Study on the Effectiveness of Cu^{2+} Ions Removal from Aqueous Solutions Using the Purolite S920 Ion Exchange Resin

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Abstract

Anthropogenic environmental pollution with heavy metals remains a significant problem, especially when they occur in a form that facilitates bioaccumulation. In the case of natural and process waters or industrial wastewater, there is still a need to improve methods, which provide to reduce heavy metal content.

In this study has been shown to the Purolite S920 is useful to eliminating Cu^{2+} ions from aqueous solutions. In the tested concentration range, 92% purification of single-component solutions from Cu^{2+} ions were achieved at pH=4 (in laboratory conditios).

The process of copper (II) ion removal using the chelating ion exchange resin was interpreted based two of the most popular isotherm models: Langmuir and Freundlich.

Keywords: *sorption, copper (II) ions, Purolite S920, Langmuir and Freundlich isotherm*

INTRODUCTION

The development of technology and human industrial activity contributes to the increase in environmental pollution with heavy metals, which include elements with atomic numbers in the range of 21–92, densities above 4.5 g/ml, and the ability to form cations through chemical processes. Lead, cadmium, mercury, nickel and copper are particularly hazardous to living organisms due to their bioaccumulation potential. [1-3] Their occurrence in the natural environment is primarily associated with processes such as rock weathering, volcanic eruptions, ocean evaporation, forest fires, and soil-forming. The sources of anthropogenic environmental contamination with these metals include mining and processing of polymetallic ores, the metallurgical and electrochemical industries, the energy sector, and municipal utilities [4]. Toxic metals from these sources disperse and penetrate into the soil, water, air and enter the bodies of animal and human directly or through plants. Excessive bioaccumulation of heavy metals disrupts metabolic balance and can lead to numerous diseases and even death. Their concentration in the aquatic environment depends on physical and chemical properties, including solubility, the presence of other contaminants, pH, oxidation-reduction potential and chemical reactivity at the site of occurrence. In the case of process waters and industrial wastewater, there is still a need to implement technologies that reduce heavy metal content.

Various physicochemical methods are used to remove and recover heavy metal ions, including chemical precipitation and co-precipitation, coagulation, solvent extraction, electrochemical and membrane processes, adsorption, and ion exchange. The choice of method depends primarily on the type and composition of the wastewater, the form and concentration of the components to be removed, and the required degree of purification. Process efficiency and cost are also important.

The conventional methods, as mentioned earlier, are often unfavourable, especially for large volumes of material with low heavy metal ion content. In general, these ions precipitate as hydrated metal oxides or hydroxides, sulphides, etc. This process is accompanied by flocculation or coagulation which provide to the generation of large amounts of hazardous sludge. Additionally, these processes are complicated, when precipitates are in the form of colloids or amorphous gels or create the complexes formation with inorganic or organic ligands. Such circumstances reduce the effectiveness of toxic metals elimination.

Ion exchange, on the other hand, enables the removal of all ions from a solution or the selective separation of wastewater components, achieving the required degree of decontamination. This process involves the exchange of ions of the same sign and in equivalent quantities between the solution and the ion exchanger surface, while maintaining electronegativity. An additional advantage of ion exchange process is the wide range of ion-exchange resins, both synthetic and natural [5-7]. It should be emphasized that in most cases, ion exchange process allows for the replacement of an undesirable ion with another, environmentally neutral one [8].

The effectiveness of ion exchange depends among others, on the structure of the ion exchanger particles, the type of ions being exchanged, the type and number of functional groups in the ion exchanger, and the efficiency of its regeneration [9]. The basic parameter characterizing the ion exchanger its exchange capacity, which indicates the number of ions that can be exchanged with the solution, expressed per gram of dry or swollen ion exchange resin. The pH of the purified solution is also crucial, as it determines the degree of dissociation of the ion exchanger functional groups, which directly affects the effectiveness and dynamics of the process [10].

Fig. 1. Purolite S920 equivalent thiouronium chelating ion exchange resin [16]
Rys. 1. Żywica jonowymienna chelatująca timocznikowa Purolite S920 [16]

Tab. 1. Typical physical and chemical characteristics of Purolite S920 resin [17]
Tab. 1. Typowe właściwości fizyczne i chemiczne żywicy Purolite S920 [17]

Parameter	Value
Mercury capacity min.	200 g/L
Moisture retention (H)	48-54%
Mean size of grains	0.60-0.85 mm
Uniformity Coefficient (max.)	1.70
Swlling H/Hg (max)	5
Specific Gravity	1.11 g/L
Shipping weight (approx)	700-735 g/L
Temp. Limit (H^+)	80°C
pH Limits (stability)	0-10
pH Limits (operating)	1-10

