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Research of Co^{2+} ions removal
from water solution by using ion exchangers

Introduction

Industrial development has a significant impact on the natural environment and in many cases contributes to the increase of its pollution, including natural waters. Toxic metals, due to their ability to accumulate, are particularly dangerous to the health and life of living organisms. Their presence disturbs the natural biological balance and self-cleaning processes in water reservoirs. Cobalt which is found mainly in industrial wastewater from electrochemical plants, the metallurgical and galvanic industry is also being classified to this group of toxic metals.

Chemical and physicochemical methods, such as precipitation and co-precipitation for the removal, solvent extraction, membrane processes, sorption and ion exchange are commonly used for concentration and recovery of metal ions. However, the choice of the method depends on the number of parameters such as: the kind and composition of wastewater, the form and concentration of removed forms of pollutants.

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1. Characteristics of metals removal methods
from water and wastewater

One of the simplest methods of water solutions purification from metal ions is precipitation, which is the basis of the oldest methods of the separation, detection and determination of elements. Chemical precipitation is cheapen inexpensive and relatively simple method, but it is only effective for high concentrations of removed pollutions. The formation of large amounts of sediment and sludge which are difficult to manage is also a disadvantage of this method. Non-selective elements separation takes place during the precipitation process. The obtained sediments may contain impurities as a result of the co-precipitation process. The necessity of solution neutralization after sediments the removal of also the a disadvantage of this method (Bożęcka 2013).

Hydrometallurgical processes also have an important role in obtaining metals from aqueous solutions. The possibility of selective metals separation and solutions purification is their advantage (Burzyńska et al. 2002). Additionally, the possibility of limiting emitted pollutants into the atmosphere exists compared to 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 2-ethylhexylphosphonic acid 2-ethylhexyl ester are used to separate cobalt from nickel. In order to separate cobalt from nickel in chloride solutions, tertiary amines 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 and Lee 2017; Zhang et al. 2018).

One of the youngest methods used to separate metal ions are membranes (Yenphan et al. 2010; Landaburu-Aguirre et al. 2011; Eyupoglu and Kumbasar 2015). Membrane processes are characterized by a better use of the extraction solvent which is found in the membrane material, in comparison with traditional extraction systems. The organic phase is immobilised on a porous polymer base through which ions from the purified solution are being transported. More favorable separation parameters are obtained on inclusion membranes where the synthesis is based on cellulose triacetate, o-nitrophenyl-pentyl ether and tri-n--octylamine. They are characterized by high mechanical stability (Kozłowski and Jabłońska 2003). The high operation costs and frequent contaminations of membranes are the main disadvantages of these methods.

In water and wastewater treatment, adsorption on activated carbon is also commonly used. They have selective ion exchange capacities and also remove organic pollutants from the water. In addition, they can be modified to change their structural, surface (hydrophobic and hydrophilic) properties and change the number and type of functional groups (Kołodyńska and Hubicki 2008; Sulaymon et al. 2009; Duman and Ayranci 2010; Kasaini et al. 2013).

Minerals such as zeolites, bentonites and kaolinites also belong to effective adsorbents. It is confirmed that they have an affinity to toxic metals such as: lead, chromium, cadmium, zinc, nickel and mercury (Tomczak and Sulikowski 2010). They owe this to their unique structure enabling ion exchange from ions present in their skeleton to these being in the solution.

Synthetic resins are characterized by a much higher ion exchange capacity. These materials are also selective and can be reused after the regeneration of their surfaces. The use of ion exchangers for the removal of toxic metals from water and wastewater has been the subject of numerous scientific studies e.g. Zainol and Nicol 2009; Li et al. 2012; Stefan and Meghea 2014; Li et al. 2017; Abbasi et al. 2018.

Among all ion exchangers, complexing ion exchange resins are widely used in practice. They form coordination bonds with removable metal ions (mainly transition metals). Complexing ion exchange resins also form: vinylpyridines, vinylimidazoles, vinyl amines, as well as acrylic esters and their derivatives (Floriańczyk and Penczek 1998). These resins are most often used in hydrometallurgy.

