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*Dedicated to prof. dr. I. C. Popescu*
*on the occasion of his 70th anniversary*

# REMOVAL OF COPPER FROM DILUTED AQUEOUS SOLUTIONS USING AN IMINODIACETIC ACID CHELATING ION-EXCHANGE RESIN IN A FIXED-BED COLUMN

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**ABSTRACT.** In this study, the copper removal was investigated in a fixed-bed column using a iminodiacetic acid chelating ion exchange resin (Purolite S930Plus).The influence of the resin bed height (3-6 cm) over the removal process was evaluated at a flow rate of 5 mL/min and initial Cu(II) concentration of 0.8 mM. The obtained results were analysed by linear regression using the most common sorption kinetic models such as Yoon-Nelson, Adam-Bohart, and Clark. The experimental data were in good agreement with Yoon and Nelson model. Also, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were employed to study the morphologies and the composition of the resin surface before and after sorption. The column regeneration studies were performed using 3 N $H_2SO_4$ solution. The tested resin presented a good regeneration capacity and can be successfully used to remove copper ions from diluted wastewaters.

***Keywords:*** *Copper removal, Fixed-bed column, Kinetics, Regeneration*

## INTRODUCTION

The presence of heavy metals in effluents discharged from different activities can cause serious environmental problems, because of theirs non-biodegradability and long persistence [1].

Copper is one of the metals used extensively in the technological sphere, along with other heavy metals such as lead and chromium [1]. The

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most common methods to treat these wastewaters in order to remove the copper ions are: flotation, solvent extraction, adsorption, cementation, ion exchange, ultrafiltration and electrochemical methods [2-5].

Among these methods, the ion exchange process has been successfully used for heavy metals removal. Moreover, the resins present the ability to adsorb and desorb metals for several cycles.

According to the literature, numerous studies regarding the ion exchange process can be found but many of them are still in the optimization phase in order to improve the affinity and selectivity of the resins [6, 7]. The sorption experiments performed in batch conditions can be easily used in the laboratory study, but are not appropriate for industrial applications because of the large volume of wastewaters that have to be processed [8]. Therefore, the fixed-bed column studies can be used due to their simplicity, ease of handling and operation [8-10].

In this case, the concept of breakthrough curve [8, 11-13] can be applied, analyzing the shape of the breakthrough curve and the breakthrough time [8, 14]. Various sorption kinetic models, such as Thomas, Yoon-Nelson, Clark and Adam-Bohart, can be used to evaluate the performances for heavy metals removal [8, 15-17].

The aim of this study was to investigate the capacity of the Purolite S930Plus ion-exchange resin to remove copper from diluted aqueous solutions in a fixed-bed column. The influence of resin quantity (bed height) and resin regeneration on the removal process were considered. The obtained results were analyzed by linear regression using the most common sorption kinetic models: Yoon-Nelson, Adam-Bohart and Clark. The resin surface before and after sorption was examined by SEM and EDS.

## RESULTS AND DISCUSSION

For industrial applications, the sorption experiments realized in a fixed-bed column are more suitable to be used than in batch mode. In order to evaluate the sorption abilities of the tested resin towards the Cu(II) ions removal from diluted solutions, several experiments were made using different amounts of adsorbent, at a fixed flow rate.

### Effect of resin quantity

The breakthrough curves for copper sorption on Purolite S930Plus resin were recorded for various resin quantities ranged between 100 and 200 mg (various bed heights, from 3 to 6 cm), at a flow rate of 5 mL/min and an initial Cu(II) concentration ($C_0$) of 0.8 mM (pH = 4). The obtained results, based on the effluent concentration ($C_t$) at the sampling time (t), are presented in Figure 1. It was observed that, in these conditions, copper sorption was very fast in the first minutes, afterwards, the sorption rate slowly decreased due to the resin saturation [18].

In the explored range of resin quantities, the breakthrough curves obtained did not follow the typical ‘S-shape’ curves. An incomplete ‘S’ breakthrough shape can be explained by the slow sorption kinetics of copper on the considered resin [18, 19].

