Removal of copper ions from dilute synthetic solution using staple ion exchange fibres: Equilibrium and kinetic studies

CrossMark

Rhulani N. Ntimbani [a,b], Geoffrey S. Simate [a,*], Sehliselo Ndlovu [a]

[a] School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, P/Bag 3,Wits 2050, South Africa
[b] Hydrometallurgy Division, Mintek, P/Bag X3015, Randburg 2125, South Africa

ABSTRACT

The removal of heavy metals like copper (Cu^{2+} ions) from industrial waste streams is necessary so as to prevent detrimental effects to the environment and human health. One of the effective adsorbents that can be used for the removal of heavy metals are ion exchange fibres (IEFs). Therefore, this paper focuses on equilibrium and kinetic studies of the Cu^{2+} ions removal process using IEFs. In addition, selectivity and elution tests were also conducted. The equilibrium and kinetic behaviour of Cu^{2+} ions removal was best described by the Temkin and the pseudo-second-order model, respectively. The results also indicated that the IEFs had a higher selectivity for Cu^{2+} ions than the other ions (cobalt (Co^{2+}), nickel (Ni^{2+}), zinc (Zn^{2+}), manganese (Mn^{2+}) and magnesium (Mg^{2+})) studied at pH 3 and 62 mg of Cu^{2+} ions per gram of IEFs were loaded at this pH. It was also found that the percentage of metal eluted from IEFs increased with an increase in eluent concentration. Furthermore, the ion exchange rate was found to be dependent on the number of ionizable functional groups as suggested by the pseudo-second-order model.

©2015 Elsevier Ltd. All rights reserved.

Introduction

Industrial effluent streams contain heavy metals such as copper (Cu^{2+} ions) which are harmful to the environment and human health when above certain threshold levels [1–4]. It is, therefore, necessary to treat industrial effluent streams prior to their release into the environment. However, techniques like chemical precipitation, reverse osmosis, electrolysis and coagulation that are normally used for heavy metal removal have been found to be inefficient as they result in incomplete metal removal, high reagent and energy requirements, and generate voluminous toxic sludge [5–7]. In addition, the above mentioned technologies are nearly nonselective, thus, inefficient for selective removal or separation of metals [7]. These disadvantages have brought attention to the application of ion exchangers, impregnated materials and silica gels. Thus, granular ion exchangers, impregnated materials and silica gels have been studied extensively for selective removal of metals; however, their reaction rates are generally slow [8].

Nevertheless, in the recent past, ion exchange fibres (IEFs) have found widespread applications because of their higher reaction rates due to their larger surface areas and shorter diffusion paths [2,9,10] compared to granular ion exchangers. IEFs are

functionalized to have functional groups which give them their selectivity properties and may be fabricated to either exchange anions and/or cations [9]. Furthermore, IEFs can be fabricated into different textures such as thread, felts, nonwoven cloth, etc., thus making them more versatile.

In this study, the equilibrium and kinetic behaviour describing the removal of Cu^{2+} ions from dilute synthetic solutions by IEFs were investigated in order to gain an understanding of the ions removal process. The study included investigation of the effects of pH on metal loading and the selectivity of IEFs for a solution containing Cu^{2+}, cobalt (Co^{2+} ions), nickel (Ni^{2+} ions), zinc (Zn^{2+} ions), manganese (Mn^{2+} ions) and magnesium (Mg^{2+} ions). Maximum loading tests were also carried out to determine the amount of Cu^{2+} ions that IEFs can load at the selected optimum pH. Elution tests were also conducted to determine the effects of eluent concentration on the removal of the loaded ions from IEFs.

Materials and methods

Material acquisition

IEFs referred to as Fiban X-1 were selected as the ion exchange material for the study. Fiban X-1 consists of iminodiacetate and carboxylic acid groups attached to a polyacrylic matrix [11]. The selected IEFs are generally referred to as chelating ion exchangers [11,12]. The ion exchange materials were purchased from the

* Corresponding author. Tel.: +27 11 717 7570/76 112 6959; fax: +27 11 717 7599.
  E-mail address: simateg@yahoo.com (G.S. Simate).

Table 1
Characteristics of Fiban X-1 cationic ion-exchange fibres [9,11,13].

Characteristics	Values/description
Physical form	Staple form
Maximum compression	$0.24\,kg/dm^3$
Volume density	$0.07–0.10\,kg/dm^3$
Effective diameter	$10–40\,\mu$
Colour	Yellow
Matrix	Acrylic
Functional group	Carboxylic group, iminodiacetic group
Ionic form as shipped	H^+
Total cationic capacity	3.74 meq/g
Moisture holding capacity	$0.6\,g\ H_2O/g$
pK_a	9.3
Δpk	1.0
Temperature range	0–80 °C

Fig. 1. Schematic experimental set up for loading tests.

Institute of Physical Organic Chemistry (IPOC, Minsk, Belarus). Metallic salts of the following elements: Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Mg^{2+} ions were also used for the test work. These metal sulphate salts were supplied by Merck, South Africa. Caustic soda (NaOH), hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) used in the study were also supplied by Merck, South Africa.