Chelating resins belong to the complexing ion exchange resins group and they are characterized by high selectivity to the metal ions. Their characteristic feature is their presence in the polymer matrix of active functional groups which are capable of interacting with the metal ions present in the solution to form ring-shaped chelate complexes. The sorption capacity of chelating resins depends on the type of functional groups and on the physicochemical properties of the polymer matrix. The high selectivity of chelating resins towards metal ions allows for their use in industrial conditions where the concentrations of the removed ions are very low compared to the concentrations of the accompanying ions. Due to this they have been used in recovery of many precious metals from ores or sludge and in the removal of toxic metals from water and wastewater. In conventional methods such as: liquid-liquid extraction or liquid-solid extraction, it is necessary to use environmentally unfriendly strong acids or solvents (Beauvais and Alexandratos 1998; Floriańczyk and Penczek 1998).

The use of biosorbents is competing with these methods. They are characterized by biorenewability, biodegradability and by relatively low operating costs. The sorption material can be modified, which leads to the differentiation of the metals binding mechanism and to an increase in the selectivity of their elimination. Biosorption can be carried out in an active version (alive biomass), as well as in a passive one (death biomass). The live biomass includes, among others: bacteria, fungi, yeast and algae (Zabochnicka-Świątek 2013).

Various materials, such as organic waste from the food or wood industry and residues from agriculture can be used as natural sorbents. The sorption process on organic wastes has many advantages such as: low cost, possibility of using unnecessary waste and biodegradation of the used biomass. The use of dead biomass is much more attractive in comparison to the alive biomass. The main reason is lack of impact of the toxic metals on living organisms and there is no need to use any nutrients or to maintain sterile conditions during the tests. Biosorption is also selective, efficient and effective even in low concentrations, which makes organic sorbents very competitive to conventional methods (Argun et al. 2009; Bożęcka 2013; Bożęcka et al. 2016; Bożęcka et al. 2017).

2. Cobalt – physicochemical properties, occurrence and application

Cobalt is a trace element in lithosphere and often coexists with nickel. Its mean content in magma rocks is about 25 ppm, while in ultramafic rocks is about 130 ppm (Paulo and Strzelska-Smakowska 1996). The highest content of this metal is found in shales, which are mainly rich in bitumen and organic matter. Cobalt naturally occurs in form of the sulphide, oxide and arsenic minerals. In oceans, more specifically in manganese concentrations, its content ranges from 0.2 to 1.2 weight % (Krzak and Krzak 2016). In aqueous solutions, cobalt is present in the second and third oxidation stages.

Only the ores where cobalt coexists with nickel and copper have industrial importance. These are copper stratoid deposits, copper-nickel igneous rocks deposits and nickel and iron-nickel laterite deposits. In the future, manganese concretions deposits in the Pacific can also play an important role. In Poland cobalt minerals do not occur separately. They are associated with copper and iron ores, from which cobalt is extracted on an industrial scale.

During the processing of copper ore, this metal goes into copper concentrate and reaches the content of about 1 weight % in converter slags (Smakowski et al. 2015). Unfortunately, in Poland, the worked out technology of cobalt recovery from this source is not used. Cobalt is also found in Polish hard coal deposits, but a method of its recovery has not yet been found. Other sources of cobalt are solutions after leaching (Kopytko et al. 2015). In this case cobalt can be recovered by using ion exchange resins working under acidic conditions. However, obtaining high purity cobalt compounds is not easy due to the difficulty of its separation from nickel.

As mentioned earlier, weathering rocks are the main natural source of cobalt emissions. The mining and treatment of cobalt ores, the production of alloys and sinters, the combustion of cobalt-containing wastes, phosphatic fertilizers and also nuclear tests are the anthropogenic emitters of this element (Langauer-Lewowicka and Pawlas 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.

3. Goal of the study

The aim of the study was to determine the conditions of cobalt ions removal from model water solutions, in which the concentration of the studied ions was about 30,000 mg/L (it corresponds to the cobalt concentration level in industrial wastewater, which also contain the following in its composition: nickel, chrome and aluminum with an average contents of about 32,000, 15,000, 7,000 mg/L, respectively). 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 the previous studies, the most effective resins were selected and the sorption process kinetics of was determined.

4. Experimental methods

Research were conducted on C 160, S 950, S 930, S 920 i 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 the hydrogen cycle. The main stage in the preparation of resins for research was swelling in deionized water for 24 hours. The pH of the solution with ion exchange resins ranged from 3.26 to 5.36. These values were selected according to the recommendations of the producer. In experiments, 40 g samples of the ion exchange resins were used. The initial concentration of the Co^{2+} ions in solutions was equal to 0.5 mol/L (29 465 mg/L). The solutions were prepared using hydrated cobalt(II) sulphate(VI).