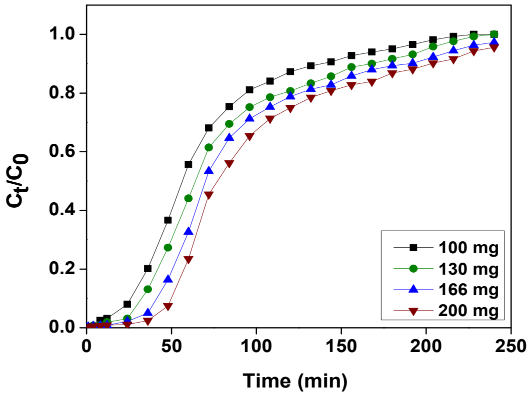

**Figure 1.** Breakthrough curves for Cu(II) sorption onto Purolite S930Plus ion exchange resin using different sorbent quantities ($C_0$ = 0.8 mM, T = 298 K, pH = 4).

The breakthrough time ($t_b$) increased by increasing the resin quantity (from 100 to 200 mg), which can be attributed to the increase of binding sites numbers, broadening the mass transfer zone [20]. The breakthrough time values were between 0.24 and 1 h when different resin quantities were used at an exhaustion time ($t_s$) of 5 hours. Also, it was noted that, increasing the resin quantity in the studied range, the values of sorption capacity ($q_t$) at $t_s$ increased from 95 mg/g to 97 mg/g. The sorption capacity was calculated using the following equation:

$$q_t = \frac{C_0 - C_t}{M} \cdot \frac{V}{1000} + q_{t-1} \tag{1}$$

where $q_{t-1}$ is the sorption capacity at time (t-1) (mg/g), V is the volume of copper solution (L) and, M is the mass of the resin (g) [18].

### Regeneration studies

When the output effluent concentration passes the breakpoint values, the feed of the column is discontinued and the column should be regenerated [21]. The regeneration of Purolite S930Plus resin (100 mg) was made using a

3 N $H_2SO_4$ solution at a flow rate of 0.125 mL/min. The obtained results, presented in Figure 2, showed that the copper concentration in the effluent becomes very high in the first minutes, after that it decreased slowly until the resin was completely regenerated. A volume of 60 mL 3 N $H_2SO_4$ ensured the complete regeneration of the Purolite S930Plus resin, further desorption is negligible [22].

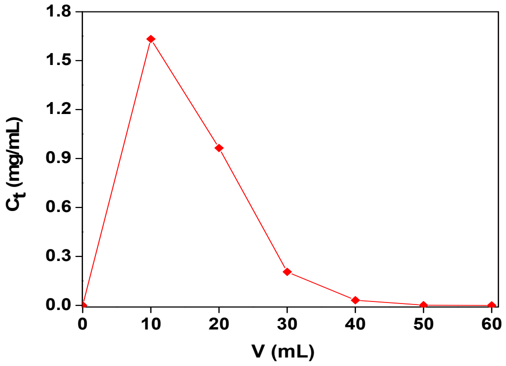

**Figure 2.** Copper concentration in effluent during the regeneration cycle.

### SEM and EDS analysis

The morphology of Purolite S930Plus resin surface before and after Cu(II) adsorption were examined by SEM and the obtained images are presented in Figure 3. The smooth surface of resin turned thicker and coarser with granular flake material after adsorption of Cu(II), suggesting that the cooper was loaded on the surface of the resin [22]. Further, the presence of the adsorbed cooper on the resin surface was confirmed by the metal peaks that appear on the EDS spectra presented in Figure 4.

