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Arch. Min. Sci. **63** (2018), 3, 633-646

Electronic version (in color) of this paper is available: http://mining.archives.pl

DOI 10.24425/123688

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THE USE OF ION EXCHANGERS FOR REMOVING COBALT AND NICKEL IONS FROM WATER SOLUTIONS

WYKORZYSTANIE WYMIENIACZY JONOWYCH DO USUWANIA JONÓW KOBALTU I NIKLU Z ROZTWORÓW WODNYCH

The paper presents results of research on cobalt and nickel ions removal from monocomponent solutions using Purolite ion exchange resins. It has been shown that C 160 ion exchange resin has the best sorption properties for both ions (Q_e – 72.5 mg Co/g and 88.2 mg Ni/g). Regeneration process of this ion exchanger has high efficiency, achieving about 93% for cobalt ions and about 84% in case of nickel ions. It has been shown that the use of ion exchange method with suitable ion exchange resins guarantees effective removal of cobalt and nickel ions from solutions with very high concentrations corresponding to contents of these metals in industrial wastewaters (e.g. galvanic). In case of C 160 ion exchange resin, after the sorption process is carried out in one 50 minute cycle, the cobalt concentration decreased from about 30 000 mg/L to about 9 500 mg/L (approx. 68%), whereas nickel concentration reached about 6 300 mg/L (approx. 79%). Studied chelating resins don't have such high sorption capacities. In their case, it is required to convert cobalt and nickel ions into complex forms. The kinetics of studied processes were described by pseudo-second order equations.

Keywords: Ion exchange resins, cobalt ions, nickel ions, ion exchange kinetics

Rozwój przemysłu znacznie wpływa na stan środowiska naturalnego. Zanieczyszczenia emitowane do wód, gleb i powietrza na skutek działalności człowieka stanową zagrożenie dla zdrowia i życia organizmów żywych. Wśród tych substancji, jako szczególnie niebezpieczne wymienia się metale toksyczne. W ich grupie znajduje się również kobalt i nikiel, których głównym źródeł emisji do środowiska jest przemysł elektrochemiczny i metalurgiczny. Pierwiastki te są stosunkowo rzadkimi i cennymi metalami, dlatego ważne jest poszukiwanie dodatkowych źródeł i metod ich odzysku.

Przedmiotem badań były żywice jonowymienne firmy Purolite, które zastosowano do usuwania jonów kobaltu i niklu z roztworów monoskładnikowych o stężeniach odpowiadających zawartościom tych metali w ściekach galwanicznych (ok. 30 000 mg/dm^3). W oparciu o wyniki badań można stwierdzić, że najlepsze właściwości sorpcyjne zarówno w stosunku do jonów kobaltu jak i niklu wykazuje kationit C 160. Zdolności sorpcyjne pozostałych jonitów maleją w szeregu S 950 > S 930 > S 910 > S 920.

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W kolejnym etapie sprawdzono możliwość regeneracji badanych jonitów za pomocą 10% roztworów kwasu azotowego(V) lub kwasu solnego. Proces regeneracji jonów kobaltu zachodzi z większą wydajnością w porównaniu do jonów niklu.

Wykazano, że metodą wymiany jonowej z użyciem odpowiednich żywic jonowymiennych można skutecznie usuwać jony kobaltu i niklu z roztworów o bardzo wysokich stężeniach, odpowiadających zawartościom tych metali w ściekach przemysłowych (m.in. galwanicznych). W przypadku jonitu C 160, po procesie sorpcji wykonanym w jednym, 50 minutowym cyklu, stężenie kobaltu obniżyło się z ok. 30 000 mg/dm^3 do wartości ok. 9500 mg/dm^3 (ok. 68%), natomiast stężenie niklu osiągnęło wartość ok. 6300 mg/dm^3 (ok. 79%) (Tab. 2 i 3). Badane jonity chelatujące nie osiągają tak wysokich pojemności sorpcyjnych. W ich przypadku wymagane jest przeprowadzenie jonów kobaltu i niklu w formy kompleksowe.

Słowa kluczowe: Żywice jonowymienne, jony kobaltu i niklu, kinetyka wymiany jonowej

1. Introduction

Trace amounts of cobalt and nickel are present in all spheres of the environment. In most deposits, these elements occur together and can be selectively separated only after they have been converted to solution. However, obtaining high-purity cobalt and nickel compounds is associated with a great difficulty in their separation because of significant seminaries of their chemical properties. Interest in these elements is steadily increasing because they belong to valuable metal group, which makes that it important to look for additional sources of their recovery.

