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Equilibrium and kinetics of copper ions removal from wastewater by ion exchange

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ABSTRACT

The removal of copper ions from wastewater by ion exchange has been studied using an iminodiacetate resin. The capacity of the resin for the copper ions has been determined to be $2.30 \text{ mmol} \cdot \text{g}^{-1}$ by measuring the equilibrium isotherm at $25 \text{ }^\circ\text{C}$ and initial pH value of 3.5 where the final equilibrium pH value is 5. An analysis of equilibrium isotherm models showed that the best fit model was the Langmuir–Freundlich. The kinetics of the ion exchange process have been investigated and four kinetic models have been tested namely: Ritchie model, pseudo-second order model, pseudo-first order model and the Elovich model. The pseudo-second order model provides the best fit to the kinetic data.

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1. Introduction

Copper is a well-known metal in human history and it has been in use for over 10000 years. Nowadays, the use of copper is still widespread in different industries, for instance, the manufacture of alloys and the production of printed circuit boards (PCBs). The human body, a daily micro- to milligram scale intake of copper is required. It plays an essential role in the development and performance of the human nervous and cardiovascular systems [1]. Ingestion of gram quantities of copper salt daily may, however, cause harmful effects to the human body, although copper is not classified as a carcinogenic material by US EPA [2]. The Guidelines for Drinking Water Quality (GDWQ) of World Health Organisation (WHO) recommended that the daily average copper requirements are $12.5 \text{ } \mu\text{g} \cdot \text{kg}^{-1}$ of body weight for adults and about $50 \text{ } \mu\text{g} \cdot \text{kg}^{-1}$ of body weight for infants [3]. The Institute of Medicine (IOM) advocated $10 \text{ mg} \cdot \text{d}^{-1}$ as a tolerable upper intake level for adults from foods and supplements [4].

Nowadays, numerous methods have been developed for treating metal ion containing waste solution. The basic principles of treating waste solution are the removal of ions from the waste solution or concentrating the ions in the waste solution in the same phase or different phases. In chemical precipitation, copper ions react with hydroxide ions and form an insoluble copper precipitate at alkaline (high pH) condition. It is, however, sensitive to pH, ion concentration and composition, and non-compatible with any soaps or surfactants

[5]. Evaporation may be used to produce a more concentrated solution which can sometimes be reused in the electroplating industry or reprocessed to produce a metal salt. The evaporated water can be condensed for rinsing purposes. This is one of the suitable waste treatment methods for the electroplating industry. In membrane filtration processes cross flow filtration method is used. Depending on the specific requirement microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), or reverse osmosis (RO) membranes can be used. Membranes separate the wastewater into two streams. One (the concentrate) contains contaminants and the other, cleaned water. Electrochemical coagulation has been investigated [6] but produces a waste floc.

Ion exchange is an effective technology to remove heavy metal ions from water. Natural ion exchangers, such as peat [7–9], have found some success for the removal of copper and other heavy metals. Other biomass, sources have also the exchange/chelating capacity to exchange with copper ions in solution [10–12]. Ion exchange materials can be found naturally or artificially synthesized [13]. Synthetic ion exchange materials can be divided into two categories: inorganic material and organic material. Inorganic ion exchange materials can be classified by their own chemical characteristics and include: hydrous oxides, acidic salts of multivalent metals, salts of heteropolyacids, insoluble ferrocyanides and aluminosilicates. Most inorganic ion exchange materials have high selectivity to alkali metals [14]. Synthetic ion exchange resins are high molecular weight polymer carrying ionic groups as integral parts of the polymer structure. Cation exchange resin attracts cations since its ionic group is phenolic, sulfonic, carboxylic or phosphoric acid group [15]. Cation resins can be further classified into strong acid resin and weak acid resin depending on which ionic group it contains. The

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strong acid resins carry sulfonic acid functional group, correspondingly, weak acid resin has carboxylic acid functional groups and slightly dissociate in solution. Weak acid resins are highly affected by the pH value of the solution [16].

The present study investigates the ion exchange capacity and the rate of ion exchange of an iminodiacetate weak acid resin to remove copper ions from wastewater. Equilibrium isotherms are determined and the reaction kinetics are analyzed. The results are useful for industrial adsorber design.

2. Materials and Methodology

2.1. Materials

2.1.1. Ion exchange resin

The ion exchange resin is a synthetic organic material with polystyrene polymeric base. The chelating resin (D401) used in experiments was supplied by the Suqing Group Limited, Beijing, China. This chelating resin is the sodium form of a weak acid cation resin, but it has high degree of selectivity for heavy metal cations because it forms stable complexes with heavy metal ions due to its functional iminodiacetate group.

Fig. 1 shows the functional group and ion-exchange process and Table 1 lists the physical and chemical properties of D401 resin, respectively [17,18]. The uptake mechanism of heavy metals is:

2.1.2. Adsorbate

Analytical grade copper(II) chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) used in the experiments was supplied by Acros Chemicals, Geel, Belgium. Stock solutions of metal ions were prepared using deionized (DI) water. The pH values of the copper solutions were adjusted to 3.5 at the commencement of each experiment since PCB effluents are acidic in nature.