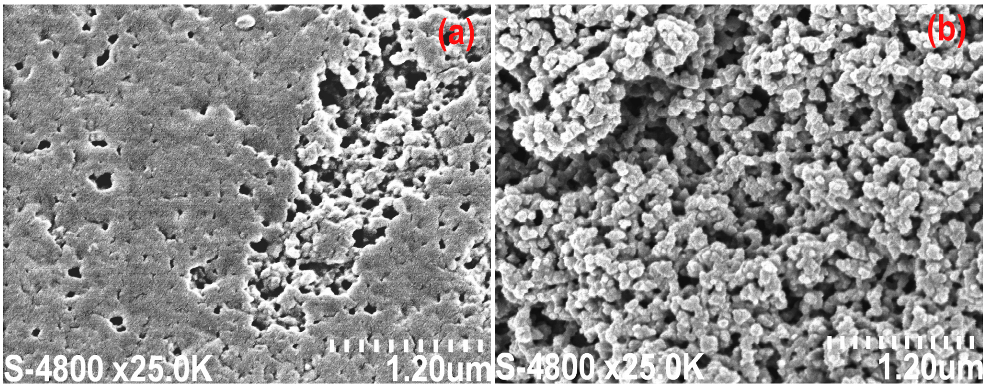

**Figure 3.** SEM images for Purolite S930Plus resin before (a) and after sorption (b)

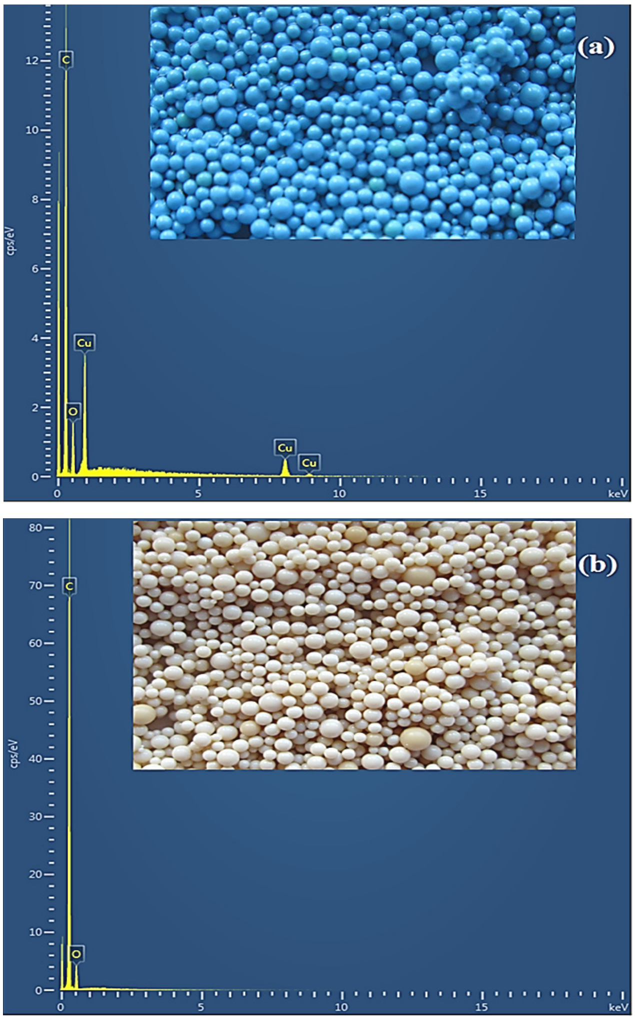

**Figure 4.** EDS spectra of Purolite S930Plus resin after Cu(II) sorption (a) and after regeneration (b).

## Reaction kinetic models

In order to study the kinetics of copper sorption, three kinetic models (Yoon-Nelson, Adams-Bohart and Clark) were considered [8, 17, 23].

Yoon-Nelson model is based on the assumption that the rate of decrease in the probability of adsorption of the adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough [23]. The Yoon-Nelson model for a single component system is expressed as:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = tk_{YN} - \tau k_{YN} \tag{2}$$

where, $k_{YN}$ (1/min) is the Yoon-Nelson constant and $\tau$ (min) is the time required for 50% adsorbate breakthrough [23, 24].

