Sorption recovery of copper(II) and zinc(II) from aqueous chloride solutions
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Abstract: The present investigation was devoted to the simultaneous sorption recovery of copper(II) and zinc(II) ions on some commercial anion exchangers with different physico-chemical properties. The initial concentrations of zinc and copper were 1–3 mmol L⁻¹ and the recovery was performed in 0.01 and 2 M hydrochloric acid solutions. It was shown that the investigated anion exchangers possess good sorption and kinetic properties. After the recovery of copper and zinc from the strongly acidic solutions, their selective elution was realized by means of 2 M hydrochloric acid solution (zinc recovery) and 2 M ammonia solution (copper recovery). In the weakly acidic solutions, copper and zinc were separated during sorption, as zinc sorption did not proceed in this case. The subsequent copper(II) elution was performed using 2 M ammonia solution. The anion exchangers Purolite S985, Purolite A500 and AM-2B could be recommended for zinc and copper recovery from acidic industrial solutions and wastewater.

Keywords: anion exchange; copper; zinc; anion exchangers; hydrochloric acidic solutions.

INTRODUCTION
The rapid growth in the demand for non-ferrous metals in metallurgy and the chemical industry was followed by an increase in their production volumes.¹ The most widespread non-ferrous metals are copper and zinc, which are extensively used in electrical engineering and the chemical industry. Zinc is used for galvanization of steel products, whereas copper is applied as a catalyst, and brasses, the alloys of copper and zinc with 5–45 % zinc content, are widely used for the

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production of automotive parts, chemical and heat technology equipment, bearings and jewelry.1–3

Simultaneously, the growth in output of non-ferrous metals (including copper and zinc) entailed the growth in the amounts of solid and liquid wastes arising from the processing of ores and secondary raw materials. These wastes include mine and dump water of mining plants, and waste water from the facilities in which non-ferrous metals are manufactured facilities.2,4,5 Waste emission leads to environmental damage through toxic solutions, and to the loss of valuable components, such as copper and zinc.1,4,5

This situation led to the urgent need for the utilization and decontamination of wastewaters containing heavy metal ions. A simple illustration of this could be as follows. It is known that acid washing sewages after etching usually contain about 60–120 mg L⁻¹ of copper(II) and 50–200 mg L⁻¹ of zinc. However, according to EU regulations, the maximum permissible concentrations (MPC) of these components are 0.5 mg L⁻¹ for copper and up to 5 mg L⁻¹ for zinc. The standards of the Russian Federation generally imply that the MPC values are 0.1 mg L⁻¹ for both copper and zinc, but in case of drinking water (or water for fishery purposes), the MPC values are more stringent, i.e., 0.001 mg L⁻¹ for copper and 0.01 mg L⁻¹ for zinc.7 Besides being an illustration of the high quality purification requirements, this also indicates the toxicity of these components, given the strict regulations imposed on water supply. It is known that copper and zinc induce respiratory tract infections, gastrointestinal issues and functional disorders of the nervous system.8 Although zinc is less hazardous than copper, the content of both components in water is strictly controlled.

The basic technologies for wastewater purification from heavy metals include chemical (reagent) methods (when soluble compounds are converted into sparingly soluble ones, and the precipitates are separated), microbiological methods, and physical (sorption) methods.8–15 The sorption technologies are being increasingly used for sewage treatment, mostly because they imply eco-friendly processes. For these purposes, various kinds of sorbents are used: inorganic (zeolites),5 activated carbon,15 sorption materials based on natural compounds,16–18 as well as organic ion exchangers.19–27 Many researchers modify the sorbents, to improve their sorption properties.5,15,17,20,21 The ion exchange recovery of heavy metals from wastewater is realized on cation exchangers or on chelate sorbents,4,8,9,11,19–21 because of the presence of the cation form of the recovered ions in solution. However, it is known28–31 that copper(II) and zinc(II) form anionic complexes in acidic media, so that they could be adsorbed on anion exchangers. Previously, the sorption recovery of zinc from chloride and chloride–sulfate (i.e., mixed) solutions was studied32 on some anion exchangers. The present work was focused on the simultaneous recovery of copper(II) and zinc(II) from chloride solutions on some anion exchangers.
EXPERIMENTAL

Solutions of copper(II) and zinc(II) with concentrations of 1–3 mmol L\(^{-1}\) were used. Accurately weighed salt samples CuCl\(_2\)·2H\(_2\)O and ZnCl\(_2\) were dissolved in hydrochloric acid solutions with concentrations 2 and 0.01 mol L\(^{-1}\). The acidity of the solutions and initial concentrations of Cu\(^{2+}\) and Zn\(^{2+}\) were chosen to make the experiment conditions similar to those of real industrial conditions, i.e., similar to wastewaters from the galvanic industry, or to technical solutions obtained after treatment of secondary copper–zinc raw materials. All the reagents were of analytical purification grade.