Copper and nickel ores (in which cobalt occurs in the form of sulphides, oxides and arsenic) are main raw materials of cobalt (Craig et al., 2003). Some cobalt is also present in oceanic concretions (Sanak-Rydlewska & Gala, 2011). This element is obtained on an industrial scale in the form of an intermediate product (sulphide concentrate) during the hydrometallurgical process of copper and nickel ores. The characteristic feature of cobalt obtaining technology is dominant share of hydrometallurgical processes. This is mainly pressure leaching using oxygen and then secretion of metallic cobalt by hydrogen pressure reduction. In first stage, sulphide copper and nickel ores, containing cobalt are enriched by flotation. Then, obtained concentrate is leached with ammonia. A mixed method of copper-nickel melt smelting and its leaching under oxidative conditions using sulphuric(VI) acid can also be used. Laterite ores are processed by metallurgical method (obtaining ferronickel) or subjected to reductive calcination and next ammoniacal pressure leaching. After removal of copper from solution in form of sulphide and next iron and thiosulphates, pressure hydrogen reduction is applied in order to separate metallic nickel and then metallic cobalt. Cobalt in the CoS form can be recovered after ammoniacal leaching under oxygen pressure. In acid method, concentrates, oxide ores, as well as nickel stones are leached using sulphuric(VI) acid. Obtained solution is purified from iron and then nickel salt is precipitated in order to obtain metallic nickel. In the solution, Co(III) is reduced to Co(II) using metallic cobalt and then metallic cobalt is released in hydrogen pressure reduction. Hydrogen pressure reduction is a process that enables production of materials with unique properties and applications on an industrial scale, such as: composite powders, fine cobalt powders used for the production of special paints (Kołodziej et al., 2002).

Cobalt occurrence in the natural environment is mainly related to rocks weathering, volcanic eruptions and forest fires. Mining and treatment of cobalt ores, production of alloys or sinters, combustion of cobalt-containing wastes and nuclear tests are the anthropogenic emitters of this element. Also, cobalt gets into soil with phosphorus fertilizers. From soil it penetrates into plants as an indispensable factor for their growth. Food and drinking water are the main supplier of cobalt for human body. Cobalt is present mainly in mushrooms, green onions, tomatoes, cabbage, leafy vegetables, potatoes and rice (Langauer-Lewowicka & Pawlas, 2012).

In human body content of this element is estimated at about 1.2-1.5 mg irrespective of age (Legget, 2008). Its presence has been found in all tissues, organs and body fluids. Cobalt is excreted from body with urine (0.4-1.2 mg/L) and faeces (Langauer-Lewowicka &Pawlas, 2012). Cobalt is one of the most common contact allergens. It can cause allergies to people who wear jewellery. This element also permeates from placenta to foetus. The radioactive cobalt isotope emitted during nuclear tests is very dangerous for living organisms. Metallic cobalt dusts are classified as carcinogenic. In case of smoke or dust, cobalt Threshold Limit Value (TLV) is 0.02 mg/m^3 (Sapota & Darago, 2012). People who work in metallurgy, metalworking, printing houses, ceramics production (cobalt dyes), paint production and in agriculture may be exposed to cobalt and its compounds. In addition, people who live near landfills containing cobalt compound wastes and industrial emitters are also exposed.

Cobalt can occur on second or third oxidation degree. Cobalt compounds on second oxidation degree are stable in aqueous solutions. This element is more commonly present on third oxidation degree in complex compounds. Its form in aqueous solution is conditioned by concentration and pH value. Co^{2+} and $[CoOH]^+$ cations are present in acidic environments. At pH 6.2-7.5 (depending on concentration) cobalt precipitates as $Co(OH)_2$, while in alkaline medium it forms $[Co(OH)_3]^-$ and $[Co(OH)_4]^{2-}$ anionic forms (Takeno, 2005; Minczewski & Marczenko, 2012).

In the natural environment nickel occurs mainly in laterite ore and sulphide minerals as pentlandite. It is often accompanied by cobalt and iron minerals (Craig et al., 2003). It is also present in coal and crude oil (Seńczuk, 2002). In aqueous solutions nickel is present in form of Ni^{2+}, $[NiOH]^+$ and $[Ni(OH)_3]^-$ ions (Takeno, 2005; Minczewski & Marczenko, 2012). Its concentration in drinking water can range from 2 to 10 μg/L, while in air of industrial areas it ranges from 0.1 to 3 ng/m^3 (Seńczuk, 2002).

This metal is used for the production of alloys with high corrosion and temperature resistance and stainless steel. It is used in the chemical industry, food industry, production of plastics, laboratory equipment, electrodes, batteries and for galvanic metal coatings (Seńczuk, 2002). As already mentioned, nickel recovery takes place through flotation enrichment and metallurgical refining.

This element is emitted to air by coal and liquid fuels (diesel engines) combustion and asbestos production. Cocoa, soy, legumes, nuts and oatmeal include large nickel amounts. Aquatic plants and fish also accumulate this element to a large extent. In polluted water, nickel concentration in plants can range from 0.2 to 20 mg/kg d. m. Nickel is toxic to plants at concentrations above 50 mg/kg d. m. Elevated concentration of nickel is also present in animals, but it has not been shown that this metal undergoes biomagnification in food chain (Seńczuk, 2002).

The human body can absorb nickel orally with food, but also from utensils and kitchenware.

