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Removal of copper ions from dilute synthetic solution using staple ion exchange fibres: Dynamic studies



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ABSTRACT

Heavy metals such as copper (Cu^{2+}) ions can have detrimental effects on the environment and human health if present at high concentrations in industrial effluent streams. Unfortunately, conventional techniques are ineffective in removing these metals from effluent streams. Therefore, it is imperative that new methods with exceptional qualities are found. This paper presents the removal of Cu^{2+} ions using ion exchange fibres (IEFs). The study focused on the effect of bed packing density and flow rate on loading and elution of Cu^{2+} ions. The optimal bed packing density, superficial velocity and residence time which corresponded to the highest removal of Cu^{2+} ions were $0.16\,\mathrm{g/cm^3}$, $5.2\,\mathrm{cm/min}$ and $2\,\mathrm{min}$, respectively. Overall, metal removal increased with a decrease in packing density and flow rate. All the loaded Cu^{2+} ions were completely eluted in all the bed packing densities and flow rate studied. Nevertheless, the elution rate of Cu^{2+} ions was not affected by bed packing density, but it increased with an increase in acid flow rate. Amongst the fitted empirical models, the Yoon-Nelson model best described the adsorption of Cu^{2+} ions from synthetic wastewater onto the selected IEFs .

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1. Introduction

Heavy metals such as copper (Cu²⁺ ions) contained in waste streams from electroplating, mining, extracting and printing units are harmful to the environment and human health when the concentration of the metal ions are above certain threshold levels [1–5]. Therefore, waste streams containing heavy metals need to be treated to prevent accumulation in the biosphere and avoid negative health effects [1,6]. Consequently, numerous wastewater treatment methods have been developed in the past. For example, various wastewater treatment adsorbents such as granular ion exchangers, impregnated materials and silica gels have been used for selective removal of metals; though, their reaction rates are generally slow [7].

Other techniques (chemical precipitation, reverse osmosis, electrolysis, coagulation, etc) normally used for metal removal are also inefficient as they result in incomplete metal removal, high reagent and energy requirements, and generate toxic sludge [8,9] which may require special treatment and/or disposal facilities.

Furthermore, extraction techniques such as chemical precipitation are more effective for streams composed of medium to high concentrations of metal ions [10]. Extraction techniques may also generate secondary pollutants particularly when removing metal ions present in low concentrations [10].

In view of many disadvantages of conventional processes, it is imperative that new methods with exceptional qualities are found. Amongst emerging technologies and materials, ion exchange fibres (IEFs) have been the focus of considerable studies. IEFs are a novel kind of adsorption materials. Compared to the conventional ion-exchange beads, IEFs are preferred due to their high reaction rates as well as high selectivity rates and loading capacities when compared with conventional ion exchangers [11,12]. Generally, IEFs have a higher ion exchange rate due to their shorter diffusion distances [2,12,13]. Moreover, IEFs can be used repeatedly without a change in sorption activity [14]. For example, some studies [12] report that IEFs were effective in 29 cycles as compared to 5 cycles when using conventional ion-exchange beads. The fact that IEFs can be used in many cycles shows that they can withstand osmotic shock, thus making them more mechanically stable than resins [15].

Unlike solvent extraction, IEFs may be used to remove metal ions present in trace quantities with less sludge formation, if any, and IEFs can ensure that the resulting solution meets the

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environmental discharge requirements [10]. For example, the IEFs onto which Cu²⁺ ions adsorb may be regenerated using sulphuric acid and the Cu²⁺ ions can be directly recovered by electrowinning [10]. At the same time, the eluent used (sulphuric acid) is recovered.

The other advantage of IEFs is that they can be fabricated into different textures such as fibre, thread, felts, nonwoven cloth, etc, [12] thus making them more versatile. Furthermore, with respect to ion-exchange membranes (IEMs), the IEFs have better mechanical properties and are also characterized by a high hydrophobicity [12]. Practically, applications of IEFs seem to favour sorption-desorption with packed bed columns.

Researchers [5,16–18] have shown that IEFs containing iminodiacetic (IDA) group can be used to remove Cu²⁺ ions from dilute solutions. The Cu²⁺ ions form strong bonds with the two oxygen atoms of the carboxylic acid and nitrogen atom of the IDA group [16,17]. The use of IEFs is also employed for the removal of other heavy metal ions such as cobalt (Co²⁺), nickel (Ni²⁺), zinc (Zn²⁺), manganese (Mn²⁺) and magnesium (Mg²⁺). Nevertheless, Ntimbani et al., [5] found that IEFs containing IDA functional group have a higher selectivity for Cu²⁺ ions than Co²⁺, Ni²⁺, Zn²⁺, Mn²⁺ and Mg²⁺ ions at pH 3. However, the effective use of IEFs requires the measurement of the optimal superficial velocity and residence time under conditions that simulate a continuous ion exchange process [19,20]. Continuous ion exchange processes are simulated by breakthrough tests conducted in laboratory scale columns [19,20].

Thus, in this study, the optimal packing density, superficial velocity and residence time required to effectively remove Cu^{2+} ions from dilute synthetic solutions were investigated using packed bed columns. The variables which were investigated include, (1) effect of bed packing density and feed flow rate on Cu^{2+} ions removal by IEFs, and (2) effect of bed packing density and eluent (acid) flow rate on elution of Cu^{2+} ions from IEFs. It must be noted that the effects of bed packing density and feed flow rate need to be studied as efficiency depends on these parameters [16]. Some of the well-established empirical models such as the Adam-Bohart model, Thomas model and the Yoon-Nelson model were fitted into the experimental data from the Cu^{2+} ions removal tests so as to determine the dynamic behaviour of the Cu^{2+} ions removal by IEFs.

2. Materials and methods

2.1. Material acquisition

The IEFs under the trademark Fiban X-1 were selected as the ion exchange materials for the study. Fiban X-1 comprises of iminodiacetate and carboxylic acid functional groups attached to a polyacrylic matrix [18]. The selected IEFs are generally referred to as chelating ion exchangers [16,18] and they were supplied in H⁺ form [14]. The physical form of the IEFs used in this study is shown in Fig. 1. The morphology of the IEFs used in this study is given by Kosandrovich and Soldatov [12]. A detailed discussion of the functional groups found in the IEFs used in this study is also outlined in Kosandrovich and Soldatov [12].

The ion exchange materials were purchased from Institute of Physical Organic Chemistry of National Academy of Sciences of Belarus [14]. Copper sulphate (CuSO₄), hydrochloric acid (HCl) and sulphuric acid (H₂SO₄) used in the study were supplied by Merck, South Africa.

2.2. Fibre preparation

The IEFs were contacted with 1 M $\rm H_2SO_4$ to ensure that they are in $\rm H^+$ ionic form. About 10 times the volume of IEFs (10 bed volumes) was contacted with IEFs in a sealed bottle and was mixed by rolling on rollers for 2 h. After 2 h of contact, IEFs were separated from the acid by vacuum filtration. The IEFs were then washed with de-ionised water to remove any entrained acid. Thereafter, the IEFs were left to dry in air for 24 h. The characteristics of the fibres used in this study as described by the supplier [14] and other previous studies [5,12,16] are listed in Table 1.

2.3. Reagent preparations

The H₂SO₄ solution of 1 M was prepared from 98% H₂SO₄ solution. A 2 M HCl was prepared using 30% HCl solution. The studies conducted by Kose and Ozturk [21] also used HCl as an eluent to remove loaded metal ions from ion exchange materials.



Fig. 1. Ion exchange fibres (IEFs) in staple form [11].

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