Macroporous anion exchangers with different functional groups were taken for the investigations. Their physico–chemical characteristics are presented in Table I. The selection of the anion exchangers was based on their good sorption properties towards zinc, which were revealed in a previous study.32

**TABLE I. Physico–chemical characteristics of the investigated anion exchangers**

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Exchanger type</th>
<th>Copolymer</th>
<th>Functional group</th>
<th>Exchange capacity in the Cl(^{-}) form, mmol g(^{-1})</th>
<th>Swelling grade g cm(^{-3})</th>
<th>Moisture %</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purolite S985</td>
<td>Weak base</td>
<td>PAc – DVB</td>
<td>PA</td>
<td>2.3</td>
<td>1.3</td>
<td>18.8</td>
<td>Purolite (UK)</td>
</tr>
<tr>
<td>Purolite A500</td>
<td>Strong base</td>
<td>St – DVB</td>
<td>QAB</td>
<td>2.8</td>
<td>1.6</td>
<td>20.3</td>
<td>Purolite (UK)</td>
</tr>
<tr>
<td>AM-2B Intermediate base</td>
<td>St – DVB</td>
<td>SAG, TAG, QAB</td>
<td>3.0</td>
<td>2.1</td>
<td>32.8</td>
<td>Cherkassy (Ukraine)</td>
<td></td>
</tr>
</tbody>
</table>

Before use, the anion exchangers were prepared according to standard methods and loaded by 1 M HCl, to convert the resins into the Cl\(^{-}\) form.

The concentrations of non-ferrous metal ions were determined by spectrophotometrical methods: copper(II) – with rubecanic acid (ethanedithioamide)\(^{28}\) and zinc(II) – with PAN (1-(2-pyridylazo)2-naphthol)\(^{29}\) using a Specol 1300 spectrophotometer (Carl Zeiss, Germany). Before the determination of the zinc ions, the copper ions were masked with sodium thiosulfate.

The sorption of copper(II) and zinc(II) was studied under batch experiment conditions: resin mass, 0.2 g; volume of contacting solution, 20.0 mL; stirring in a thermostat at 20±1 °C. The equilibrium time was 24 h.

The efficiency of ion exchange recovery of copper(II) and zinc(II) was estimated by means of the recovery degree \(R / \%\) and the distribution coefficient \(D\), which were calculated as follows:

\[
R = 100 \frac{c_0 - c_{eq}}{c_0}
\]

\[
D = \frac{WEC}{c_{eq}}
\]

where \(c_0\) and \(c_{eq}\) are the initial and equilibrium molar concentrations of zinc (copper), respectively, and \(WEC\) is working exchange capacity of resin for zinc (copper) in mmol g\(^{-1}\). The latter was calculated using the equation:
\[ WEC = \frac{(c_0 - c_{eq})V}{m} \]  

where \( V \) in L is the volume of the contacting solution and \( m \) in g is the resin mass.

Moreover, the separation coefficient \( S \) of copper(II) and zinc(II) was calculated as follows:

\[ S = \frac{D_{Cu}}{D_{Zn}} \]

where \( D_{Cu} \) and \( D_{Zn} \) are the distribution coefficients of copper and zinc, respectively.

The sorption isotherms were plotted by varying the molar ratio of resins to the amount of copper (zinc) in contacting solution. The apparent constants of ion exchange equilibrium were calculated based on the sorption isotherms obtained according to the law of mass action for the investigated equilibria.