Average consumption of nickel in diet ranges from 100 to 300 μg/day. By inhalation this element gets into body as a result of smoking cigarettes. While by dermal route, it is absorbed by contact with objects coated with nickel (coins, jewellery) and may cause allergic reactions manifested by eczema or vesicular dermatitis. In human body nickel content is less than 30 mg. Daily absorption is from 0.3 to 0.5 mg Ni. The amount of absorbed metal depends on solubility of its compounds. Substances with low solubility are mainly deposited in the lungs (nickel metallic dust, sulphide and nickel oxide). Well-soluble compounds (such as $NiSO_4$) are absorbed through the skin from 55 to 75%. The largest amount of nickel gets into the body through serum albumin and is stored in the liver, kidneys and intestines (Seńczuk, 2002).

Nickel carbonyl which is absorbed by dermal and inhalation routes is the most dangerous compound for humans. It causes headaches and dizziness, vomiting, coughing, shortness of breath and pneumonia or even death. Its toxic concentration is 30 mg/m^3. Nickel compounds can cause poisoning mainly in people working in plating, nickel refining, nickel-cadmium batteries, jewellery and ceramics production. Dissolved salts, dust, carbonyl, sulphide and oxide of nickel are the main causes of cancer of lungs, paranasal sinus and gastrointestinal tract in humans. Nickel compounds may cause DNA synthesis disorders. Absorbed nickel is eliminated from the body with urine, sweat and saliva. Nickel concentration in serum and urine is a good environmental and occupational indicator of human exposure (Seńczuk, 2002).

Physiological concentration of nickel in human organs varies and ranges from about 1.6 μg/kg in lungs to about 1 μg/kg in hair. Environmental concentration of nickel in serum is 4.6 g/L, while occupational concentration is three times greater. Content of this element in urine is approx. 8 μg/L and in case of occupational exposure it can rise up to 130 μg/L (Environmental Health Criteria 108, 1991).

Nickel concentration in the air varies from 0.23 to 0.86 mg/m^3. Detection of nickel concentration above 500 g/L in urine indicates air contamination with this element. In Poland, nickel TLV (Threshold Limit Value) equal 0.25 mg Ni/m^3. For nickel carbonyl it is 0.007 mg/m^3 (Seńczuk, 2002).

2. Methods of cobalt and nickel removing from aqueous solutions

Wastes containing cobalt and nickel are produced by technological processes in many industries, e.g. in metallurgy and electrical engineering. Usually conventional methods such as precipitation, ion exchange or membrane processes are used for removing and recovering of these elements.

Precipitation (S^{2-}, OH^-), coagulation and filtration are most commonly used due to their relatively low cost. However, formation of large amounts of sediments and sludges which are difficult to manage are disadvantages of these methods. In addition, organic compounds and ammonia which are often present in wastewater significantly reduce efficiency of these processes.

In water and wastewater treatment, adsorption on activated carbon is also commonly used. They have selective ion exchange capacities. In addition, they can be modified to change their structural, surface (hydrophobic and hydrophilic) properties and change the number and type of functional groups (Sulaymon et al., 2009; Duman &Ayranci, 2010; Kasaini et al., 2013).

Minerals such as zeolites, bentonites and kaolinites also belong to effective adsorbents. They owe it to their unique structure enabling ion exchange from those present in their skeleton to ions being in the solution. Clinoptilolite – natural aluminosilicate with characteristic skeletal structure with free spaces filled with Ca, Mg, Na, K and water molecules is an example of such mineral. Its selectivity to studied toxic metal ions is given in the following series $Pb^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Cr^{2+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$ (Tomczak & Sulikowski, 2010).

Synthetic resins are characterized by much higher ion exchange capacity. Their characteristic feature is presence of active functional groups in polymer matrix which are capable to interact with metal ions present in the solution. The use of ion exchangers for removal of toxic metals (including nickel and cobalt) from water and wastewater has been the subject of numerous scientific studies e.g. (Zainol & Nicol, 2009; Li et al., 2012; Stefan & Meghea, 2014; Li et al., 2017; Abbasi et al., 2018).

Hydrometallurgical processes also have an important role in obtaining metals from aqueous solutions and waste water. A possibility of solutions purification, selective and easy separation of pure metals or their compounds is their advantage (Burzyńska et al., 2002). There is also a possibility of limiting emission of pollutants to the atmosphere comparing to existing pyrometallurgical processes.

Extraction, electrochemical processes and pressure reduction with gases (such as hydrogen sulphide or hydrogen) are used to recover metals from ammonia, chloride or sulphate solutions. Organic extracts such as organophosphorus acids and their esters, e.g. D2EHPA – di-(2-ethylhexyl) phosphoric acid; Cyanex 272 – bis(2,4,4-trimethylpentyl) phosphonic acid; PC-88A – 2ethylhexylphosphonic acid 2-ethylhexyl ester are used to separate cobalt from nickel. Use of these three extracts in an organic MSB 210 solvent to separate cobalt from nickel from their 0.1 mol/L sulphate solution and at pH = 4, gives separation factor equal 14 for D2EHPA, 280 for PC-88A and 7000 for Cyanex 272. In order to separate cobalt from nickel in chloride solutions, tertiary amines are used. In order to separate cobalt from nickel in chloride solutions, tertiary amines, (e.g. triisooctylamine) are used (Szymanowski, 1997). The extraction is an effective method of separating cobalt from nickel from sulphate and chloride solutions, which is confirmed by numerous scientific studies carried out in the last few years (Nadimi et al., 2014; Wang & Lee, 2017; Zhang et al., 2018).

