Cooper Removal and Recovery from Aqueous Solutions by Using Selected Synthetic Ion Exchange Resins (Part 2)

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http://doi.org/10.29227/IM-2020-02-02
Submission date: 03-07-2020 | Review date: 23-07-2020

Abstract

In paper the possibility of Cu2+ ions removing from aqueous solutions on selected synthetic ion exchange resins (Purolite S 910, S 930, S 940, S 950, C 160) was studied. These processes were described by the Langmuir and Freundlich adsorption models. It was found that the process of Cu2+ ions removing on S 910 and S 930 ion exchangers were the best described by linear equation form of Langmuir isotherm. The fit quality of the Freundlich isotherm is the best for S 940, C 160 and S 950 ion exchangers, which is confirmed by the obtained values of correlation coefficients R.

The highest value of the maximum sorption capacity (about 69 mg/g) was obtained for C 160 cation exchange resin with sulfonic groups. For others ion exchange resins the monolayer capacity was decreasing in following order S 940 > S 930 > S 950 > S 910. The S 940 and S 930 ion exchangers were characterized by the highest affinity for Cu2+ ions. The amidoxime polyacrylic chelating resin S 910 was the least efficient. The differences in the affinity of the studied resins towards to Cu2+ ions can be explained by their different chemical or physical structure and particles size.

In case of the studied ion exchange resins, the 1/n parameter values of the Freundlich isotherm were in range of 0.21–0.32. Therefore, it can be concluded that energy heterogeneity of the studied sorption system and intensity of Cu2+ ion removal on above ion exchangers are moderate. The K parameter value of the Freundlich equation was also highest for ion exchangers S 930 and S 940.

Keywords: copper, ion exchange resins, Langmuir isotherm, Freundlich isotherm

Introduction

Nowadays, human activity generates significant amounts of waste. This includes also wastewater, which pose a significant threat to living organisms. Among the substances emitted into the natural environment there are also copper compounds.

Copper is a toxic metal, but it is also a micronutrient necessary for proper functioning of living organisms. The basic function of copper in human body is its participation in oxidation-reduction processes. This element is in enzymes active centres which are involved in cell metabolic processes. Its deficiency causes a significant reduction in copper-dependent enzymes, which leads to inhibition of cells life processes (Ogórek et al. 2017).

However, copper excess is toxic to living organisms. One of its main consequences is formation of reactive oxygen forms, causing development of oxidative stress. In cell, this process can damage proteins and lipids thus cell structures and genetic material. Its excess in diet is mainly associated with changes in liver, followed by damage to kidneys, brain tissue, coronary vessels and cardiac muscle (Piontek et al. 2014; Ogórek et al. 2017). Copper is one of the factors responsible for appearance and progression of Alzheimer’s and Parkinson’s diseases. Disorders of copper metabolism in body also lead to Menkes’ and Wilson’s diseases (Hu et al. 2017).

Copper is a valuable element, widely used in many industries. It has the highest electrical and thermal conductivity of all base metals, therefore it is widely used in electrical industry as well as in production of alloys (brass, bronze, alloys with aluminium, manganese and beryllium). It is also used for wood impregnation and for production of insecticides and fungicides (Al-Saydeh et al. 2017). Therefore, in untreated industrial and municipal sewage, copper compounds concentration is usually at a high level. Considerable copper environmental pollution is also found near mines and smelters of this metal (Seiczkuk 2017).

The current requirements for plants which discharge sewage into the municipal and industrial sewage system or watercourses determine that concentration of copper ions cannot exceed 0.1 mg/L. For water from the ceramic industry and 0.5 mg/L for other types of wastewater (Dz. U. 2014.1800). Exceeding of these acceptable standards affects surface water quality and poses a special threat to living aquatic organisms in these ecosystems. This is also important for the raw water intake and production of drinking water with suitable quality, for which copper ions concentration cannot exceed 2 mg/L (Dz. U. 2017.2294).

For the copper ions removal from aqueous solutions, methods such as: precipitation (Lundström et al. 2016), electrochemical processes (Jack et al. 2014; Rincón and La Motta 2014; Li et al. 2017) and membrane processes (Ahmad and Ooi 2010; Tran et al. 2012), adsorption (Prakash and Arungalai Vendan 2016; Shahamirfard et al. 2016; Dil et al. 2017) and ion exchange (Lin and Juang 2007; Bulai et al. 2009; Kolodynska 2009; Gurule and Dhopa 2012; Rudnicki et al. 2014; Al-Saydeha et al. 2017) are commonly used. Choice of water and wastewater treatment methods always depends on the number of parameters, including: kind and composition
of wastewater as well as form and concentration of removed pollutants. The method's effectiveness and economic reasons are also important.