The kinetic behavior of copper(II) and zinc(II) sorption by the investigated resins was studied by the “limited bath” method. The resin quantities (0.1 g) were stirred with 10.0 mL of zinc and copper solution at 20±1 °C over a period from 1 min to 24 h. The saturation times were 1, 2, 3, 5, 15, 20, 30 and 45 min and 1, 2, 3, 6 and 24 h. The suspensions were intensively stirred (more than 800 rev min\(^{-1}\)). After a certain time, the resins and solutions were quickly separated by filtration through a porous glass filter. Then the concentrations of copper and zinc were determined in the solutions by the spectrophotometrical methods. Using the obtained results, the saturation degree \( F \) was calculated using the equation:

\[ F = \frac{Q_t}{Q_{\infty}} \]

where \( Q_t \) and \( Q_{\infty} \) in mmol are the amounts of copper (zinc) sorbed at time \( t \) and at equilibrium, respectively.

Then the kinetic curves were plotted as dependences \( F = f(t) \), and the half-exchange times, \( t_{1/2} \) in s, were determined from these curves at \( F = 0.5 \). Subsequently, the diffusion coefficients of copper and zinc ions in a resin grain, \( D_{R} \) in cm\(^2\) s\(^{-1}\), were calculated from the following formula:

\[ D_{R} = \frac{r^2}{4\pi t_{1/2}} \]

where \( r \) in cm is the radius of the resin grain.

Moreover, the process rate, \( v \) in mmol g\(^{-1}\) s\(^{-1}\), was calculated from the equation:

\[ v = \frac{a_t}{t_i} \]

where \( a_t \) in mmol is the quantity of copper (zinc) sorbed per 1 g of the resin at time \( t_i \) in s.

The obtained results were statistically processed by standard methods. The average experimental error was less than 6 %.

RESULTS AND DISCUSSION

As mentioned above, the ion exchange recovery of copper(II) and zinc(II) is usually realized on cation exchangers or chelate sorbents. However, the ionic state of these elements depends on the acidity of the medium. Thus, cop-
per(II) is present in solution in the form of complexes $[\text{CuCl}_4]^{2-}$ when the HCl concentration is 1–4 mol L$^{-1}$, but in stronger acidic solutions (5–10 M HCl) its polymeric species $[\text{Cu}_2\text{Cl}_6]^{2-}$ are formed. With dilution and decrease in the acidity, the complexes $[\text{Cu(H}_2\text{O})_6]^{2+}$ appear in the system. In weaker acidic media in the presence of chloride ions (0.5–1 mol L$^{-1}$), the following transformation occurs:

$$2\text{CuCl}_2 \Leftrightarrow \text{CuCl}_3^+ + \text{CuCl}^+$$  \hspace{1cm} (8)

The ionic state of zinc also depends on the acidity of the medium. For instance, complexes $[\text{ZnCl}_4]^{2-}$ are present in strong acidic solutions (1–6 M HCl). On decreasing the acidity to 0.01–0.001 M HCl, the formation of the species $[\text{ZnCl}]^+$ and $[\text{ZnCl}_2]^0$ occurs. These species co-exist with the complex $[\text{ZnCl}_4(\text{H}_2\text{O})_2]^{2-}$.

Therefore, the presence of anionic complexes of copper(II) and zinc(II) in acidic solutions gives an opportunity to use anion exchangers for their recovery. In this work, the simultaneous sorption of Cu(II) and Zn(II) on anion exchangers with different basicity (Table I) was studied, which is a matter of scientific and practical importance.

The results of the sorption recovery of copper and zinc on the investigated anion exchangers from strong and weak acidic solutions for various initial concentrations are presented in Table II. It can be seen from these data that zinc was not adsorbed from weak acidic media when copper was present (regardless of initial concentrations of both ions). However, in a previous study, the recovery of 53–71 % zinc on the same anion exchangers from individual weak acidic solutions was studied.