One of the newest method used to separate metal ions are membranes (Yenphan et al., 2010; Landaburu-Aguirre et al., 2011; Eyupoglu & Kumbasar, 2015). Membrane processes are characterized by a better use of extraction solvent which is present in the membrane material comparing to traditional extraction systems. The organic phase is immobilised on porous polymer base through which ions from the purified solution are being transported. More favourable separation parameters are obtained on inclusion membranes where synthesis is based on cellulose triacetate, onitrophenyl-pentyl ether and tri-n-octylamine. They are characterized by high mechanical stability (Kozłowski & Jabłońska, 2003). The membranes are also used in metal electrolytic separation (Kołodziej et al., 2002). They are based on differences in normal potentials of metallic electrodes. For nickel, cobalt and copper, at 25°C, they are respectively: $Ni/Ni^{2+} = -0.250$ V; $Co/Co^{2+} = -0.277$V; $Cu/Cu^{2+} = +0.337$ V.

For example, cobalt electrolytic separation is based on melting of cobalt and nickel scraps, carburizing and anode casting. Then, anode is hydrometallurgically digested in chloride solutions in two stages: solution purification and cobalt and nickel electrodeposition in cathode space of DMEC electrolyser. This is an electrolyser with two membranes which separate anode from cathode. The anolytic impurities stop on membrane part and are discharged through waste catholyte stream flowing through it (Kołodziej et al., 2002).

Gaseous reducers (e.g. H_2 or H_2S) are also used to extract metals and their compounds from aqueous solutions, which results in high purity of products. With respect to very widespread metals, reduction with pressurized gases can be a complement to commonly used fire or electrochemical methods. Due to costs and risks, only small amounts of semi-finished products or metallurgical wastes may be treatment. Pressure reduction methods are most commonly used for the extraction of metals associated with copper ores (including cobalt and nickel) from various technological solutions in copper industry. This includes, e.g. nickel(II) sulphate(VI) processing into nickel powder or obtaining metallic cobalt, nickel or composite powders. Cobalt and nickel powder can be obtained by pressure reduction using hydrogen gas from ammoniacal leach solutions. Solution after leaching of lateritic with sulphuric(VI) acid at 500°C is used to precipitation of nickel and cobalt with hydrogen sulphide in sulphides form. These settlements are digested in sulphuric acid, aluminium, chromium and iron compounds are removed in form of hydroxides and resulting cobalt and nickel solutions is pressure reduced with hydrogen.

Competing with these methods is the use of biosorbents. They are characterized by biorenewability, biodegradability and by relatively low operating costs. Sorption material can be modified, which leads to differentiation of metals binding mechanism and to increase in selectivity of their elimination. Biosorption can be carried out in active version (alive biomass), as well as in passive one (death biomass).Various materials, such as bacteria, fungi, yeast and algae, organic waste from food or wood industry and residues from agriculture can be used as natural sorbents (Argun et al., 2009; Bożęcka et al., 2016; Ivanova et al., 2016; Jancarova et al. 2017; Foroutan et al., 2017).

3. Aim of the study

The aim of the study was to determine conditions of cobalt and nickel ions removal from monocomponent water solutions, in which concentration of studied ions was approx. 3 0000 mg/L (level of cobalt and nickel content in an industrial wastewater).The ion exchange method with the C 160 cation exchanger and the S 910, S 920, S 930 and S 950 chelating resins produced by Purolite was used. Based on obtained results, the most effective resins for studied ions removal and ion exchanger regeneration were selected. The kinetics of studied processes were described by pseudo-second order equations.

4. Methods of the study

Research were conducted on C 160, S 950, S 930, S 920 and S 910 ion exchange resins produced by Purolite. Their characteristics are presented in Table 1 (Purolite, 2017). All of the applied synthetic ion exchange resins worked in hydrogen cycle. The main stage in resins preparation for research was swelling in deionized water for 24 hours. The pH of the solution with ion exchange resins ranged from 2.88 to 5.41. These values were selected according to the recommendations

TABLE 1

Characteristics of selected parameters of Purolite ion exchangers: C 160, S 950, S 930, S 920 and S 910 (Purolite, 2017)