The Yoon-Nelson kinetic parameters, $k_{YN}$ and $\tau$, were obtained from the slope and the intercept of the linear plot $\ln[C_t/(C_o-C_t)]$ against time (t), and presented in Table 1.

**Table 1.** Yoon-Nelson, Adams-Bohart and Clark parameters for the sorption of copper on Purolite S930Plus for different resin quantities

| **Sorbent quantity (mg)** | **Yoon-Nelson** | | | **Adams-Bohart** | | | **Clark** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **$\tau$ (min)** | **$k_{YN}\cdot10^{-2}$ (1/min)** | **$R^2$** | **$k_{AB}$ $10^{-4}$ (L/mg·min)** | **$N_0$ (mg/L)** | **$R^2$** | **A** | **$r\cdot10^{-2}$ (min)** | **$R^2$** |
| 100 | 91.6 | 3.44 | 0.82 | 3.46 | 14.61 | 0.58 | 1.84 | 5.01 | 0.72 |
| 130 | 99.2 | 3.52 | 0.80 | 3.78 | 11.10 | 0.64 | 1.97 | 5.47 | 0.82 |
| 166 | 111.5 | 3.69 | 0.91 | 4.22 | 8.98 | 0.68 | 2.07 | 5.57 | 0.80 |
| 200 | 120.1 | 3.71 | 0.97 | 4.54 | 7.57 | 0.72 | 2.15 | 5.74 | 0.81 |

From Table 1, it can be seen that the values of $k_{YN}$ increased as the resin quantity increased. Based on correlation coefficients values, the model presents a good applicability for copper removal using Purolite S930Plus resin at a sorbent quantity higher than 166 mg.

Adams-Bohart model is based on the assumption that the rate of adsorption is proportional with the concentration of the adsorbing species and the residual capacity of the adsorbent and is used for the description of the initial part of the breakthrough curve [17,18, 25].

The Adam-Bohart expression is given as:

$$\ln\frac{C_t}{C_0} = k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{U} \tag{3}$$

where $k_{AB}$ is the kinetic constant (L/mg·min), $N_0$ is the saturation concentration (mg/L), Z is the bed height of the column (cm) and U is the linear velocity of solution (cm/min).

The parameters describing the characteristic operations of the column ($k_{AB}$ and $N_0$) were determined from the linear plot of ln $(C_t/C_0)$ vs. time (t), using the slope and intercept values, respectively [17, 18, 25].

The calculated values of $N_0$, presented in Table 1, decreased with the increase of the bed height. Based on the obtained correlation coefficients, the Adams-Bohart model does not fit adequately the experimental data for the Purolite S930Plus resin, so its assumptions were not validated.

The Clark kinetic model is based on the use of a mass-transfer concept in combination with the Freundlich isotherm and has a precise analytical solution enabling determination of dynamic adsorption rate constants [17, 18]. In previous equilibrium studies, it was found that the Freundlich model was valid for the Cu(II) adsorption on Purolite S930Plus resin, which allows the use of the Freundlich constant (n = 1.97) [26] to calculate the parameters in the Clark model.

$$\ln\left[\left(\frac{C_0}{C_t}\right)^{n-1}-1\right]=\ln A-rt \tag{4}$$

where n is the Freundlich constant, A and r are the Clark constants [17].

The values of r and A, presented also in Table 1, were determined from the slope and the intercept of the linear plot of $\ln[(C_0/C_t)^{n-1}-1]$ vs. time (t). Based on the calculated correlation coefficients (Table 1), it was concluded that the Clark model does not fit adequately the experimental data.

