Abstract
The paper presents results of research on removal of Cu\(^{2+}\) ions from aqueous solutions by ion exchange method in concentration range of 10–1000 mg/L. For this purpose, following Purilite synthetic ion exchange resins were used: S 910, S 930, S 940, S 950 and C 160. The obtained results were interpreted based on the degree of solution purification and microstructural investigations. The regeneration possibility of used ion exchangers with a 10% hydrochloric acid solution was also investigated.

Based on obtained results, it was determined that studied ion exchangers efficiently removed copper(II) ions from aqueous solutions, especially in low concentrations. Microstructural investigation made for tested materials after the sorption process clearly indicate that Cu\(^{2+}\) ions removal process was in accordance with ion exchange mechanism, which was confirmed by recorded SEM images. All ion exchangers except S 910, purified solutions from Cu\(^{2+}\) ions with an efficiency greater than 90% up to a concentration of 100 mg/L. In case of S 930 and S 940 ion exchangers, their efficiency was close to 100%. For higher concentrations, efficiency of studied ion exchangers decreased significantly. The lowest decrease in degree of copper(II) S 910 chelating resin with amidoxime groups was the least efficient. All studied ion exchangers can be regenerated with a 10% hydrochloric acid solution. The efficiency of this process varies from 53.1% to 80.5% depending on the used resins.

Keywords: copper ions, ion exchange, ion exchanger resins, microstructural research

Introduction
Copper belongs to the 11th group of periodic table and it's average content in Earth's crust is approx. 0.0055%. In the nature it occurs mainly in form of sulfide minerals (chalcolite – Cu\(_2\)S, covellite – CuS, chalcocpyrite – CuFeS\(_2\)), oxide minerals (carmite – CuO), carbonate minerals (malachite – Cu\(_2\)(OH)\(_2\)CO\(_3\)), azurite – Cu\(_2\)(OH)(CO\(_3\)) and less frequently silicate minerals (Bielański 2013). About 1% of total copper amount is in its native form. Its content in ores is estimated at about 6% (Sierczuk 2017). In pure natural waters, copper compounds are relatively rare, wherein water from wetlands or peat lands may contain traces of it – up to about 0.01 mg/L. Most of dissolved copper is bound in stronger complexes with various inorganic as well as organic ligands. In natural water, insoluble copper compounds, such as sulfides hydroxides or carbonates, may also occur (Hermanowicz et al. 1999).

Copper is considered to be an essential element for human body, however its excessive doses may cause various disease (Górecki et al. 2017). This element shows a particularly high susceptibility to bioaccumulation from aquatic environment. Its toxicity in water depends on: pH, water hardness, dissolved oxygen concentration, presence of chelating agents, presence of humic acids, content of suspended solids and interactions between individual metals (Piontek et al. 2014). In surface waters elevated amounts of copper compounds usually are caused by wastewater from metallurgical, paint, textile and chemical industries (Thomas et al. 2014). It can also penetrate into water from installations made of copper, brass or bronze as a result of its corrosive action. The conditions that should be met while disposing of sewage into natural environment, define that concentration of copper ions cannot exceed 0.1 mg/L for wastewater from the ceramic industry and 0.5 mg/L for other types of wastewater (Dz. U. 2014.1800).

In order to remove, concentrate and recover metal ions, various physicochemical methods are used, e.g. chemical precipitation and coprecipitation (Lundström et al. 2016; Zhou et al. 2018), coagulation (Chang and Wang 2007; El Samrani et al. 2008; Heredia and Martín 2009), solvent extraction (Wanga et al. 2018; Elizaldé et al. 2019), electrochemical and membrane processes (Ahmad ang Ooi 2010; Jack et al. 2014; Rincón and La Motta 2014; Li et al. 2017; Hosseini et al. 2018), adsorption (Prakash and Arungalai Vendan 2016; Shahamirifard et al. 2016; Dil et al. 2017), ion exchange (Gurnule and Dhote 2012; Kuz'min and Kuz'min 2014; Al-Saydeha et al. 2017) and biotechnological processes (Foroutana et al. 2017; Wena et al. 2018; Nanchaaraih et al. 2019). Selection of method depends on type and composition of sewage, form and concentration of removed components and desired degree of purification. Effectiveness and cost of method are also taken into account.