Ion exchanger	**Typical physical and chemical characteristics**			
	Functional group	**Ionic form**	**Total capacity**	**pH limit**
C 160	R-SO_3^-	Na^+	min 2.4 mval/mL – Na^+ form	0–14
S 950	R-$CH_2NHCH_2PO_3^{2-}$	Na^+	min 2.0 val /L Na^+ form	2–6 – H^+ form 6–11 – Na^+ form
S 930	R-NH_2-N-($CH_2COONa)_2$	Na^+	35g Cu^{2+}/L – H^+ form 50g Cu^{2+}/ L – Na^+ form	2–6 – H^+ form 6–11 – Na^+ form
S 920	R-S-C(NH_2)NH	H^+	min 1.6 val/L – H^+ form	1 – 9
S 910	–C(NH_2)NOH	free base	min 1.9 val/L – free base form	0–14

of the producer. In experiments, a 40 g samples of the ion exchange resins were used. The initial concentration of the Co^{2+} and Ni^{2+} ions in solutions were equal to 0.5 mol/L (29 465.0 mg Co/L and 29 345.0 mg Ni/L). The monocomponent solutions were prepared using hydrated cobalt(II) and nickel(II) sulphate(VI).

Conditions of ion exchange processes were the same for all studied ion exchange resins. For this purpose, 100 mL of Co^{2+} and Ni^{2+} ions solutions were dropped into ion exchange column with flow rate equal 2 mL/min and then samples were being collected for 50 minutes in specified time intervals. Sorption processes were also performed by one-time pouring of whole solution volume (100 mL) into column and then collecting of eluate with flow rate of 2 mL/min. Just like before, samples were being collected at the same time intervals. Additionally, for the C 160 ion exchanger, experiments in extended time (150 minutes) were carried out by pouring whole solution volume (100 mL) into the column. Taken samples were being analysed to cobalt and nickel ions content.

Cobalt and nickel ions desorption studies were carried out according to Purolite recommendations. In case of C 160 ion exchanger 10% HNO_3 solutions were used for regeneration.

But in case of S 910, S 920, S 930, S 950 ion exchangers, 10% HCl solutions were used. The desorbing reagent was poured into the column and then it was passed through the ion exchange bed with 2mL/min flow rate. After regeneration, ion exchange bed was flushed with demineralised water according to recommendations of the producer (Purolite, 2017). Samples after regeneration were analysed to cobalt and nickel ions content.

Concentration of cobalt and nickel ions in solutions was determined by colorimetric method using UV-VIS spectrometer. Absorbance of cobalt solutions was measured at 510 nm wavelength and nickel at 720 nm.

The purification degree of solutions for Co^{2+} and Ni^{2+} ions, X (%), was calculated using formula (1):

$$X = \frac{c_0 - c_e}{c_0} \cdot 100\% \tag{1}$$

where: c_o and c_e – are the initial and equilibrium concentrations of studied ions in solutions (mg/L)

The metal ion concentration on the ion exchange resins after time t, Q_t (mg/g), was calculated according to formula (2):

$$Q_t = \frac{V\left(c_0 - c_e\right)}{m} \tag{2}$$

where: V – is the volume of the solution (L), c_o and c_e – are initial and equilibrium concentrations of studied ions in solution (mg/L), m – mass of the ion exchange resin (g).

The pseudo-second-order model (3), which is the most coonly used in case of chemical sorption, was used to describe the kinetics of removal of Co^{2+} and ions.

$$\frac{dQ_e}{dt} = k_2 (Q_e - Q_t)^2 \tag{3}$$

where: Q_t and Q_e – metal ion concentration on the ion exchange resin after time t and in equilibrium, k_2 – the rate constant of the pseudo-second-order equation (Sari & Tuzen, 2008).

The value of rate constants, k_2, and ion exchange capacities in equilibrium conditions, Q_e, were determined using the linearized form of the equation (4):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} \cdot t \tag{4}$$

5. Discussion of the results

In order to determine time after which studied systems achieved equilibrium, cobalt and nickel ions sorption experiments for C 160 ion exchange resin were carried out, taking samples from the ion exchange column with flow rate of 2 mL/min during 150 minutes (every 15 minutes). Obtained results were presented in Fig. 1. Studies on sorption process kinetics show that for both studied ions sorption capacity of ion exchanger gradually increases with extending contact time from about 7 to 64 mg Co/g and 7 to 78 mg Ni/g. This increase is fastest in time period from 5 to 50 minutes. The equilibrium of ion exchange process starts at 50 minutes, resulting in saturation of ion exchange bed (Fig. 1). Thus, in further studies, duration of process was limited to 50 minutes.

From comparison of relationships shown in Fig. 1, it can be said that nickel ions are more efficiently removed from aqueous solutions by resin C 160. The sorption capacity of this ion exchanger was about 78 mg/g at 150 minutes, while for cobalt it was about 14% lower.