## CONCLUSIONS

In this study, the performance of an iminodiacetic acid chelating ion exchange resin (Purolite S930Plus) resin for copper removal was evaluated in a fixed-bed column. The obtained results revealed a classic behavior, showing that the increase of the used resin quantity and, implicitly, of the bead height induces the increase of the breakthrough time. The Purolite S930Plus resin was successfully regenerated using 3 N $H_2SO_4$. A volume of 60 mL ensured the complete regeneration (100 %) for 100 mg of resin. Based on the correlation coefficients values, the following series of kinetic models was depicted: Yoon-Nelson > Clark > Adam-Bohart. Also, the correlation coefficients values for Yoon-Nelson model indicate a better linearity at increased resin quantities, while, for the other models, lower correlation coefficients were obtained for copper removal using the Purolite S930Plus resin. According to the obtained results, it can be concluded that Purolite S930Plus resin is a good ionic exchanger for copper removal from diluted aqueous solutions, presenting also a good regeneration capability.

## EXPERIMENTAL SECTION

The Purolite S930Plus resin, especially designed for heavy metals removal, was activated according to the supplier specifications [27]. Before usage, the dry resin was placed in double-distilled water for 24 h at a mass-volume ratio ($M_{resin}:V_{water}$) of 1:10.

Stock solution of 1000 ppm Cu(II) was prepared in double-distilled water using solid $CuSO_4 \cdot 5H_2O$ (from Merck, analytical grade). The initial pH of aqueous solutions was adjusted in the range 1.0 – 6.0 by adding small amounts of 0.1 M $H_2SO_4$ or 0.1M NaOH. In order to preserve the solution pH at the desired value, the resin was supplementary conditioned in a blank solution having similar acidity.

A plastic column, having an inner diameter of 0.45 cm and a total height of 7.0 cm, was used for the experiments. The column was equipped with two layers of nitrocellulose membranes (45 μm) to prevent the escape of the resin beads. The scheme of the experimental setup is presented in Figure 5.

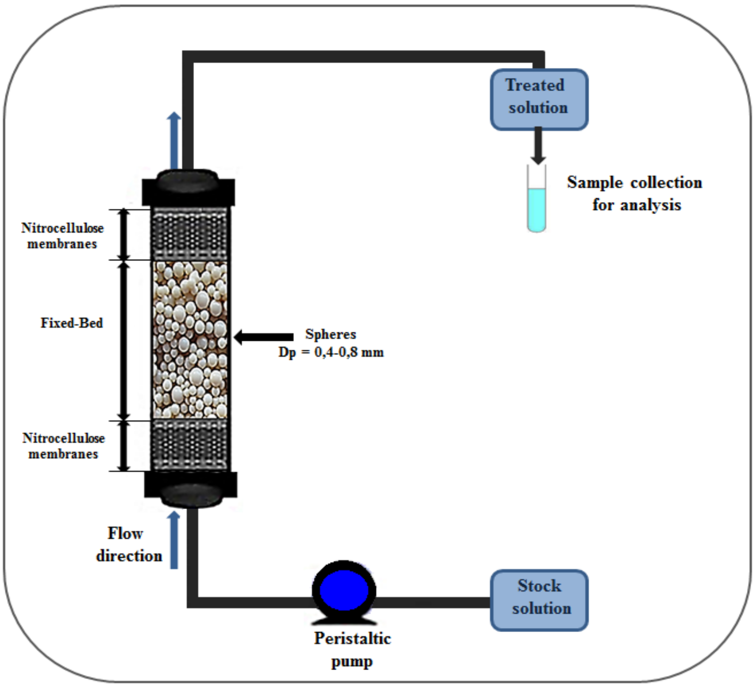

**Figure 5.** The experimental setup.

The synthetic solution, having an initial copper concentration of 0.8 mM, was allowed to pass through the column in continuous up-flow mode, at a 5 mL/min flow rate, using a peristaltic pump Reglo Digital (Ismatec, Switzerland). The treated solution was collected from the outlet of the column at different time intervals and analyzed by flame atomic absorption spectrometry using an Avanta PM spectrometer (GBC, Australia) exploited in the air-acetylene flame mode.

The surface morphology and the composition of the resin before and after copper sorption were analysed using a scanning electron microscope (SEM) combined with an energy-dispersive X-ray spectrometer (EDS) model Hitachi S-4500.

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