Among previously mentioned methods, ion exchange has a significant role in modern technologies of metal ions removal from wastewater. In initial phase of technology development for synthetic ion exchangers production, their use was mainly related to the need of water treatment. Gradually, ion exchange resins were also used to treat industrial wastewater, from which it was possible to recover not only water, but also other components, e.g. precious metals. However, used conventional ion exchangers were characterized by limited ion exchange capacity. Therefore, work has been begun to improve their selectivity (Greluk and Hubicki 2011).

The much greater selective sorption ability of one ion in the presence of other was obtained for chelating resins. They are characterized by presence of active functional groups capable to react with metal ions contained in solution with which they form cyclic chelate complexes. The sorption abilities of these ion exchangers depend on type of functional groups and on physicochemical properties of polymer matrix (Bożęcka and Sanak-Rydlewskia 2018).

High selectivity of chelating ion exchangers on selected metal ions allows their use in industrial conditions, when concentrations of adsorbed ions are even very low compared to concentrations of accompanying ions. This is an important advantage compared to traditional liquid-liquid or liquid-solid extraction methods where it is necessary to use environmentally harmful solvents (Bożęcka and Sanak-Rydlewskia 2018).

The aim of this study was to determine and compare ion exchange properties of selected synthetic ion exchange resins towards Cu$^{2+}$ ions. This kind of experimental and theoretical studies are valuable in search of new, more effective sorption materials used to remove and recovery valuable metals, including copper. Therefore, it is planned to continue this problem.

### Materials and methods

The Purolite S 910, S 930, S 940, S 950 and C 160 cation exchanger were subject of the research. Their physicochemical characteristics are presented in Table 1. The main stage in resins preparation for the research was swelling them in deionized water for 24 hours.

The Cu$^{2+}$ ions sorption experiments were performed in 250 mL Erlenmeyer flasks. The 0.5 g sample of ion exchanger and 100 mL of studied solutions were introduced into each flask. Copper solutions were prepared from hydrated copper(II) nitrate(V) $[Cu(NO_3)_2 \cdot 3H_2O]$ by ACROS ORGANICS. The Cu$^{2+}$ ions concentrations were in the range of 10–1000 mg/L. Solutions with ion exchangers were shaken for 60 min by using laboratory shaker with a constant speed equal to 180 rpm. After this time system reached equilibrium. The pH up to value 4.0 was regulated by addition of nitric acid solution.
Before measurements, all samples were filtered to remove solid particles. Concentration of Cu\(^{2+}\) ions was determined by using UV-VIS Cadas 200 spectrometer from Dr. Lange. The analysis were carried out in an ammonia-citrate medium at pH 8.0–9.5. Absorbance of copper solutions was measured at 600 nm wavelength.

The sorption capacity was calculated using Formula 1:

\[
Q = \frac{V(c_0 - c_e)}{m}
\]  

(1)

where: \(Q\) is the amount of adsorbed Cu\(^{2+}\) ions per gram of ion exchanger in equilibrium [mg/g], \(V\) – is the volume of the solution [L], \(c_0\) and \(c_e\) are the initial and equilibrium concentrations of Cu\(^{2+}\) ions [mg/L], \(m\) is the quantity of dry mass of the ion exchanger [g].

The removal of Cu\(^{2+}\) ions on selected ion exchangers was described by two most popular adsorption isotherm models (Langmuir and Freundlich). Despite the increasing number of recent achievements in modelling adsorption processes, these isotherms are still often used for both micro- and macroporous materials (Bulai et al. 2009; Greluk and Hubicki 2011; Edebali and Pehlivan 2016; Yuanfeng et al. 2016). The equations of these two isotherms and their linear forms were shown in Table 2.

For the Langmuir equation a dimensionless division factor, \(R_L\), was determined in accordance with Formula (6) (Bożęcka et al. 2017):

\[
R_L = \frac{1}{1 + b \cdot C_0}
\]  

(6)

where: \(C_0\) is the highest initial concentration of adsorbate in solution [mg/L]. It is related to the shape and determines the intensity of the adsorption process according to the following dependences:

- \(R_L > 1\) – adsorption occurs poorly (unfavourable character);
- \(R_L = 1\) – the linear course depends on the adsorbate concentration;
- \(0 < R_L < 1\) – intensive course (favourable character)
- \(R_L = 0\) – the process is irreversible.

### Discussion of the results

For mathematical description of experimental data, often used empirical dependencies of Langmuir and Freundlich isotherms were applied. Parameter values of these isotherms for all studied experimental systems were given in Table 3.