The conditions of ion exchange processes were the same for all the studied ion exchange resins. 100 mL of the solution was dropped to the ion exchange column with a flow rate of 2 mL/min and then samples were collected for 50 minutes in specified time intervals. Sorption processes were also performed by the the one-time pouring of the entire volume of the solution (100 mL) into the column and then collecting of eluate at the same time intervals with a flow rate of 2 mL/min. Additionally, for the C 160 ion-exchanger, experiments in extended time (150 minutes) were carried out by pouring the entire the solution volume (100 mL) to the column. The taken samples were analyzed for the cobalt ions content.

Cobalt ions desorption studies were carried out according to Purolite recommendations. In the case of the C 160 ion-exchanger, 10% HNO_3 solutions were used for regeneration. But in the 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 it was then passed through the ion exchange bed at a 2 mL/min flow rate. After regeneration, the ion exchange bed was flushed with demineralized water according to the producer's recommendations (Purolite 2017). Samples after regeneration were analyzed for the cobalt ions content.

The concentration of Co^{2+} ions in solutions was determined by the colorimetric method using a UV-VIS spectrometer. The absorbance of cobalt solutions was measured at a 510 nm wavelength.

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

$$X = \frac{c_o - c_k}{c_o} \cdot 100\%$$
(1)

✍ c_o and c_k – the initial and final concentrations of the studied ions in the solutions [mg/L].

The sorption capacity of the ion exchange resins, Q [mg/g], was calculated according to the following formula (2):

$$Q = \frac{V(c_o - c_k)}{m} \tag{2}$$

☝ V –   the volume of the solution (L),
c_o and c_k –   the initial and final concentrations of the studied ions in the solution (mg/L),
m –   mass of the ion-exchange resin (g).

Table 1.   Characteristics of selected parameters of Purolite ion-exchangers: C 160, S 950, S 930, S 920 i S 910 (Purolite 2017)

Tabela 1.   Charakterystyka wybranych parametrów jonitów Purolite: C 160, S 950, S 930, S 920 i S 910

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

5. Discussion of the results

In order to determine when the studied systems achieved equilibrium, the Co^{2+} ions sorption experiments for C 160 ion exchange resin were carried out during 150 minutes. The obtained results were presented graphically in Fig. 1. Studies on sorption process kinetics show that ionic sorption capacity for Co^{2+} ions gradually increases with extending the contact time from about 7 to 64 mg/g. The obtained results show that this increase is the fastest in the time period from 5 to 50 minutes (Fig. 1). It can be assumed that the equilibrium of the ion exchange process starts at 50 minutes, resulting in the saturation of the ion exchange bed. Thus, in further studies, the duration of the process was limited to 50 minutes.
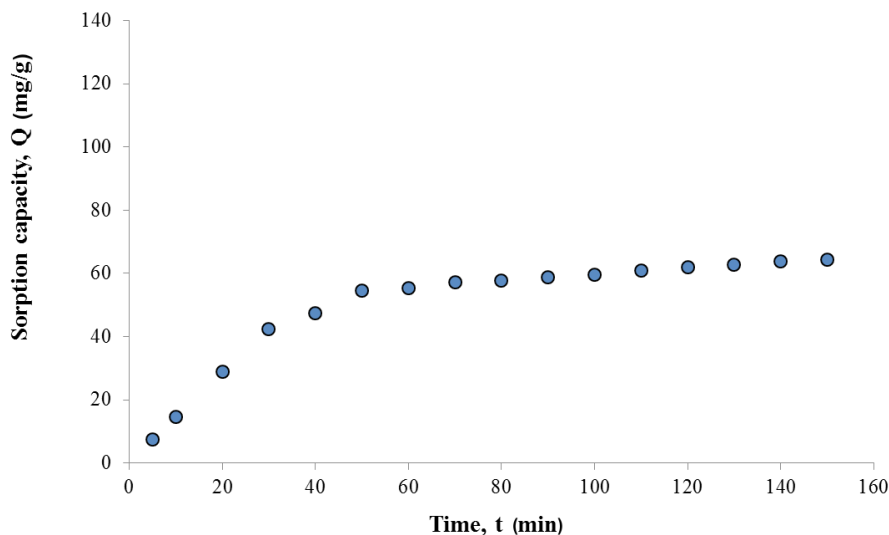
Fig. 1. Effect of contact time on the removal of Co^{2+} ions by the C 160
ion exchange resin by pouring the entire volume of the solution into an ion exchange column