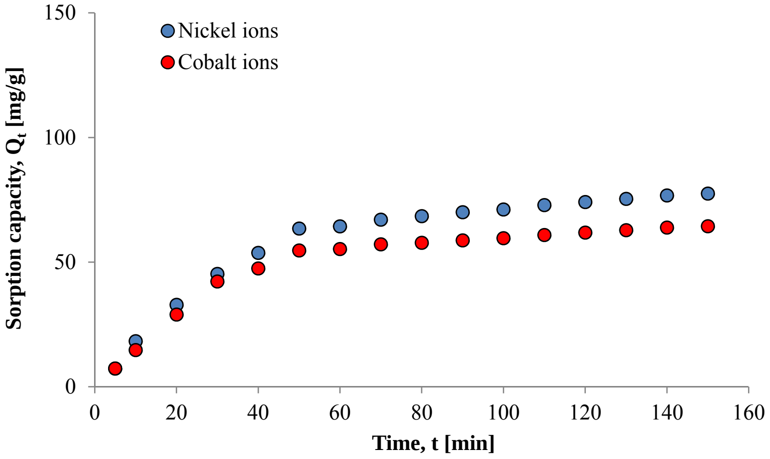

Fig. 1. Effect of contact time on removal of Co^{2+} and Ni^{2+} ions by C 160 ion exchange resin by pouring of whole volume of solution into an ion exchange column

In the next part of experiments, based on results obtained at 50 minutes, sorption properties of C 160 cation exchanger and S 950, S 930, S 920, S 910 chelating resins were compared (Figs. 2-5; Tab.2 and 3). In addition, for all selected ion exchange resins, effect of solution introducing method into an ion exchange column on Co^{2+} and Ni^{2+} ions separation degree has been determined. Studied solutions were dropped into an ion exchange column at a flow rate of 2 mL/min (1st method) or poured at once (2nd method).

Analysis of obtained dependencies shows that after 50 minutes, the C 160 ion exchange resin has the best sorption properties for cobalt and nickel ions. For other ion exchange resins values of sorption capacity is decreasing in the following order S 950 > S 930 > S 910 > S 920 (Tab. 2 and 3). Obtained results confirm that by using studied ion exchangers, cobalt and nickel ions can be efficiently removed from solutions with very high concentrations corresponding to contents in an industrial wastewater (e.g. galvanic). In case of C 160 ion exchange resin, after sorption process was carried out in one 50 minute cycle, cobalt concentration decreased from about 30 000 mg/L to about 9500 mg/L (approx. 68%), while nickel concentration decreased to about 6 000 mg/L (approx. 79%) (Tab. 2 and 3).

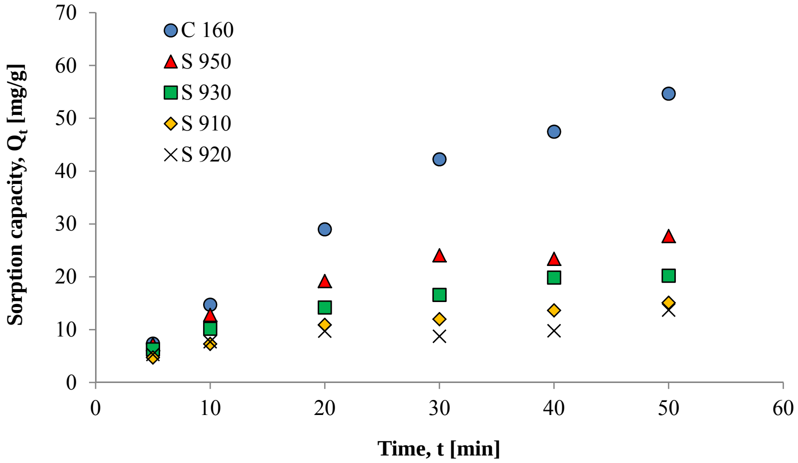

Fig. 2. Effect of contact time on removal of Co^{2+} ions by C 160, S 950, S 930, S 920 and S 910 ion exchange resins by pouring of whole volume of solution into an ion exchange column

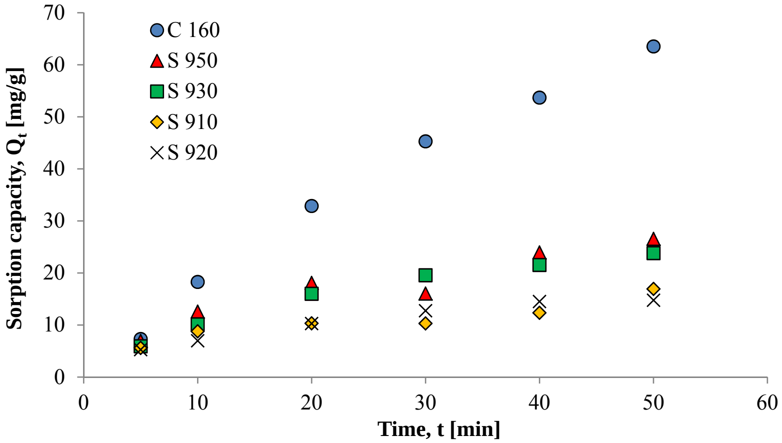

Fig. 3. Effect of contact time on removal of Ni^{2+} ions by C 160, S 950, S 930, S 920, S 910 ion exchange resins by pouring of whole volume of solution into an ion exchange column