Data analysis showed that the process of Cu\(^{2+}\) ions removing on S 910 and S 930 ion exchangers was the best described by using linear equation of Langmuir isotherm. For other resins, isotherms fit to experimental data is also quite good, which is confirmed by obtained values of correlation coefficients \(R\).

The Langmuir model assumes that surface of adsorbent is homogeneous. When localized adsorption occurs the molecule cannot move freely across the surface. Lateral interactions between the adsorbed molecules are irrelevant. Therefore, it is a monolayer adsorption (Atkins 2012; Bożęcka et al. 2017). Langmuir’s theory works well when total number of active sites is saturated, as shown by course of obtained adsorption isotherms (Figure 1).

The linear form of the Langmuir isotherm was used to determine the capacity of obtained monolayer, i.e. amount of adsorbate covering adsorbent surface with a monomolecular layer. The state of maximum adsorption, corresponding to occupancy of all active centres is determined by \(q_{\text{max}}\) parameter of the isotherm. The highest value of this parameter, equal to 68.96 mg/g, was obtained for C 160 cation exchanger with sulfonic groups. The monolayer capacity values determined for other chelating ion exchangers (S 910, S 950, S 930, S 940) differed from each other and were 35.60 mg/g; 46.32 mg/g; 48.33 mg/g; 50.08 mg/g; respectively (Table 3).

Based on intersection point of linear form of Langmuir isotherm with axis of ordinates, values of \(b\) constants were determined, which defining affinity of studied ion exchange resins to Cu\(^{2+}\) ions. The higher value of \(b\) parameter the greater affinity and the more steep course of Langmuir equation. For most of the studied ion exchange resins, obtained \(b\) parameter values of the Langmuir equation were quite high (Table 3). The highest value was obtained for S 940 ion exchanger (\(b = 0.1197\ L/mg\)). A very similar result was obtained for S 930 chelating resin (\(b = 0.1141\ L/mg\)). For other ion exchangers

<table>
<thead>
<tr>
<th>Resin Purolite</th>
<th>Langmuir Isotherm</th>
<th>Freundlich Isotherm</th>
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<tr>
<td></td>
<td>(q_{\text{max}}) [mg/g]</td>
<td>(b) [L/mg]</td>
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<tr>
<td>S 910</td>
<td>35.60</td>
<td>0.0253</td>
</tr>
<tr>
<td>S 930</td>
<td>48.33</td>
<td>0.1141</td>
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<tr>
<td>S 940</td>
<td>50.08</td>
<td>0.1197</td>
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<tr>
<td>S 950</td>
<td>46.32</td>
<td>0.0623</td>
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<tr>
<td>C 160</td>
<td>66.96</td>
<td>0.0667</td>
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</tbody>
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Tab. 3. Langmuir and Freundlich isotherms coefficients for studied Purolite ion exchangers: S 910, S 930, S 940, S 950 and C 160
(C 160; S 950 and S 910) b parameter values were lower and reached respectively 0.0667 L/mg; 0.0623 L/mg and 0.0253 L/mg. Generally a good sorbent should have high values of both \( q_{\text{max}} \) and \( b \) constants.

Dimensionless division factor \( R_L \) was calculated in order to determine degree of resins suitability for \( Cu^{2+} \) ion removal process. Its values are in the range \( 0 < R_L < 1 \), thus confirming that course of the studied ion exchange processes is favourable.

The Freundlich isotherm is an experimental equation, which well describes adsorption at energetically heterogeneous surface and microporous adsorbents. Freundlich theory assumes, that upon complete covering of adsorbate surface by adsorbent particles, their number cannot be greater than number of surface active sites. This equation well describes reversible adsorption from diluted solutions (Atkins 2012; Bożęcka et al. 2017).

Data presented in Table 3 show that fit quality of the Freundlich isotherm to experimental data is also good, as evidenced by the obtained value of correlation coefficients \( R \). Freundlich model describes the best removal process of \( Cu^{2+} \) ions for ion exchangers S 940 (\( R = 0.9981 \)); C 160 (\( R = 0.9964 \)) and S 950 (\( R = 0.9866 \)).

The graph of \( \log Q = f (\log c_e) \) is a straight line, which easily allowed to determine \( K \) and \( 1/n \) constants from Freundlich equation and to describe the experimental systems by using these parameters (Figure 1 and Table 3). The \( K \) constant determines sorption capacity of studied ion exchangers at equilibrium concentration of \( Cu^{2+} \) ions in solution. Parameter \( 1/n \) is a measure of surface heterogeneity. The more value of this constant is closer to zero, the more adsorbent surface is energetically inhomogeneous (Atkins 2012; Bożęcka et al. 2017).