2.2. Experimental set up

2.2.1. Pre-treatment of resin

The chelating resin supplied was in the sodium form. However, the sodium content of the resin may not be consistent. Pre-treatment of resin, therefore, was required to ensure consistent experimental results. The pre-treatment procedure was similar to the regeneration of exhausted resin.

First the resins were immersed into DI water for more than 30 min and then the resin was immersed in 8 wt% hydrochloric acid with a portion of 180 ml $\text{HCl} \cdot \text{L}^{-1}$ resin for more than 45 min to replace all the sodium ions by protons. The acid treated resin was washed with DI water to remove the acid residue until the solution pH was above 2. Then the resin was immersed in 4 wt% sodium hydroxide solution for 45-min to replace the protons by sodium ions with the sodium content being $3 \text{ mmol} \cdot \text{g}^{-1}$ of the resin. The resins were then washed with DI water and

dried at 100–110 °C for 3 days before allowed to cool to ambient temperature in a desiccator. The resins used are 710–1000 μm in particle sizes.

2.2.2. Contact agitation time for sorption isotherm studies

The equilibrium time for the sorption isotherm must be established before any other experiments are conducted. The highest concentration of Cu ions solution, which was to be used in the equilibrium sorption isotherms, was used in these experiments. A fixed mass of 0.100 g resin was added to 50 ml of copper metal ion solution, transferred into a screw cap jar and shaken at a speed of $200 \text{ r} \cdot \text{min}^{-1}$ at $(25 \pm 2)^\circ\text{C}$. Each jar was removed from the shaker at a pre-specified time and the copper ion solution was sampled and its copper content was measured utilizing an Inductively Coupled Plasma-Atomic Emission Spectrophotometer (ICP-AES), a Perkin Elmer Optima Model 3000XL. The removal percentages can then be calculated as a function of time.

Although the equilibrium was considered reached after 72 h, the agitation time of 96 h was adopted in all further isotherm experiments to ensure all isotherms achieved equilibrium.

2.2.3. Equilibrium sorption isotherms

The sorption capacity (q_e) of the resin was calculated from the mass balance:

$$m(q_0 - q_e) = -V(C_0 - C_e) \quad (1a)$$

$$q_e = \frac{V}{m}(C_0 - C_e) \quad (1b)$$

where

C_0 = initial concentration of metal ion solution ($\text{mmol} \cdot \text{L}^{-1}$)

C_e = equilibrium concentration of metal ion solution ($\text{mmol} \cdot \text{L}^{-1}$)

m = mass of resin (g)

q_e = equilibrium metal ion concentration on resin ($\text{mmol} \cdot \text{g}^{-1}$)

V = volume of metal ion solution (L)

Since fresh resin was used in the experiments, the initial metal ion concentration on resin ($\text{mmol} \cdot \text{g}^{-1}$), q_0 , is zero.

2.2.4. Batch kinetic studies

Batch kinetic experiments were conducted to investigate the influence of different parameters on the adsorption rate. A standard configuration of adsorption vessel and stirrer developed by Furusawa and Smith [17] was employed in all of the experiments. The dimension of each component was designed based on the inner diameter of the tank D_i .

Fig. 2 shows the experimental vessel setup. A 2-L plastic vessel was used as the adsorption tank with the inner diameter $D_i = 0.13 \text{ m}$ to hold 1.70 L metal ion solution for the kinetic experiment. A flat plastic impeller with six blades provided the mixing effect to the solution. The

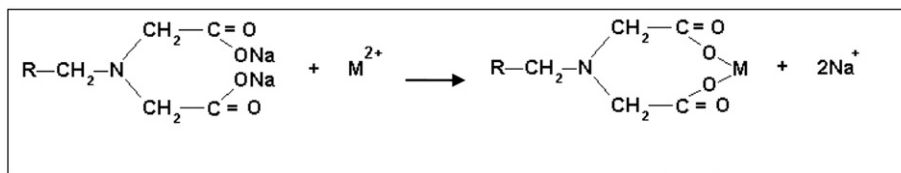


Fig. 1. Functional group of D401 resin (Na^+ form).

Table 1
Physical and chemical properties of D401 resin

Ionic form	Total capacity $\text{min}/\text{mmol} \cdot \text{ml}^{-1}$	Water retention/%	Shipping $\text{mass}/\text{g} \cdot \text{ml}^{-1}$	Specific $\text{density}/\text{g} \cdot \text{ml}^{-1}$	Maximum reversible swelling	Remarks
Na	0.6 (Cu^{2+})	52–58	0.72–0.78	1.15–1.25	H → Na 40%	Macroporous iminodiacetate resin. Highly selective for multi-valence metals.

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