The high selectivity is achieved through new types of ion exchanger with specific affinity for specific metal ions or groups of heavy metals, as well as alkali and alkaline earth metals. These are chelating ion exchange resins with a microporous structure, developed in the 1970s [11-13]. Their characteristic feature is the presence of chemically active functional groups in the polymer matrix capable of binding metal ions from solution in the form of cyclic chelate complexes. The sorption capacity of these resins depends primarily on the nature of the functional groups and, to a lesser extent, on grain size or other physical properties [14]. It should be emphasized that chelating resins are very effective in concentrating and removing metal ions with very low concentrations in solution [15].

This study assessed the effectiveness of removing Cu^{2+} ions from aqueous solutions under laboratory conditions for various initial ion concentrations and pH<7. Solutions containing copper (II) ions as Cu^{2+} were chosen because in this form they exhibit high chemical activity and are toxic in strongly acidic and low-hardness waters. The similar behaviour exhibits two ionized forms of copper hydroxides: $CuOH^+$ and $Cu_2OH_2^{2+}$.

As a sorbent, Purolite S920 resin, recommended by the producer for the selective removal of mercury ions, was used. An additional goal was to verify the suitability of this chelating resin for the elimination of copper (II) ions, as few studies on this topic were found in the literature.

MATERIAL AND METHODS

Sorbent preparation

The subject of the study was the S920 ion exchange resin produced by Purolite. It is a macroporous, polystyrene-based, chelating resin containing thiourea groups, primarily used for the selective removal of mercury and the recovery of precious metals from industrial wastewater. The characteristics of the ion exchanger are presented in Table 1. In this study, the Purolite S920 resin operated in a hydrogen cycle. Prior to the study, the resin was subjected to swelling in demineralized water for 24 hours. For the experiments, samples of the resin weighing 0.5 g were used. Figures 1 present Purolite S920 ion exchange resin in dry (wet) form.

Adsorption test

The study used copper solutions with initial concentrations ranging from 6.3 mg/L to 109.4 mg/L at pH values of 2.0 and 4.0 (±0.1), with a constant ionic strength of 0.02 mol/L The pH of the solutions was adjusted using 0.2 M HNO_3 and 0.02 M HNO_3. To adjust the ionic strength, a 0.04 M KNO_3 solution was used. All reagents of analytical purity were sourced from POCH S.A.

Ion exchange processes were carried out using a mechanical stirrer. For this purpose, 100 mL of the solutions, along with the ion exchange resin, were placed in a beaker, which was then immersed in a thermostatic bath at a constant temperature of 298±0.5 K. The contents of the beaker were thermostated for 15 minutes, and then continuously stirred for 60 minutes at a stirring speed of 120 rpm. Samples for analysis were taken after one hour, as equilibrium was achieved by this time. The experimental conditions were determined during previous studies [2]

The final concentration of Cu^{2+} ions in the solutions after the ion exchange process was determined using the cuprizon method with UV-VIS spectroscopy, employing the standard curve method. The cuprizon measurements were carried out in an ammonia-citrate medium at pH 8.0–9.5. The absorbance of the solutions was measured at a wavelength of 600 nm.

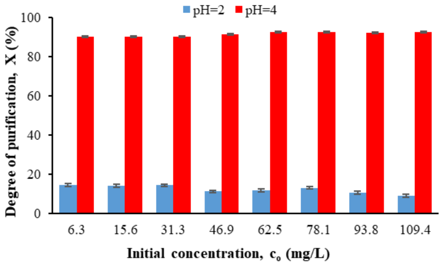
Theoretical analyse for copper ions adsorption

The degree of purification of the solutions from Cu^{2+} ions, X (%), was calculated using formula (1):

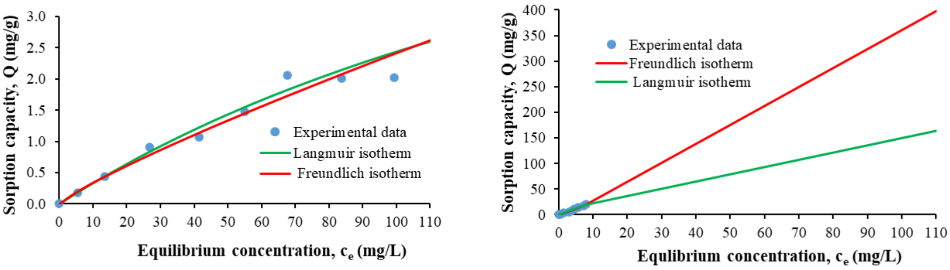
$$X = \frac{c_0 - c_e}{c_0} \cdot 100\% \tag{1}$$

where: c_o and c_e are the initial and equilibrium concentrations of copper(II) ions in the solution (mg/L).