Rys. 1. Wpływ czasu kontaktu na usuwanie jonów Co^{2+} za pomocą jonitów C 160
metodą wlania całej objętości roztworu do kolumny jonowymiennej

Next the sorption properties of C 160 cation exchanger and S 950, S 930, S 920, S 910 chelating resins from Purolite were compared. The obtained results are shown in Figures 2 and 3 and in Table 2. In addition, for all selected ion exchange resins, the effect of the solution introducing the method into the ion exchange column on Co^{2+} ions separation degree was determined. Studied solutions were dropped at a flow rate of 2 mL/min and poured into the ion exchange column once.

The analysis of obtained dependencies shows that after 50 minutes, the C 160 ion exchange resin has the best sorption properties for Co^{2+} ions (54.7 mg/g). For others ion exchange resins values of the sorption capacity is decreasing in the following order S 950 < S 930 < S 910 < S 920 (Table 2). It has been shown that by using ion exchange method, cobalt ions can be efficiently removed from solutions with very high concentrations corresponding to the contents in industrial wastewater (e.g. galvanic). In the case of the C 160 ion exchange resin, cobalt concentration decreased from about 30 g/L to about 9 g/L after sorption process carried out in one 50 minute cycle (Table 2). For chelating resins, the degree of solutions purification was below 30%, suggesting that cobalt ions should first be converted into complex forms. This problem will be the subject of further studies.

It has also been shown that the method of introducing a solution into an ion exchange column has no significant effect on the efficiency of the cobalt ion exchange process. The obtained sorption capacity values aren't significantly different from each other, although slightly better results were obtained for pouring of solution method for majority of used ion exchangers.

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

Tabela 2. Parametry procesu usuwania jonów Co^{2+} za pomocą jonitów Purolite C 160, S 950, S 930, S 920 i S 910 po 50 minutach, W – roztwór wlano, K – roztwór wkroplono

| Ion exchanger		pH_0 (resin)	pH_0 (solution)	Final concentrations c_k (mg/L)	Degree of purification X (%)	Regeneration (%)	Sorption capacity Q (mg/g)
C 160	W	4.68	2.31	9 476.9	67.8	92.8	54.7
	K	5.36	2.29	9 840.6	66.6	85.3	51.8
S 950	W	4.84	2.33	20 832.2	29.3	88.0	27.7
	K	4.11	2.29	20 627.6	30.0	93.5	29.0
S 930	W	4.14	2.38	23 571.6	20.0	86.4	20.2
	K	3.64	2.38	23 594.3	19.9	80.6	19.5
S 910	W	4.00	2.27	24 947.0	15.3	67.2	15.1
	K	3.94	2.32	26 345.1	10.6	89.9	12.8
S 920	W	3.26	2.35	25 253.9	14.3	73.8	13.7
	K	3.26	2.37	25 594.9	13.1	100.0	13.2
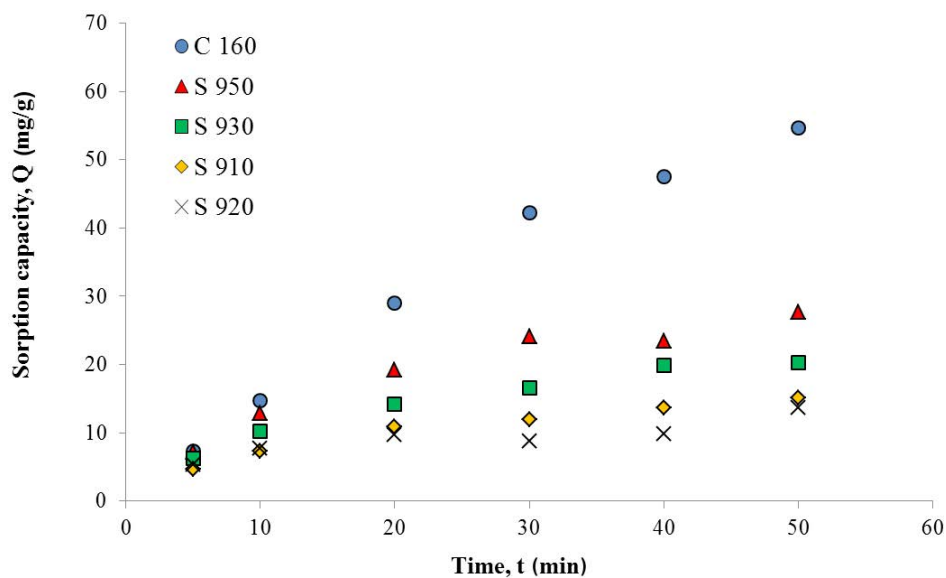
Fig. 2. The effect of contact time on the removal of Co^{2+} ions by the C 160, S 950, S 930, S 920, S 910 ion exchange resin by pouring the entire volume of the solution into an ion exchange column