**Table II.** Simultaneous recovery of copper(II) and zinc(II) from chloride solutions of different acidity on the investigated anion exchangers

<table>
<thead>
<tr>
<th>Trade name</th>
<th>$e_0$(HCl) mol L$^{-1}$</th>
<th>Initial concentrations of copper(II) and zinc(II)</th>
<th>$c_0$(Cu) = $c_0$(Zn) = 3 mmol L$^{-1}$</th>
<th>$c_0$(Cu) = $c_0$(Zn) = 1 mmol L$^{-1}$</th>
<th>$c_0$(Cu) = 3 mmol L$^{-1}$; $c_0$(Zn) = 1 mmol L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purolite</td>
<td>2</td>
<td>86 ±5</td>
<td>345 ±20</td>
<td>91 ±25</td>
<td>408 ±14</td>
</tr>
<tr>
<td>S985</td>
<td>±4 ±12</td>
<td>±4 ±5</td>
<td>±20 ±4</td>
<td>±25 ±5</td>
<td>±6 ±3</td>
</tr>
<tr>
<td>Purolite</td>
<td>74 ±4</td>
<td>74 ±5</td>
<td>232 ±5</td>
<td>81 ±10</td>
<td>327 ±7</td>
</tr>
<tr>
<td>A500</td>
<td>±3 ±12</td>
<td>±3 ±5</td>
<td>±20 ±3</td>
<td>±25 ±5</td>
<td>±6 ±3</td>
</tr>
<tr>
<td>AM-2B</td>
<td>63 ±3</td>
<td>63 ±4</td>
<td>198 ±5</td>
<td>90 ±10</td>
<td>405 ±4</td>
</tr>
<tr>
<td>Purolite</td>
<td>0.01</td>
<td>– –</td>
<td>97 ±24</td>
<td>485 ±24</td>
<td>– –</td>
</tr>
<tr>
<td>S985</td>
<td>±3 ±3</td>
<td>±3 ±5</td>
<td>±29 ±3</td>
<td>±29 ±5</td>
<td>±5 ±3</td>
</tr>
<tr>
<td>Purolite</td>
<td>– –</td>
<td>94 ±5</td>
<td>479 ±24</td>
<td>93 ±24</td>
<td>465 ±27</td>
</tr>
<tr>
<td>A500</td>
<td>±5 ±5</td>
<td>±5 ±5</td>
<td>±24 ±5</td>
<td>±24 ±5</td>
<td>±27 ±5</td>
</tr>
<tr>
<td>AM-2B</td>
<td>– –</td>
<td>95 ±5</td>
<td>481 ±24</td>
<td>95 ±24</td>
<td>484 ±27</td>
</tr>
</tbody>
</table>

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tions was observed. This indicates to the joint action of simultaneously sorbed ions, leading to the increase in the selectivity of the resins to copper(II). The probable reason is an acid effect, affecting the anion exchanger phase and facilitating the sorption of the component with more stable anionic complexes. Given that zinc in weak acidic media is present not only in the form of anionic complexes, but also in the form of cationic and neutral species, the affinity of anionic complexes of copper(II) to the anion exchanger is greater, so that the sorption centers are occupied by copper and copper is recovered almost completely. From the practical point of view, this facilitates the complete separation of copper and zinc in dependence on the stage of their sorption on investigated anion exchangers.

In strong acidic solutions, a similar result was obtained for the strong basic anion exchanger Purolite A500 during zinc and copper sorption at 1 mmol L\(^{-1}\) initial concentration of zinc, whereas when its concentration was 3 mmol L\(^{-1}\), its sorption recovery was observed (Table II). Probably the decrease in the initial zinc concentration in the presence of copper(II) reduces the affinity of the anion exchanger for zinc and improves its affinity for copper. Overall, the sorption recovery of copper(II) and zinc(II) in strong acidic media was affected by the functional groups of the investigated anion exchangers. The greatest affinity for copper(II) ions was revealed for the complex-forming polyamine anion exchanger Purolite S985 (Table II). In addition, the degree recovery of copper(II) also depended on the initial concentrations of the components, and with decreasing zinc concentration, it grew to almost complete recovery. In turn, the recovery of zinc depended positively on its initial concentration.

Therefore, the obtained data for simultaneous recovery of copper(II) and zinc(II) demonstrated the good sorption properties of investigated anion exchangers, and also indicated the possibilities for separation of copper and zinc during their sorption from weak acidic solutions (or from strong acidic solutions onto the strong basic anion exchanger Purolite A500).

The separation coefficients presented in Table III also indicate that copper(II) and zinc(II) ions could be separated during their sorption from 2 M HCl solutions. It can be seen from the data that all the values exceeded 1 and that the anion exchanger Purolite S985 provides the most favorable conditions for separation at initial zinc concentration 1 mmol L\(^{-1}\) (Table III).