The sorption capacity, qe (mg/g), was determined as the amount of Cu^{2+} ions contained in the dry mass of the ion ex-



Rys. 2. Porównanie wpływu stężenia wyjściowego roztworów na proces wymiany jonowej jonów Cu^{2+} na jonicie S920 przy pH równym 2 i 4
Fig. 2. Comparison of the influence of the initial concentration of solutions on the ion exchange process of Cu^{2+} ions on the S920 ion exchange resin at pH=2 and 4



Rys. 3. Porównanie izoterm Langmuira i Freundlicha dla usuwania jonów Cu^{2+} na jonicie S920 dla a) pH=2, b) pH=4 roztworów
Fig. 3. Comparison of Langmuir and Freundlich isotherms for removal Cu^{2+} ions on the S920 ion exchange resin for a) pH=2 and b) pH=4 of solutions

Tab. 2. Współczynniki izoterm Langmuira otrzymane dla jonów Cu^{2+} na jonicie S920 w roztworach o pH równym 2 i 4
Tab. 2. Langmuir isotherm coefficients obtained for Cu^{2+} ions on the S920 ion exchange resin in solutions with pH values of 2 and 4

pH of the solution	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	b (L/mg)	R	K (L/g)	1/n	R
2±0.1	8.137	0.0043	0.9988	0.0473	0.8536	0.9908
4±0.1	416.667	0.0062	0.9937	1.8463	1.1409	0.9974

change resin, depending on the concentration in the aqueous solution, according to formula (2):

$$q_e = \frac{V(c_0 - c_e)}{m} \tag{2}$$

where: V – volume of the solution (L), m – amount of dry resin mass (g).

The removal of Cu^{2+} ions on unmodified ground coffee was described by often used the Langmuir and Freundlich isotherm models. The equation of this isotherm and their linear form were described in detail in our previous study [18, 19].

Results and Discussion

Influence of Cu^{2+} ion concentration on their removal process using S920 ion exchange resin, depending on the pH of the aqueous solution.

Comparison of the determined degree of purification of the solutions from Cu^{2+} ions using the S920 ion exchange resin as a function of the initial concentration at pH 2 and 4 is presented graphically in Figure 3.

The obtained results clearly indicate that the pH of the treated solution has a significant impact on the effectiveness of Cu^{2+} ion removal on the tested S920 ion exchange resin (Fig. 3). For a pH of 4, the ion exchange process efficiency is greater than 90% for all tested concentrations (Fig. 2). The maximum degree of purification (92.7%) was achieved for the solution with the highest concentration tested, 109.4 mg/L (Fig. 2). On the other hand, for copper (II) solutions at pH 2, the obtained process efficiencies are very low. In this case, the degree of purification is less than 15% (Fig. 1). The lowest ion exchange process efficiency was achieved for the solution with the highest Cu^{2+} ions concentration of 109.4 mg/L (only 9.2%).

The pH value of the treated solution determines the degree of dissociation of the functional groups of the ion exchange resin, which directly affects the effectiveness and dynamics of the ion exchange process.

Figure 3 directly compares the degree of purification (X) of the solutions from copper (II) ions, using the S920 ion exchange resin for both tested pH values. The obtained results allow us to conclude that, in very acidic solutions, the efficiency of the ion exchange process decreases.

Interpretation of the sorption results of the tested ions based on the Langmuir adsorption model

The process of Cu^{2+} ion removal using the chelating resin S920 was interpreted based on two of the most popular isotherm models: Langmuir and Freundlich [18, 19].

The Langmuir adsorption isotherm model is described using formula (3):

$$Q = \frac{q_{max} \cdot b \cdot c_e}{(1 + b \cdot c_e)} \tag{3}$$

where: Q – the amount of metal ions adsorbed per unit mass of the ion exchange resin (mg/g), c_e – the equilibrium concentration of metal ions in the solution (mg/L), q_{max} (mg/g) and b (L/mg) – Langmuir constants.

The constants qmax and b were determined based on the linear form of the Langmuir isotherm described by equation (4):

$$\frac{1}{Q} = \frac{1}{q_{max} \cdot b} \cdot \left(\frac{1}{c_e} + b\right) \tag{4}$$

The Freundlich isotherm is an empirical equation expressed by the following formula (5):

$$Q = K \cdot {c_e}^{1/n} \tag{5}$$

where Q is the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g), ce is the equilibrium concentration of adsorbate in the solution (mg/dm3), K (L/g) and 1/n are the Freundlich constants.