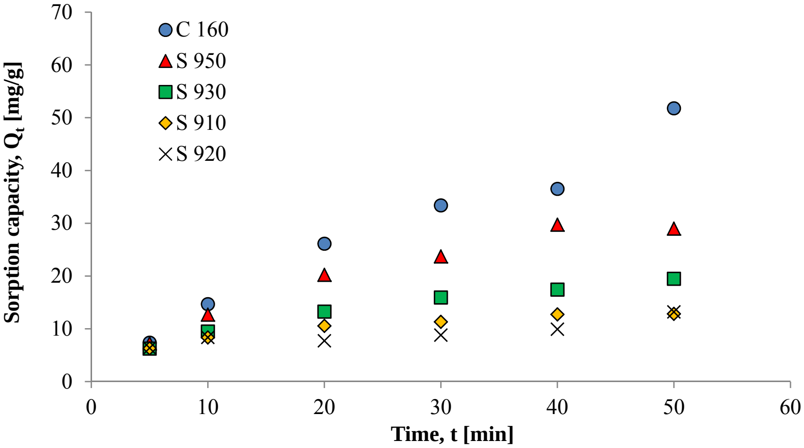

Fig. 4. Effect of contact time on removal of Co^{2+} ions by C 160, S 950, S 930, S 920, S 910 ion exchange resins by dropping of solution into an ion exchange column

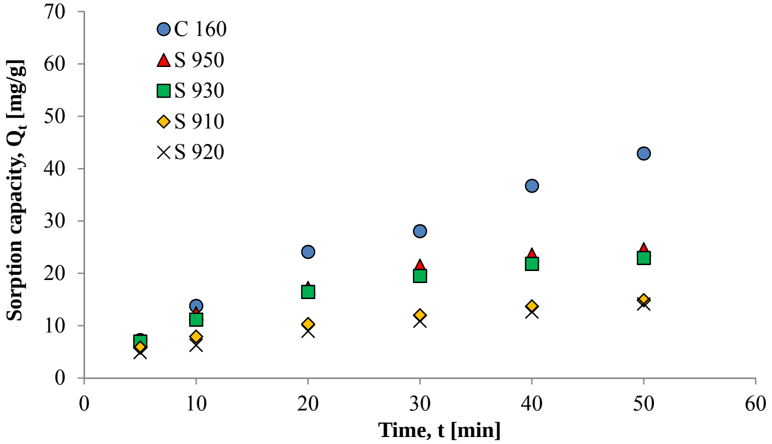

Fig. 5. Effect of contact time on removal of Ni^{2+} ions by C 160, S 950, S 930, S 920, S 910 ion exchange resins by dropping of solution into an ion exchange column

It has also been shown that the method of introducing of solution into an ion exchange column has significant effect only in case of nickel removal by using C 160 ion exchanger. For others ion exchangers obtained sorption capacity values are not significantly different from each other, although for majority of exchangers, used slightly better results were obtained for pouring the solution method. The differences in sorption capacities are probably related to different contact surfaces of solution with an ion exchange resin. If all volume of solution is poured into column, contact with ion exchange bed is faster.

In the next step, regeneration possibility of selected resins with 10% solutions of nitric acid(V) or hydrochloric acid was studied (according to producer recommendation). Process of cobalt ions regeneration achieved the highest efficiency for S 920 (100%), S 950 (93.5%) and C 160 (92.8%) ion exchange resins. Other exchangers S 910 and S 930 reduce cobalt ions at 89.9% and 86.4%, respectively. For nickel ions, efficiency of regeneration process is lower. The best results were achieved for the S 930 (approx. 87%), S 950 (85%) and C 160 (approx. 84%) ion exchanger. S 920 and S 910 ion exchanger reduce nickel ions in the range from about 55 to about 65%.

Considering values of sorption capacity and regeneration efficiency, it was concluded that C 160 resin is the best cobalt and nickel ions ion exchanger. It is effective at high concentrations, also is reusable and allows recovery of studied metals. Chelating resins do not have such high sorption capacities. In their case, it is required to convert cobalt and nickel ions into complex forms to increase their affinity for studied ions. By comparing obtained results, it can also be concluded that nickel ions are more efficiently removed from aqueous solutions than cobalt ions. In turn, regeneration process of cobalt ions occurs with much higher efficiency (Tab. 2 and 3).