For this purpose, there are often used, methods based on ion exchange, due to its advantages, among which there is high selectivity in removing impurities, as well as vast diversity of used ion exchangers, both: synthetic and natural (Alyüz and Veli 2009; Naushad 2009). Thanks to ion exchange, all ions can be removed from solution or one substance can be separated from other one. Choosing one of these options depends, most of all, on composition of solution, as well as on desired level of purification. Ion exchange process involves substitution of ions being a part of the ion exchanger, for equivalent quantity of other ions of the same charge that are included in
purified water solution. Ion exchangers are macromolecular substances, practically insoluble in water, which have ability to exchange positively or negatively charged ions from electrolyte solution to equivalent amounts of ions contained in ion exchangers (Inamuddin and Luqman 2012). Among wide group of ion exchangers, chelating resins have great practical importance. Their unique feature distinguishing them from other types of sorbents is presence in their polymer matrix of chemically active functional groups, which are capable to interact with metal ions found in solution and form chelated complexes as a consequence. Sorption abilities of chelating resins depend mainly on nature of functional groups, and with lesser extent on size of grain or other physical properties. They are characterized by a much higher ability of selective sorption of one ion in presence of other ones, in comparison to typical ion exchangers. Thanks to that, they are used in recovery of precious metals from sludges, as well as in removal of toxic heavy metals from surface water and wastewater (Bożęcka and Sanak-Rydlewska 2018). In particular, they enable selective sorption of transition metal ions from wastewater containing large amounts of sodium ions. Most of ion exchangers can be regenerated with mineral acids, which result in obtaining concentrates of adequate salts that can be then reused in technological processes.

The use of ion exchangers to remove copper(II) ions from water and sewage is subject of many scientific studies, including (Bulai et al. 2009; Kołodyńska 2009; Greluk and Hubicki 2011; Rudnicki et al. 2014; Bożęcka et al. 2016; Edebali and Pehlivan 2016). Results of mentioned studies are summarized in Table 1.

### Materials and methods

The aim of this study was to compare degree of purification of aqueous solutions from copper(II) ions using different Purolite ion exchangers. The possibility of their regeneration and ability to recover copper was also examined. In addition, surface morphology of used ion exchangers was determined using a Scanning Electron Microscope (SEM). These analyses have been extended with chemical research in micro areas (EDS).

Five different synthetic ion exchange resins from Purolite were used for research. Four of them are chelating resins: S 910, S 930, S 940, S 950 and one is strongly acid cation ion exchanger C 160. Table 2 presents their physicochemical characteristics. A crucial step in the preparation of resins for this research was to subject it to swell in deionized water for 24 hours.

The 0.5 g sample of ion exchange were used for studies. Range of initial concentrations of Cu\(^{2+}\) ions in tested solutions ranged from 10 to 1000 mg/L. Copper solutions were prepared from hydrated copper(II) nitrate(V), \([Cu(NO_3)_2 \cdot 3H_2O]\), by ACROS ORGANICS. The pH of studied solutions was 4.0 (± 0.1). For the pH adjustment 0.02 M HNO\(_3\) had been used.

Ion exchange processes were carried out with a dynamic method using laboratory shaker. For this purpose, 100 ml of the solution with ion exchanger was placed in a 250 ml Erlenmeyer flasks and shaken with a constant speed of 180 rpm. Sample for analysis was collected after one hour (at that time system reached equilibrium). Solutions after ion exchange processes were filtered to isolate solid particles. Final concentration of Cu\(^{2+}\) ions in solutions was determined with cuprizone method using a UV-VIS spectrophotometer Cadas 200 Dr. Lange. Analysis were carried out in an ammonia-citrate medium at pH 8.0–9.5. The absorbance of the solutions was measured at 600 nm wavelength.

The degree of purification of studied solutions from copper(II) ions, X (%), was calculated using Formula 1:

\[
X = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%
\]

where \(C_{in}\) is initial concentration of copper ions and \(C_{out}\) is final concentration of copper ions after ion exchange process.
Observed differences in efficiency of purification of aqueous solutions from Cu\(^{2+}\) ions by tested resins resulted from both different structure of ion exchangers, as well as from differences in functional groups. Ion exchangers: S 930 with the iminodiacetic groups, S 940 containing aminophosphonic groups and C 160 with sulfonic groups proved to be the most effective in ion exchange process. Slightly lower solutions purification level from copper(II) ions was observed for S 950 chelating resin, which possesses the same functional groups as S 940 ion exchanger but shows a greater diversity of particles size. A S 910 ion exchanger, which contained amidoxime groups was the least efficient.