The Freundlich constants K and 1/n were determined using the linear form of the Freundlich isotherm Equation (6):

$$logQ = log\,\mathrm{K} + \frac{1}{n} \cdot log\, c_e \tag{6}$$

The plotted Langmuir and Freundlich isotherms are shown in Figure 3.

The qmax and b coefficients of the Langmuir isotherm were determined based on its linear form (equation 4). All parameters and their uncertainties were calculated using the Microsoft Excel software. The obtained values of these coefficients are summarized in Table 2.

Analysing the course of the isotherms presented in Figure 7, it can be observed that both isotherms fit the experimental data well at both tested pH values.

The correlation coefficient R value above 0.99 in both cases (pH=2 and 4) indicates a good fit of these models to the experimental data points. According to the data presented in Figure 3 a i b, for both tested pH values, the sorption capacity increases until saturation and equilibrium are reached. A significantly higher value of the q_{max} coefficient, determining the maximum sorption capacity of the ion exchange resin, was obtained for Cu^{2+} ions in aqueous solutions at pH=4. This value was 416.667 (mg/g). For copper (II) solutions at pH=2, this parameter reached a value of only 8.137 (mg/g) (Table 1). The S920 resin shows a higher affinity for Cu^{2+} ions in solutions with pH=4. In this case, the value of the coefficient b was 0.0062 L/mg (Tab. 2).

The dependency graph log Q = f (log c_e) is a straight line (R values of 0.991 and 0.997), which allows calculation of the constants K and 1/n of the Freundlich equation and description of experimental systems using these parameters (Fig. 3 and Tab. 2). The constant K defines the sorptive capacity of the tested resin at the equilibrium concentration of Cu^{2+} ions in the solution. In solutions with pH=2, the value of this parameter is significantly lower (K=0.0473 L/g) than in solution with pH=4 (K=1.8463 L/g), indicating poorer sorptive abilities of the tested resin towards Cu^{2+} ions in a more acidic 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. The 1/n exponent also makes it possible to determine the intensity of the Cu^{2+} ions removal process from the aqueous phase using S920 resin.

In the solution with pH=2, the value of the parameter 1/n is less than 1, which suggests a moderate intensity of Cu^{2+} ion removal by the S920 ion exchange resin. In the solution with pH=4, the value of this parameter is even higher.

CONCLUSION

Based on the conducted studies, the following conclusions can be drawn:

- the Purolite S920 resin is an efficient ion exchanger resin for Cu^{2+} in aqueous solutions with a pH of 4.
- in the tested concentration range, the highest degree of purification of the solutions from Cu^{2+} ions, was approximately 92%.
- for copper(II) ion solutions at pH 2, the degree of purification is significantly lower, reaching a maximum of only about 15%.
- based on the interpretation of the Langmuir equation coefficients, it can be concluded that the studied resin exhibits significantly greater sorption capacities for Cu^{2+} ions in solutions with pH=4.
- at the same pH, the Purolite S920 resin also exhibits a higher affinity (value of the coefficient b) for copper(II) ions, which is 0.0062 L/mg.
- the values of the Freundlich constants K and 1/n indicate significantly better sorption properties of the Purolite S920 toward copper ions in solutions with pH=4.

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Badanie skuteczności usuwania jonów Cu^{2+} z roztworów wodnych przez jonit Purolite S920

Antropogeniczne zanieczyszczenie środowiska metalami ciężkimi pozostaje istotnym problemem, zwłaszcza kiedy występują one w postaci sprzyjającej bioakumulacji. W przypadku wód naturalnych i procesowych oraz ścieków przemysłowych nadal istnieje potrzeba udoskonalenia metod zapewniających redukcję zawartości metali ciężkich.

W niniejszym badaniu wykazano, że Purolite S920 jest przydatny do eliminacji jonów Cu^{2+} *z roztworów wodnych. W badanym zakresie stężeń uzyskano 92% oczyszczenie roztworów jednoskładnikowych z jonów* Cu^{2+} *przy pH=4 (w warunkach laboratoryjnych). Proces usuwania jonów miedzi(II) za pomocą chelatującej żywicy jonowymiennej zinterpretowano w oparciu o dwa najpopularniejsze modele izoterm: Langmuira i Freundlicha.*

Słowa kluczowe: *sorpcja, jony miedzi(II), Purolite S920, izoterma Lanmguira i Freundlicha*