TABLE 2

Parameters of process of Co^{2+} ions removal by ion exchange resins C 160, S 950, S 930, S 920 and S 910 after 50 minutes, W – solution was poured, K – solution was dropped

Ion exchanger		**pH_0 (resin)**	**pH_0 (solution)**	**Equilibrium concentration, c_e [mg/L]**	**Degree of purification, X [%]**	**Regeneration, [%]**
C160	W	4.68	2.31	9 476.9	67.8	92.8
	K	5.36	2.29	9 840.6	66.6	85.3
S 950	W	4.84	2.33	20 832.2	29.3	88.0
	K	4.11	2.29	20 627.6	30.0	93.5
S 930	W	4.14	2.38	23 571.6	20.0	86.4
	K	3.64	2.38	23 594.3	19.9	80.6
S 910	W	4.00	2.27	24 947.0	15.3	67.2
	K	3.94	2.32	26 345.1	10.6	89.9
S 920	W	3.26	2.35	25 253.9	14.3	73.8
	K	3.26	2.37	25 594.9	13.1	100.0

TABLE 3

Parameters of process of Co^{2+} ions removal by ion exchange resins Purolite C 160, S 950, S 930, S 920 and S 910 after 50 minutes, W – solution was poured, K – solution was dropped

Ion exchanger		**pH_0 (resin)**	**pH_0 (solution)**	**Equilibrium concentration, c_e [mg/L]**	**Degree of purification, X [%]**	**Regeneration, [%]**
C160	W	5.41	2.23	6 291.9	78.6	84.2
	K	5.20	2.23	13 925.9	52.5	74.4
S 950	W	3.50	2.27	20 829.3	29.0	85.0
	K	3.87	2.25	22 013.5	25.0	81.5
S 930	W	3.73	2.38	21 811.9	25.7	70.6
	K	3.76	2.36	22 567.7	23.1	86.9
S 910	W	4.42	2.28	23 928.3	18.5	55.1
	K	4.09	2.36	25 087.2	14.5	64.4
S 920	W	2.89	2.39	25 062.0	14.6	64.0
	K	2.88	2.39	24 810.1	15.5	56.0

The aim of the performed studies was also determination of the studied process rate constants, k_2, and ion exchange capacities in equilibrium conditions, Q_e, by using the pseudo-second-order equation. The resulting calculation data were summarized in Tab. 4. They indicate that the used of kinetic model describe the tested ion-exchange processes well, as evidenced by the high values calculated correlation coefficients R.

The analysis of reaction rate constants shows that their values are higher for chelating ion exchangers than for C 160 ion exchanger. The highest value of k_2 constant was obtained for S 920 resin in the Co^{2+} ion removal process. The Q_e parameter changed from 10.6 mg/g to 88.2 mg/g, the highest value was obtained for the C 160 ion exchanger (Tab. 4).

TABLE 4

The value of rate constants, k_2, and ion exchange capacities in equilibrium conditions, Q_e, determined by using the pseudo-second-order equation; W – solution was poured, K – solution was dropped

Ion exchanger		**Cobalt**			**Nickel**		
		k_2 [g/mg · min]	**Q_e [mg/g]**	**R**	**k_2 [g/mg · min]**	**Q_e [mg/g]**	**R**
C160	W	0.0007	72.5	0.9992	0.0005	88.2	0.9992
	K	0.0006	60.7	0.9939	0.0006	58.2	0.9752
S 950	W	0.0015	35.7	0.9851	0.0014	36.5	0.9983
	K	0.0011	41.1	0.9989	0.0016	33.8	0.9987
S 930	W	0.0021	27.4	0.9961	0.0014	32.9	0.9993
	K	0.0024	25.2	0.9967	0.0018	31.2	0.9998
S 910	W	0.0030	19.6	0.9965	0.0101	13.9	0.9896
	K	0.0090	14.7	0.9984	0.0042	18.2	0.9934
S 920	W	0.0228	10.6	0.9928	0.0029	20.1	0.9887
	K	0.0473	9.8	0.9899	0.0039	16.8	0.9867

6. Conclusions

Based on obtained results, it can be concluded that, the C 160 ion exchange resin has the best sorption properties for cobalt and nickel ions (Q_e – 72.5 mg Co/g and 88.2 mg Ni/g). Regeneration process of this ion exchanger has also high efficiency, achieving value of about 93% for cobalt ions and about 84% in case of nickel ions (Tab. 2 and 3). It has been shown that use of suitable ion exchange resins guarantees effective removal of cobalt and nickel ions from solutions with very high concentrations corresponding to contents of these metals in an industrial wastewater (e.g. from galvanic industry). In case of C 160 ion exchange resin, after sorption process was carried out in one 50 minute cycle, cobalt concentration decreased from about 30 000 mg/L to about 9 500 mg/L (approx. 68%), whereas nickel concentration reached about 6 300 mg/L (approx. 79%) (Tab. 2 and 3). Studied chelating resins do not have such high sorption capacities. In their case, it is required to convert cobalt and nickel ions into complex forms. It has also been proven that efficiency of nickel ions removal from aqueous solutions by using studied ion exchange resins is greater than for cobalt ions. However, regeneration of ion exchange resins is more efficient for cobalt ions (Tab. 2 and 3).

Based on obtained results, it was found that the processes of Ni^{2+} and Co^{2+} ions removing using by tested ion-exchange resins occur in accordance with the pseudo-second-order reaction, as evidenced by the values of correlation coefficients R (Tab. 4).

The study was carried out as part of the AGH research programme number 11.11.100.196

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