The results of regeneration are presented in Figure 3. Among all tested resins, the highest efficiency of regeneration process was achieved for ion exchanger C 160 (80.5%) and S 910 (64.5%). Recovery of copper after regeneration for remaining three chelating resins (S 930, S 940 and S 950) is significantly smaller and reaches about 54%. Cation exchanger C 160 regenerates much better than chelating resins, which is probably due to their different structure and differences in mechanism of ion exchange process. In case of chelating resins, stability of formed complexes is a function of solution pH. Therefore, smaller efficiency values of regeneration process are observed for ion exchangers S 930, S 940 and S 950 in comparison with resin S 910. Ion exchanger S 910 forms stable complexes with copper only at pH > 3. Other remaining resins have lower minimum pH values below which removal of Cu\(^{2+}\) ions from purified solution is no longer possible (Purolite, 2019). In addition, reducing volume of 10% HCl (50 ml) compared to volume of solution submitted to sorption process (100 ml), allowed to concentrate solution and reduce consumption of regenerating reagent.

**Summary**

Based on obtained results, it was found that studied ion exchangers removed effectively copper(II) ions from aqueous solutions, especially in low concentration range. This process took place in accordance with ion exchange mechanism. On the surface of tested resins, no microprecipitations were observed. All ion exchangers, except of S 910, purified solutions from Cu\(^{2+}\) ions with efficiency greater than 90% up to a concentration of 100 mg/L. In case of S 930 and S 940 chelating resins their efficiency was close to 100%. For the concentration above 100 mg/L, efficiency of tested ion exchangers decreased significantly. The lowest decrease in degree of Cu\(^{2+}\) ions separation was observed for C 160 cation ion exchanger. In this case, for the highest concentration (1000 mg/L) purification level reached 43.7%. A S 910 chelate resin turned out to be the least effective (for a concentration of 1000 mg/L) – degree of copper separation was only 16.1%.

**Results and Discussion**

Photos of surface morphology of tested ion exchangers were recorded for materials after the ion exchange process. Examples of SEM images and EDS spectra of examined materials are shown in Figure 1.

A S 910 and S 940 resins are characterized by a porous surface (Figure 1 a, g), while S 930, S 950 and C 160 have a more smooth surface with numerous cracks and grooves (Figure 1 d, j, m). Microstructural investigations performed for studied materials after sorption process clearly indicate that Cu\(^{2+}\) ion removal process occurred in accordance with ion exchange mechanism, which was confirmed by recorded SEM images (Figure 1). No microprecipitations were observed on the surface of tested ion exchangers.

Determined degree of solutions purification from Cu\(^{2+}\) ions with use of synthetic ion exchange resins as a function of initial concentration is shown graphically in Figure 2.

For all tested ion exchangers the highest degree of purification was observed at low concentrations (Figure 2). All ion exchangers, except for S 910, purified solutions from Cu\(^{2+}\) ions with efficiency greater than 90% up to a concentration of 100 mg/L. In case of S 930 and S 940 chelating resins their efficiency was close to 100%. For the concentration above 100 mg/L, efficiency of tested ion exchangers decreased significantly. The lowest decrease in degree of Cu\(^{2+}\) ions separation was observed for the C 160 cation ion exchanger. In this case, for the highest concentration (1000 mg/L) purification level reached 43.7%. A S 910 chelate resin turned out to be the least effective (for a concentration of 1000 mg/L) – degree of copper separation was only 16.1%.

\[
X = \frac{c_i - c_e}{c_i} \times 100\% \quad (1)
\]

where: \(c_i\) and \(c_e\) – initial and equilibrium concentration of Cu\(^{2+}\) ions in solutions [mg/L].

In the next stage of research, regeneration possibility of used resins with 50 ml of 10% hydrochloric acid solution was studied. Reagent selection and regeneration conditions were in line with manufacturer’s instructions (regeneration time - 30 minutes) (Purolite 2019).

In order to determine surface morphology of studied ion exchangers, photos were recorded using Scanning Electron Microscope (SEM) from FEI Quanta 200 FEG company. These analyses were extended with microchemical studies. They were performed using an EDS detector. This tests were carried out in high vacuum mode. Samples were coated with carbon before analysis. Acceleration voltage was 20 kV.