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Initial concentrations of copper(II) and zinc(II)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(c_0^\text{Cu} = c_0^\text{Zn} = 3 \text{ mmol L}^{-1})</td>
<td>(c_0^\text{Cu} = c_0^\text{Zn} = 1 \text{ mmol L}^{-1})</td>
</tr>
<tr>
<td>Purolite S985</td>
<td>1.17±0.07</td>
<td>3.47±0.21</td>
</tr>
<tr>
<td>Purolite A500</td>
<td>1.41±0.08</td>
<td>–</td>
</tr>
<tr>
<td>AM-2B</td>
<td>2.06±0.12</td>
<td>1.59±0.11</td>
</tr>
</tbody>
</table>
Therefore, taking into account the ionic state of zinc and copper and the results on their sorption recovery, it could be concluded that the sorption of copper and zinc from strong acidic solutions on the investigated anion exchangers proceeded as follows:

\[
2\text{RCI} + [\text{CuCl}_4^{2-}] \rightleftharpoons \text{R}_2[\text{CuCl}_4] + 2\text{Cl}^- \quad (9)
\]

\[
2\text{RCI} + [\text{ZnCl}_4^{2-}] \rightleftharpoons \text{R}_2[\text{ZnCl}_4] + 2\text{Cl}^- \quad (10)
\]

where R indicates the resin phase and the bar indicates the sorbate. In weak acidic medium, the sorption recovery of copper(II) proceeded according to Eq. (9).

The sorption isotherms for the simultaneous recovery of copper(II) and zinc(II) from strong acidic solutions are presented in Fig. 1 for an initial concentration of 3 mmol L\(^{-1}\) for both ions in the contacting solution. It should be noted that the curves obtained for the other concentrations of copper and zinc were similar to those presented in Fig. 1.

Fig. 1. Isotherms of copper sorption in the presence of zinc (a) and of zinc sorption in the presence of copper (b) from strong acidic chloride solutions on the investigated anion exchangers. \(c_0(\text{Cu}) = c_0(\text{Zn}) = 3 \text{ mmol}\ L^{-1}; c_0(\text{HCl}) = 2 \text{ mol}\ L^{-1}; 1 – \text{Purolite S985}; 2 – \text{Purolite A500}; 3 – \text{AM-2B}; \) [Me] is the equilibrium concentration of copper (zinc) in the contacting solutions; \(WEC\) is working exchange capacity for copper (zinc) at equilibrium.
It is known\textsuperscript{33,34} that the shape of the sorption isotherms is evidence of the sorption selectivity. As could be seen in Fig. 1, the sorption isotherms were S-shaped curves, which were steep upward sloping and almost parallel to the ordinate axis. This is evidence of the high selectivity of the copper and zinc recovery.

Using the isotherms, the apparent constants of the ion exchange equilibria (9) and (10) were calculated and the obtained data are presented in Table IV. These constants correlate with the selectivity of the investigated anion exchangers, since they define free energy and, consequently, determine the ion exchange affinity.\textsuperscript{33,34} It can be seen from Table IV that the apparent constants show the high affinity of the anion exchangers for zinc ions, and higher affinity for copper(II) ions.

Table IV. Apparent constants of the ion exchange equilibrium during copper(II) and zinc(II) recovery from strong acidic chloride solutions on the investigated anion exchangers ($c_{0}(HCl) = \text{2 mol L}^{-1}$)

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Initial concentrations of copper(II) and zinc(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$c_{0}(\text{Cu}) = c_{0}(\text{Zn}) = 3 \text{ mmol L}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Cu(II)</td>
</tr>
<tr>
<td>Purolite S985</td>
<td>55.1±3.3</td>
</tr>
<tr>
<td>Purolite A500</td>
<td>43.1±2.2</td>
</tr>
<tr>
<td>AM-2B</td>
<td>58.4±3.5</td>
</tr>
</tbody>
</table>

Furthermore, the kinetics of the recovery of copper(II) and zinc(II) from weak and strong acidic chloride solutions on anion exchangers were studied. It should be noted that the rate of experiment is very important for a number of practical tasks, such as sorption optimization and selection of the best available sorbent for a particular case.\textsuperscript{33–35}