Rys. 2. Wpływ czasu kontaktu na usuwanie jonów Co^{2+} za pomocą jonitów C 160, S 950, S 930, S 920, S 910 metodą wlania całej objętości roztworu do kolumny jonowymiennej
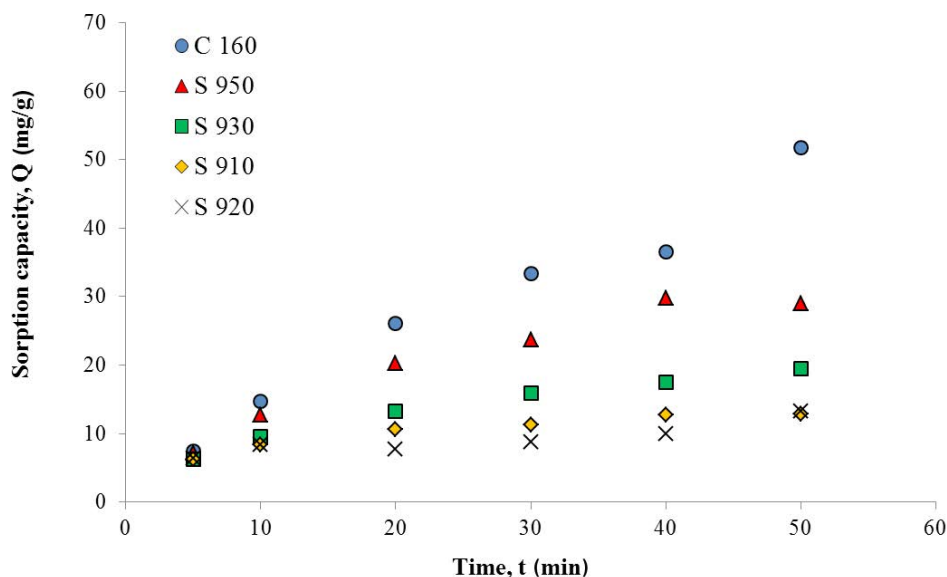
Fig. 3. Effect of contact time on the removal of Co^{2+} ions by the C 160, S 950, S 930,
S 920, S 910 ion exchange resin by dropping the solution into an ion exchange column

Rys. 3. Wpływ czasu kontaktu na usuwanie jonów Co^{2+} za pomocą jonitów C 160, S 950, S 930,
S 920, S 910 metodą wkraplania roztworu do kolumny jonowymiennej

The differences in sorption capacities are probably related to the different contact surfaces of solutions with the ion exchange resin. If the entire volume of the solution is poured into the column, the contact with the ion exchange bed is faster.

Later, the possibility of the regeneration of the selected resins with 10% solutions of nitric acid(V) or hydrochloric acid was studied (according to producer recommendation). The regeneration process achieved the highest efficiency for S 920 (100%), S 950 (93.5%) and C 160 (92.8%) ion exchange resins. The results are also satisfactory for other S 910 and S 930 ion exchange resins. In their case, the efficiency of 89.9% and 86.4% was obtained, respectively.

Considering the values of sorption capacity and regeneration efficiency, it was concluded that C 160 resin is the best cobalt ion exchanger. It is effective in high concentrations of cobalt, and is also reusable and allows for the recovery of this element.

Conclusions

Based on obtained results, it can be concluded that, the C 160 ion exchange resin has the best sorption properties for Co^{2+} ions (54.7 mg/g in time of 50 min). The regeneration of this ion-exchanger has the higher efficiency and achieving value of about 93% (Table 2).