The analysis of data shows that in the case of studied ion exchange resins, values of \( 1/n \) constant are in the range of 0.21–0.32 (Table 3). Therefore, it can be concluded that there is a moderate energetic inhomogeneity of studied sorption system. Exponent \( 1/n \) also allows to determine the intensity of the removal of \( Cu^{2+} \) ions from the aqueous phase by using studied ion exchangers. When the \( 1/n = 1 \), the isotherm is linear, which confirms that the enthalpy of process is constant throughout all range of concentrations. When \( 1/n < 1 \), the isotherm is a growing concave course, from which it can be concluded that a larger number of molecules at surface increases enthalpy and thereby further enhances adsorption (Greluk and Hubicki 2011). In analysed cases, parameter values indicate a moderate intensity of \( Cu^{2+} \) ion removal on studied ion exchangers (\( 1/n < 1 \)) (Table 3).
Summary

In this paper, the possibility of removing Cu^{2+} ions from aqueous solutions by using selected ion exchange resins produced by Purolite (S 910, S 930, S 940, S 950, C 160) was studied. The studied processes were described by the Langmuir and Freundlich adsorption models.

It was found that the process of Cu^{2+} ions removing on S 910 and S 930 ion exchangers were the best described by using linear equation of Langmuir isotherm. Fit quality of the Freundlich isotherm is the best for S 940, C 160 and S 950 ion exchangers. For other resins, isotherms fit to experimental data is also quite good, which is confirmed by obtained values of correlation coefficients R.

The highest value of maximum sorption capacity (about 69 mg/g) was obtained for C 160 cation exchanger with sulfonic groups. For other ion exchange resins, monolayer capacity was decreasing in following order S 940 > S 930 > S 950 > S 910.

For most of studied ion exchange resins, obtained values of b parameter of the Langmuir equation were quite high. Ion exchangers: S 940 containing aminophosphonic groups and S 930 with the iminodiacetic groups were characterized by the highest affinity to Cu^{2+} ions. The amidoxime polyacrylic chelating resin S 910 was the least efficient. Differences in affinity of studied resins towards Cu^{2+} ions can be explained by their different chemical and physical structure and particles size.

In case of studied ion exchange resins, the 1/n parameter values of the Freundlich isotherm were in range of 0.21–0.32. Therefore, it can be concluded that there is moderate energetic inhomogeneity of studied sorption system. This parameter also indicates a moderate intensity of Cu^{2+} ions removal process on above ion exchangers (1/n < 1). The K parameter value of the Freundlich equation was also the highest for ion exchangers S 930 and S 940.

Literatura – References

Usuwanie i odzysk miedzi z roztworów wodnych przy użyciu wybranych syntetycznych żywic jonowymieniowych (część 2)

Wykorzystanie modeli izoterm adsorpcji do opisu procesów usuwania jonów Cu\(^{2+}\) z roztworów wodnych na wybranych syntetycznych żywicach jonowymieniowych

W pracy zbadano możliwość usuwania jonów Cu\(^{2+}\) z roztworów wodnych za pomocą syntetycznych żywic jonowymieniowych firmy Purolite. Do badań wytypowano jonity chelatujące S 910, S 930, S 940, S 950 oraz kationit C 160. Badane procesy opisano za pomocą modelu adsorpcji Langmuira i Freundlicha.

Stwierdzono, że liniowa forma równania izotermy Langmuira najlepiej opisuje proces usuwania jonów Cu\(^{2+}\) na jonicie S 910 i S 930. Jakość dopasowania izoterm Freundlicha jest najlepsza w przypadku jonitów S 910; C 160 i S 930 w porównaniu do jonitu C 160 z grupami sulfonowymi. Pojemność monowarstwowa jonitów chelatujących była zależna od postaci grup ionicznych. Największą pojemność maksymalną jonów Cu\(^{2+}\) uzyskano dla jonitu C 160 oraz jonitów C 930 i S 940. Pojemność chemiczna jonitów chelatujących była mniejsza w porównaniu z grupami sulfonowymi. W przypadku jonitów chelatujących, pojemność jonowa ulegała zmniejszeniu w silniejszym zjawisku w związku z zasadowaniem jonów Cu\(^{2+}\) w silniejszym zjawisku w związku z zasadowaniem jonów Cu\(^{2+}\).

Słowa kluczowe: miedź, żywice jonowymienne, izoterna Langmuira, izoterna Freundlicha