The dependence of ion exchange rate on time during the simultaneous recovery of copper(II) and zinc(II) on the anion exchanger Purolite S985 is shown in Fig. 2. It could be seen that the process rate increased sharply in first seconds of contact between the resin and solution and then decreased gradually with the saturation of the sorbent, reaching equilibrium over 24 h. Moreover, the sorption rate of copper(II) was higher than that of zinc(II) (Fig. 2). It should be noted that in approximately 1.5 h, the saturation of anion exchanger Purolite S985 from strong acidic chloride solution reaches \approx 75 % for copper and \approx 60 % for zinc of the equilibrium exchange capacity of the resin for these ions. For the anion exchangers Purolite A500 and AM-2B, these values were slightly lower and amounted to \text{68–70} % for copper and \text{48–52} % for zinc. Therefore, it could be concluded that the saturation rates of the resins were high and the investigated sorbents possessed good kinetic properties.
Fig. 2. Kinetic curves of anion exchanger Purolite S985 saturation during simultaneous recovery of copper (1) and zinc (2) from strong acidic solutions. \( c_0(Cu) = c_0(Zn) = 3 \text{ mmol L}^{-1}; c_0(\text{HCl}) = 2 \text{ mol L}^{-1}. \)

The calculated main kinetic parameters – half-exchange time and diffusion coefficients – are presented in Table V. The order of diffusion coefficients complies with the data obtained previously\(^{40-42}\) for the kinetics on the selected ion exchangers. The values of half-exchange times indicate the good kinetic properties of the investigated anion exchangers.\(^{43}\)

**TABLE V. Kinetic parameters during simultaneous recovery of copper(II) and zinc(II) from strong acidic chloride solutions on anion exchangers investigated \( c_0(Cu) = c_0(Zn) = 3 \text{ mmol L}^{-1}; c_0(\text{HCl}) = 2 \text{ mol L}^{-1} \)**

<table>
<thead>
<tr>
<th>Trade name</th>
<th>( t_{1/2}/s )</th>
<th>( D_{b}\times10^8/\text{cm}^2\text{s}^{-1} )</th>
<th>( t_{1/2}/s )</th>
<th>( D_{b}\times10^8/\text{cm}^2\text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purolite S985</td>
<td>820±49</td>
<td>6.91±0.35</td>
<td>1207±72</td>
<td>1.79±0.11</td>
</tr>
<tr>
<td>AM-2B</td>
<td>945±57</td>
<td>4.82±0.24</td>
<td>1568±94</td>
<td>1.68±0.11</td>
</tr>
</tbody>
</table>

Furthermore, the desorption of copper and zinc after their simultaneous recovery from chloride solutions on anion exchangers were studied. The system with 3 mmol L\(^{-1}\) initial concentrations of copper and zinc in strong acidic solution was chosen for the investigation. A solution of hydrochloric acid solution (2 mol L\(^{-1}\)) was selected as the eluent, as solutions of mineral acids are, as a rule, applied for desorption of non-ferrous metals.\(^{21-27,38}\) The results are summarized in Table VI.

It can be seen from these data that zinc was eluted practically completely, whereas copper desorption proceeds to the level of experimental error. Obviously, the high desorption of zinc could be explained by the lower selectivity of the investigated anion exchangers for zinc, as discussed above when considering the sorption of copper and zinc.
TABLE VI. Desorption degree, %, using 2 M HCl. of copper and zinc after their simultaneous recovery on the investigated anion exchangers. The sorption was realized at $c_0(\text{Cu}) = c_0(\text{Zn}) = 3 \text{ mmol L}^{-1}$ from a strong acidic solution

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Ion</th>
<th>Cu(II)</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purolite S985</td>
<td>6</td>
<td>96±4</td>
<td></td>
</tr>
<tr>
<td>Purolite A500</td>
<td>6</td>
<td>96±4</td>
<td></td>
</tr>
<tr>
<td>AM-2B</td>
<td>6</td>
<td>95±5</td>
<td></td>
</tr>
</tbody>
</table>

The subsequent recovery of copper(II) was performed in the systems where copper remained in the resin after zinc removal, as well as in weak acidic solutions where zinc was not sorbed. A solution of ammonia (2 mol L$^{-1}$) was chosen as the eluent, because copper and ammonia form stable complexes.$^{28,44}$ The results are presented in Table VII.

