. DOI: 10.1016/j.poly.2017.04.022

Kondratenko, Y., Zolotarev, A.A., Ignatyev, I., Ugolkov, V. & Kochina, T. (2020). Synthesis, crystal structure and properties of copper(II) complexes with triethanolamine and carboxylic acids (succinic, salicylic, cinnamic), *Transition Metal Chemistry*, 45, 1, pp. 71–81. DOI: 10.1007/s11243-019-00359-7

Kowal, A.L. & Świderska-Bróż, M. (1981). Removal of heavy metals in water rejuvenation, *Ochorona Środowiska*. http://www.os.not.pl/docs/czasopismo/1981/Kowal_4_1981.pdf (in Polish)

Kurama, H. (2009). Treatment and recovery of nickel rich precipitate from plating plant waste, *Journal of Environmental Engineering and Landscape Management*, 17, 4, pp. 212–218. DOI: 10.3846/1648-6897.2009.17.212-218

Kurniawan, T.A., Chan, G.Y.S., Lo, W.H. & Babel, S. (2006). Physico--chemical treatment techniques for wastewater laden with heavy metals, *Chemical Engineering Journal*, 118, 1–2, pp. 83–98. DOI: 10.1016/j.cej.2006.01.015

Li, C., Xie, F., Ma, Y., Cai, T., Li, H., Huang, Z. & Yuan, G. (2010). Multiple heavy metals extraction and recovery from hazardous electroplating sludge waste via ultrasonically enhanced two--stage acid leaching, *Journal of Hazardous Materials*, 178, 1–3, pp. 823–833. DOI: 10.1016/j.jhazmat.2010.02.013

Lin, S.H. & Kiang, C.D. (2003). Chromic acid recovery from waste acid solution by an ion exchange process: Equilibrium and column ion exchange modeling, *Chemical Engineering Journal*, 92, 1–3, pp. 193–199. DOI: 10.1016/S1385-8947(02)00140-7

Liu, H.L., Chen, B.Y., Lan, Y.W. & Cheng, Y.C. (2004). Biosorption of Zn(II) and Cu(II) by the indigenous Thiobacillus thiooxidans, *Chemical Engineering Journal*, 97, 2–3, pp. 195–201. DOI: 10.1016/S1385-8947(03)00210-9

Lochynski, P., Kowalski, M., Szczygiel, B. & Kuczewski, K. (2016). Improvement of the stainless steel electropolishing process by organic additives, *Polish Journal of Chemical Technology*, 18, 4, pp. 76–81. DOI: 10.1515/pjct-2016-0074

Lugo-Lugo, V., Barrera-Díaz, C., Bilyeu, B., Balderas-Hernández, P., Ureña-Nuñez, F. & Sánchez-Mendieta, V. (2010). Cr(VI) reduction in wastewater using a bimetallic galvanic reactor, *Journal of Hazardous Materials*, 176, 1–3, pp. 418–425. DOI: 10.1016/j.jhazmat.2009.11.046

Łyczkowska-Widłak, E., Lochyński, P. & Nawrat, G. (2020). Electrochemical polishing of austenitic stainless steels, *Materials*, 13, 11, pp. 1–25. DOI: 10.3390/ma13112557

Malaviya, P. & Singh, A. (2011). Physicochemical technologies for remediation of chromium-containing waters and wastewaters, *Critical Reviews in Environmental Science and Technology*, 41, 12, pp. 1111–1172. DOI: 10.1080/10643380903392817

Panayotova, M. & Velikov, B. (2002). Kinetics of heavy metal ions removal by use of natural zeolite, *Journal of Environmental Science and Health – Part A Toxic/Hazardous Substances and Environmental Engineering*, 37, 2, pp. 139–147. DOI: 10.1081/ESE-120002578

Papadopoulos, A., Fatta, D., Parperis, K., Mentzis, A., Haralambous, K. J. & Loizidou, M. (2004). Nickel uptake from a wastewater stream produced in a metal finishing industry by combination of ion-exchange and precipitation methods, *Separation and Purification Technology*, 39, 3, pp. 181–188. DOI: 10.1016/j.seppur.2003.10.010

Petrinic, I., Korenak, J., Povodnik, D. & Hélix-Nielsen, C. (2015). A feasibility study of ultrafiltration/reverse osmosis (UF/RO)-based wastewater treatment and reuse in the metal finishing industry, *Journal of Cleaner Production*, 101, pp. 292–300. DOI: 10.1016/j.jclepro.2015.04.022

Priya, P.G., Basha, C.A., Ramamurthi, V. & Begum, S.N. (2009). Recovery and reuse of Ni(II) from rinsewater of electroplating industries, *Journal of Hazardous Materials*, 163, 2–3, pp. 899–909. DOI: 10.1016/j.jhazmat.2008.07.072

Rodríguez-Iznaga, I., Gómez, A., Rodríguez-Fuentes, G., Benítez--Aguilar, A. & Serrano-Ballan, J. (2002). Natural clinoptilolite as an exchanger of Ni2+ and NH4+ ions under hydrothermal conditions and high ammonia concentration, *Microporous and Mesoporous Materials*, 53, 1–3, pp. 71–80. DOI: 10.1016/S1387-1811(02)00325-6

Rubel, E., Tomassi, P. & Ziółkowski, J. (2009). Best Available Techniques (BAT) – *Wytyczne dla powierzchniowej obróbki metali i tworzyw sztucznych*. pp. 91. (in Polish)

Szymański, K., Janowska, B., Sidełko, R. & Maciołek, P. (2018). Impact of environmental conditions on transformation of mineral pollutants present in landfill leachates, *Przemysl Chemiczny*, 97, 9, pp. 1517–1519. DOI: 10.15199/62.2018.9.23

Taha, A.A., Shreadah, M. A., Heiba, H.F. & Ahmed, A.M. (2017). Validity of Egyptian Na-montmorillonite for adsorption of Pb2+, Cd2+ and Ni2+ under acidic conditions: characterization, isotherm, kinetics, thermodynamics and application study, *Asia--Pacific Journal of Chemical Engineering*, 12, 2, pp. 292–306. DOI: 10.1002/apj.2072

Thomas, M., Białecka, B. & Zdebik, D. (2018). Removal of copper, nickel and tin from model and real industrial wastewater using sodium trithiocarbonate. The negative impact of complexing compounds, *Archives of Environmental Protection*, 44, 1, pp. 33–47. DOI: 10.24425/118179

Thomas, M., Kozik, V., Bąk, A., Barbusiński, K., Jazowiecka-Rakus, J. & Jampilek, J. (2021). Removal of Heavy Metal Ions from Wastewaters: An Application of Sodium Trithiocarbonate and Wastewater Toxicity Assessment, *Materials*, 14, 3, pp. 655. DOI: 10.3390/ma14030655

Wang, Z., Li, J., Song, W., Zhang, X. & Song, J. (2019). Decomplexation of electroplating wastewater by ozone-based advanced oxidation process, *Water Science and Technology,* 79, 3, pp. 589–596. DOI: 10.2166/wcc.2018.167