It has been shown that by using the ion exchange method, cobalt ions can be removed efficiently from solutions with very high concentrations corresponding to the contents of this metal in industrial wastewater (e.g. galvanic). In the case of the C 160 ion exchange resin, after the sorption process carried out in one 50 minute cycle, the cobalt concentration decreased from about 30 g/L to about 9 g/L (Table 2). Chelating resins don't have such high sorption capacities. In their case, converting cobalt ions into complex forms is required. This problem will be the subject of further studies. It has also been shown that the method introducing the solution into an ion exchange column has no significant effect on the efficiency of the cobalt ion exchange process.

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RESEARCH OF Co^{2+} IONS REMOVAL
FROM WATER SOLUTION BY USING ION EXCHANGERS

Abstract

At present, industrial development is increasing pollution of soils, air and natural waters. These pollutants have a negative effect on the health and life of living organisms. Metals which interfere with the natural biological balance and inhibit self-cleaning processes in water bodies have particularly toxic effects. Cobalt, which gets into the environment from industrial sewage from electrochemical plants and the metallurgical industry, also belong to this group. This is also relatively rare and precious element, so it is important to look for additional sources of its recovery. Chemical and physicochemical methods such as: precipitation, extraction, membrane processes – nanofiltration, reverse osmosis, sorption and ion exchange are used to recover cobalt. The choice of method depends on: the kind and composition of wastewaters as well as on form and concentration of the pollutants.

Ion exchange resins produced by Purolite which were used to remove cobalt ions from solutions with concentrations corresponding to its contents in galvanic wastewater was the subject of the study. It has been shown that the C 160 ion exchange resin has the best the sorption properties for Co^{2+} ions (54.7 mg/g). In case of this ion exchange resin, after sorption process carried out in one 50 minute cycle, cobalt concentration decreased from about 30 g/L to about 9 g/L. The values of the sorption capacity do not depend on the method of introducing the solution into an ion exchange column (pouring or dropping). Each of the tested ion exchange resins is characterized by a high degree of cobalt concentration after regeneration using mineral acids, which can be advantageous in selecting the recovery method for this metal.

Keywords: ion exchange resins, ion exchange, wastewater, cobalt ions

BADANIA NAD USUWANIEM JONÓW Co^{2+} Z ROZTWORÓW WODNYCH
PRZY UŻYCIU WYMIENIACZY JONOWYCH

Streszczenie

Współcześnie rozwój przemysłu przyczynia się do wzrostu zanieczyszczenia gleb, powietrza i wód naturalnych. Zanieczyszczenia te negatywnie wpływają na zdrowie i życie organizmów żywych. Toksyczne działanie wykazują zwłaszcza metale, które zakłócają naturalną równowagę biologiczną oraz hamują procesy samooczyszczania w zbiornikach wodnych. W tej grupie jest również kobalt, który dostaje się do środowiska naturalnego ze ścieków przemysłowych pochodzących z zakładów elektrochemicznych oraz z przemysłu metalurgicznego. Jest to również stosunkowo rzadki i cenny pierwiastek, dlatego ważne jest poszukiwanie dodatkowych źródeł jego odzysku. Do pozyskiwania kobaltu stosuje się metody chemiczne i fizykochemiczne, takie jak: strącanie; ekstrakcja; procesy membranowe – nanofiltracja, odwrócona osmoza, sorpcja i wymiana jonowa. Wybór metody zależy od rodzaju i składu ścieków oraz postaci i stężenia usuwanych form zanieczyszczeń.

Przedmiotem badań były jonity firmy Purolite, które zastosowano do usuwania jonów Co^{2+} z roztworów o stężeniach odpowiadających zawartościom tego metalu w ściekach galwanicznych.

Wykazano, że najlepsze właściwości sorpcyjne w stosunku do badanych jonów ma kationit C 160 (54,7 mg/g). W przypadku tego jonitu po jednym, 50-minutowym cyklu, stężenie kobaltu obniża się z około 30 do około 9 g/dm^3. Wartości pojemności sorpcyjnej nie zależą od sposobu wprowadzania roztworu do kolumny jonitowej (wlanie lub wkraplanie). Każdy z badanych jonitów charakteryzuje się wysokim stopniem koncentrowania kobaltu w wyniku regeneracji przy użyciu kwasów mineralnych, co może być korzystne przy wyborze metody odzysku tego metalu.

Słowa kluczowe: jonity, wymiana jonowa, ścieki, jony kobaltu