Fibre preparation

The IEFs were converted to H^+ form by washing with $2\,M\ H_2SO_4$ for 2 h at room temperature. Acid of about 10 times the volume of IEFs 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-ionized water so as to remove entrained acid. Thereafter, the IEFs were left to dry in air for 24 h. The characteristics of the fibres used in this study are listed in Table 1. The data in Table 1 are as provided by studies conducted by Soldatov et al. [13] and the supplier, IPOC [14].
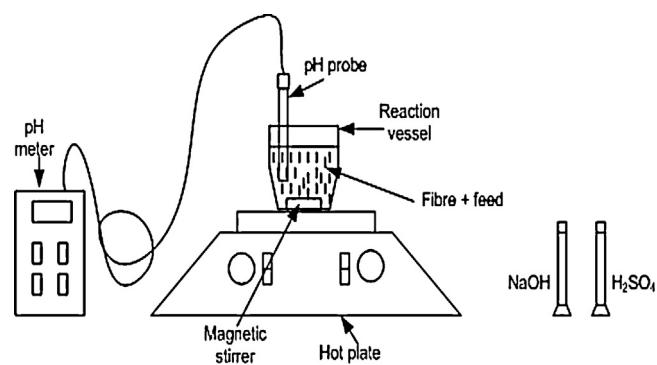
Reagent and solution preparations

NaOH and H_2SO_4 solutions of 1 and 2 M, respectively, were prepared from NaOH pellets and 98% H_2SO_4 solution. NaOH is commonly used for increasing the pH of a solution in laboratory tests [12,15,16]. On the other hand, H_2SO_4 is commonly used to decrease the pH of a solution in laboratory tests [12]. HCl of 2 M was prepared using 30% HCl solution. HCl is commonly used for eluting loaded metals from ion exchangers [17]. An equimolar (2 mM) feed solution was prepared from metal sulphates of Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Mg^{2+} ions. The amounts of metallic salts used to prepare the feed solutions are given in Table 2.

Effect of pH on extraction

Volumes of 100 mL of feed solution composed of Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Mg^{2+} ions with each metal ion at a concentration of 2 mM were contacted with 2 g of IEFs in the pH range of 1.5–5.0 to determine how selectivity varies with pH. NaOH

or H_2SO_4 was used to control the pH accordingly within 0.5 pH increment. The tests were run for 24 h and the final pH readings were noted. The IEFs were separated from the solution by vacuum filtration. Thereafter, the IEFs were washed with 100 mL of deionized water to remove any entrained solution. The wet washed fibre samples were then eluted with 200 mL of 2 M HCl solution by agitation in a beaker for 4 h. The eluted IEFs were separated from the eluent by filtration and then washed with deionized water. The washed IEFs were dried and stored for re-use. Samples of the barren feed solutions were analysed for Cu^{2+} ions using atomic absorption spectrometer (AAS). After elution, samples of the eluent were also analysed for Cu^{2+} ions after separation from IEFs. A schematic representation of the experimental set up is shown in Fig. 1.

Maximum loading capacity of copper

The tests for maximum Cu^{2+} ions loading were done to determine the amount of Cu^{2+} ions that could be loaded per g of IEFs at an optimum pH. A volume of 3.6 L containing 2 mM (127 mg/L) of Cu^{2+} ions was contacted with 0.5 g of fibre for 24 h. The volume was selected to ensure that there was excess amount of Cu^{2+} ions in solution with respect to the capacity of IEFs given by the supplier. The pH of solution was controlled at 3 (see section: Effects of pH on metal loading). After the contact time the IEFs were separated from solution and washed. The washed IEFs were eluted with 100 mL of 2 M HCl solution for 4 h as described above. Samples were collected and analysed as stated in the previous section. The fibres were dried and stored for re-use.

Generation of equilibrium adsorption isotherms

Adsorption equilibrium isotherms were generated for the loading of Cu^{2+} ions onto the IEFs by contacting fibre with synthetic Cu^{2+} ions (127 mg/L) solution at various solutions to fibre mass ratios as shown in Table 3.

The solutions containing the fibres were mechanically agitated using a magnetic stirrer (Heidolph 036110550 MR Hei-Tec Digital Hot Plate Stirrer) at 300 rpm. The pH values for the individual

Table 2
Mass of sulphate salts used to prepare the equimolar multicomponent solution.

Element	Mass of element required (g)	Mass % of element in the salt	Mass of salt required (g)	Assay of salt (g)	Actual salt mass required (g)	Amount of metal in ppm
Ni	0.235	0.223	1.051	0.990	1.062	117
Co	0.236	0.210	1.124	0.975	1.153	118
Zn	0.262	0.227	1.150	1.015	1.133	131
Mg	0.097	0.202	0.481	0.660	0.730	49
Mn	0.220	0.325	0.676	0.990	0.683	110
Cu	0.254	0.254	0.999	0.998	1.001	127