**Tab. 2. Physicochemical characteristics of the ion exchangers used for the research (Purolite, 2019)**

<table>
<thead>
<tr>
<th>Resin Purolite</th>
<th>Type functional group</th>
<th>Matrix</th>
<th>The range of particle size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S 910</td>
<td>Amidoxime -C(NH(_2))NOH</td>
<td>Macroporous crosslinked polymer</td>
<td>0.3–1.2</td>
</tr>
<tr>
<td>S 930</td>
<td>Iminodiacetate R-CH(_2)--(CH(_3)COOH)(_2)</td>
<td>Macroporous styrene-divinyl benzene</td>
<td>0.425–1.2</td>
</tr>
<tr>
<td>S 940</td>
<td>Aminophosphonic RCI(_2)NH(_2)PO(_2)</td>
<td></td>
<td>0.43–0.65</td>
</tr>
<tr>
<td>S 950</td>
<td>Aminophosphonic RCI(_2)NH(_2)PO(_2)</td>
<td></td>
<td>0.3–1.2</td>
</tr>
<tr>
<td>C 160</td>
<td>Sulfonic R-SO(_4)(^-)</td>
<td></td>
<td>0.3–1.2</td>
</tr>
</tbody>
</table>
Fig. 1. Example SEM images and EDS spectra obtained for samples of Purolite synthetic ion exchangers: S 910 (a, b, c); S 930 (d, e, f); S 940 (g, h, i); S 950 (j, k, l); C 160 (m, n, o) after Cu$^{2+}$ ions exchange process.

Fig. 1. Przykładowe zdjęcia SEM oraz widma EDS uzyskane dla próbek syntetycznych jonitów firmy Purolite: S 910 (a, b, c); S 930 (d, e, f); S 940 (g, h, i); S 950 (j, k, l); C 160 (m, n, o) po procesie wymiany jonowej jonów Cu$^{2+}$.
tested resins towards Cu\(^{2+}\) ions may be caused by a different chemical and physical structure or by size of their particles. Probably transformations of Cu\(^{2+}\) ions into complex forms will increase efficiency of their removal by tested chelating ion exchangers. This will be the subject of further research. Results obtained after the regeneration process confirmed, that studied resins can be regenerated using 10% hydrochloric acid solution. Efficiency of regeneration varies from 53.1% (for S 930 resin) to 80.5% (for C 160 resin).
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Usuwanie i odzysk miedzi z roztworów wodnych przy użyciu wybranych syntetycznych żywic jonowymieniowych (część I)

W pracy przedstawiono wyniki badań dotyczące usuwania jonów Cu\(^{2+}\) z roztworów wodnych metodą wymiany jonowej w zakresie stężeń 10–1000 mg/L. W tym celu zastosowano żywice jonowymienne firmy Purolite: S 910, S 930, S 940, S 950 i C 160. Otrzymane wyniki zinterpretowano w oparciu o stopień oczyszczenia roztworu i badania mikrostrukturalne. Zbadano również możliwość regeneracji użytych jonitów za pomocą 10% roztworu kwasu solnego.

Na podstawie otrzymanych wyników stwierdzono, że badane jonity skutecznie usuwały jony miedzi(II) z roztworów wodnych, szczególnie w niskich stężeniach. Badania mikrostrukturalne wykonane dla badanych materiałów po procesie sorpcji wyraźnie wskazują, że proces usuwania jonów Cu\(^{2+}\) zachodził zgodnie z mechanizmem wymiany jonowej, co potwierdzają zarejestrowane obrazy SEM. Na powierzchni badanych jonitów nie zaobserwowano mikrostrąceń.

Wszystkie wymienianye jonowe z wyjątkiem S 910 oczyszczały roztwory z jonów Cu\(^{2+}\) z wydajnością większą niż 90% do stężenia 100 mg/L. W przypadku jonitów S 930 i S 940 ich skuteczność było bliska 100%. W przypadku większych stężeń wydajność badanych jonitów znacząco maleła. Najmniejszy spadek stopnia wydzielenia jonów miedzi(II) zaobserwowano dla kationitu C 160 zawierającego grupy sulfonowe. Najmniej skuteczny okazał się jonit chelatujący S 910 z grupami amidoksymowymi. Wszystkie badane jonity można regenerować za pomocą 10% roztworu kwasu solnego. Wydajność tego procesu waży się od 53,1% do 80,5% w zależności od użytej żywicy jonowymiennej.

Słowa kluczowe: jony miedzi, wymiana jonowa, jonity, badania mikrostrukturalne