TABLE VII. Desorption degree, %, of copper(II) from the investigated anion exchangers using 2 mol L$^{-1}$ ammonia solution. The sorption was performed at $c_0(\text{Cu}) = c_0(\text{Zn}) = 3 \text{ mmol L}^{-1}$ from weak and strong acidic solutions; system A – desorption after elution of Zn(II) (strong acidic solutions); system B – desorption after Cu(II) sorption from weak acidic solutions (sorption of zinc was not observed)

<table>
<thead>
<tr>
<th>Trade name</th>
<th>System</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purolite S985</td>
<td>A</td>
<td>95±5</td>
<td>95±5</td>
</tr>
<tr>
<td>Purolite A500</td>
<td>A</td>
<td>≈100</td>
<td>≈100</td>
</tr>
<tr>
<td>AM-2B</td>
<td>A</td>
<td>94±5</td>
<td>95±5</td>
</tr>
</tbody>
</table>

It can be seen from these data that complete elution of copper(II) in the form of complexes with ammonia occurred. After that, the anion exchanger was converted to the hydroxyl form. The resin in hydroxyl form could be either repeatedly used, or converted into the chloride form.

Therefore, the simultaneous sorption of copper and zinc from strong acidic chloride solutions requires the selective elution for their complete separation. In the cases of copper and zinc recovery from weak acidic chloride solutions, their separation occurs in the sorption stage, and subsequently, it is necessary to elute copper only.

Thus, the investigated anion exchangers could be recommended for the purification of acidic sewages from copper and zinc ions.

CONCLUSIONS

Sorption recovery of copper(II) and zinc(II) from weak and strong acidic chloride solutions was investigated at different ratios of initial concentrations of components on anion exchangers with various physico–chemical properties. It was revealed that the investigated resins possess high sorption ability for copper(II) ions, regardless of the basicity of the resins. It was determined that...
zinc ions were not adsorbed on the investigated anion exchangers during the simultaneous recovery of copper(II) and zinc(II) from weak acidic solutions. This indicated an opportunity for the separation of copper and zinc.

The apparent constants of the ion exchange equilibrium with the participation of copper(II) and zinc(II) ions were calculated for the investigated anion exchangers. The values of these constants showed the high selectivity of the sorption process, especially towards copper(II). It was shown that investigated anion exchangers possessed good kinetic properties, since the process rate was high for both Cu(II) and Zn(II), but was higher during copper(II) recovery.

Desorption of copper(II) and zinc(II) was performed after their simultaneous recovery on the investigated anion exchangers. It was shown that zinc ions were completely eluted using 2 M hydrochloric acid, whereas copper remained in the sorbent phase. Then copper(II) could be removed by using a 2 mol L\(^{-1}\) ammonia solution.

Based on the obtained experimental data, the investigated anion exchangers (Purolite S985, Purolite A500 and AM-2B) could be recommended for purification of acidic sewages from copper and zinc ions. The novelty of the suggested method is the complete recovery of copper and zinc ions, in their simultaneous presence, from strong and weak acidic chloride solutions, as well as the complete separation of these ions by subsequent elution.

ИЗВОД

СОРПЦИОНО ИЗДВАЈАЊЕ БАКРА(II) И ЦИНКА(II) ИЗ ХЛОРИДНИХ ВОДЕНИХ РАСТВОРА

Ово испитивање је обухватило истовремено сорпционо јона бакра(II) и цинка(II) на неким анјонским измењивачима са различитим физичкохемијским својствима. Почетне концентрације цинка и бакра су биле 1–3 mmol L\(^{-1}\), а издвајање је изведено у 0,01 M и 2 M растворима хлороводоничне киселине. Показано је да испитивани анјонски измењивачи имају добра сорпциона и кинетичка својства. Након издвајања из јако киселих раствора, бакар и цинк су селективно елуирани помоћу 2 M раствором хлороводоничне киселине (издвајање цинка) и 2 M раствором амонијака (издвајање бакра). У слабо киселим растворима, бакар и цинк су раздвојени током сорпције, пошто није долазило до сорпције цинка у овом случају. Елуирање бакра(II) је затим извођено 2 M раствором амонијака. Анјонски измењивачи Purolite S985, Purolite A500 и AM-2B се могу препоручити за издвајање цинка и бакра из киселих индустријских раствора и отпадних вода.

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