



Removal of copper ions using sodium hexadecanoate by ionic flocculation

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ABSTRACT

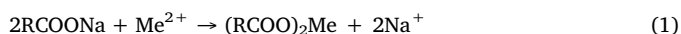
The mining, electroplating, and electronics industries release increasing amounts of heavy metals, such as copper, into aquatic ecosystems. Industrial effluent often contains metals at concentrations above the maximum limits set by law. In this study, ionic flocculation using the anionic surfactant sodium hexadecanoate is shown to be an alternative method for the removal of copper from industrial effluent. The effects of temperature, metal solution pH, and surfactant concentration on copper removal were analyzed using experimental design techniques. A statistical experimental design of the study showed that the process is directly dependent on the variations in the pH and molar ratio between sodium hexadecanoate and copper ions (Cu^{2+}) but inversely proportional (and less dependent) on the temperature. An individual study of the temperature effect shows that the process is strongly dependent on the Krafft temperature of both surfactants, i.e., that used as the extractive agent and that obtained after the reaction of the surfactant with the metal. Subsequently, the thermodynamic parameters were determined, which showed that the process is spontaneous and either endothermic or exothermic depending on the temperature range.

1. Introduction

Wastewater containing heavy metals is often directly or indirectly discharged into the environment as a result of heavy industry, especially in developing countries [1]. Certain heavy metal ions are capable of accumulating in the tissues of living organisms and, even in small amounts, cause disease and disorder [2]. In addition, they may inhibit the operation of biological treatment plants and affect aquatic life, deteriorating their self-purification power [3].

Faced with these problems, there is a need to use treatment methods that reduce or eliminate heavy metals from industrial effluent and watercourses. A variety of metal removal methods have been studied, such as chemical precipitation [4], ion exchange [5], adsorption [6,7], and membrane filtration [8,9].

Ionic flocculation [10] is an alternative removal method. In this process, an anionic surfactant forms a new water-insoluble surfactant when in contact with bivalent and trivalent metal ions. Siska [11] described this as a process of cation exchange between a sodium carboxylate and a metal ion:



This interaction depends on the alkyl chain length of the surfactant

and its concentration. The anionic surfactant formed by the reaction is a metal carboxylate that is insoluble in water but may be soluble in various organic solvents.

One of the primary advantages of this process is that the solubilities of the metal compounds formed with carboxylates are lower than those of the corresponding metal hydroxides. In addition, the carboxylates remain insoluble over a wide pH range while simultaneously precipitating a wide variety of different metals at a single pH [12].

Sodium carboxylates are easily prepared by the saponification of fatty acids or triglycerides and can be obtained from natural materials such as coconut oil, sunflower oil, and animal fat. In the chemical industry, these salts, especially those of lithium, sodium, and potassium, have great applicability as foaming agents for concrete, toilet soap bars, and for the degumming of silk [13]. Some studies have been carried out concerning the removal of metals using salts of carboxylic acids, such as sodium octanoate [14], sodium decanoate [15,16], and sodium dodecanoate [17].

These surfactants commonly show Krafft-type behavior [18]. At temperatures above the Krafft temperature, the surfactant solubility increases sharply with increasing temperature; at this point, the solubility is equal to the critical micelle concentration (CMC) [19].

This work presents an innovative approach to metal removal by

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identifying the Krafft point as a limiting factor for the ionic flocculation process. We used sodium hexadecanoate, a surfactant commonly found in natural materials, as the extracting agent. To understand the copper removal process, the thermodynamic parameters and a statistical design of the copper ion removal process were evaluated. In this statistical experimental design, the influence of three factors was considered: temperature, metal solution pH, and surfactant concentration.

2. Materials and methods

2.1. Materials

The synthetic effluent containing the copper ion was prepared using copper sulfate (VETEC). Copper sulfate, sodium hydroxide (NEON), hydrochloric acid (MERCK), and hexadecanoic acid (IMPEX) were analytical grade and used as received without purification. Sodium hexadecanoate was prepared by neutralizing hexadecanoic acid with sodium hydroxide.

2.2. Methods

2.2.1. Ionic flocculation tests

Removal tests were performed in a thermostated bath (Koehler Instrument Company, Inc., USA), showed in Fig. 1, where it was possible to control the temperature and the stirring speed of the samples throughout the experiment. The contact of the metal solution and surfactant solution in the equipment was divided into three stages: rapid mixing (stirring speed of 216 rpm for 2 min), slow mixing (stirring speed of 50 rpm for 10 min), and resting period (without stirring for 12 min) [20–22].

To obtain each experimental data point, a copper solution was placed into the tubes of the equipment, reaching a metal concentration of 124.7 ppm, and then subjected to temperature control in the thermostatic bath. Separately, the sodium hexadecanoate solution was heated on a heating plate to the same temperature as the copper solution. After the solutions were at the same temperature they were mixed, allowing the reaction between the surfactant and the metal (Fig. 2).



Fig. 1. Thermostated bath used in the removal tests.

When bivalent metals are in solution and come in contact with the anions of fatty acid soaps, they interact with these anions forming a new surfactant composed of a metal cation and two anions of the original carboxylic acid. Because of the steric hindrance between the carboxyl groups, hydrophobic parts, of this new molecule, turn to opposite sides, while the metal remains in the center.

This configuration of the new surfactant gives it a hydrophobic character, which favors the formation of colloids (Fig. 3). The agitation of the system promotes aggregation of the precipitate, forming flocs which can be separated from the system by a filtration process. It is difficult to check the size of these flocs because of their growth kinetics.

The ionic flocculation process is based on the attraction between the copper ion and the negative part of the surfactant molecule, forming a salt of low solubility, which results in an effluent with low metal concentration, making its study important as an alternative to existing processes. These flocs were separated by vacuum filtration using quantitative filter paper with a particle retention of 1–2 μm . The obtained filtrate was analyzed using an atomic absorption spectrophotometer (Spectra A-20 plus, Varian). pH control, where necessary, was achieved by adding 0.1 M HCl to the metal solution before the addition of the surfactant solution.

2.2.2. Temperature evaluation and high-pressure tests

One of the factors evaluated in the process was the temperature, because it directly affects the equilibrium. The temperature range evaluated was between 30 and 109.2 °C. To reach temperatures above 100 °C without boiling the water, a high-pressure cell was used. This apparatus has been described in detail in previous papers [23–26]. The surfactant/metal mixture was placed inside the cell, and the pressure was raised gradually to prevent the water from boiling. The temperature was gradually increased to the desired value while the system was stirred constantly.

2.2.3. Experimental design

A 2^3 -factorial design with replicas at the central points was used to investigate the influence of three factors on the copper removal process. The selected factors were: the molar ratio between sodium hexadecanoate and Cu^{2+} ions (P), initial pH of the copper solution (pH), and temperature (T). The response was the percentage of copper removed (%R). Table 1 shows the levels of each factor, used in the design matrix.

The minimum level (-1) for the temperature parameter was set at a value above the Krafft temperature of sodium hexadecanoate, 57.5 °C [27]. Therefore, to ensure that the surfactant was fully dissolved, a temperature of 60 °C was used. The maximum level ($+1$) was set to 80 °C because of the operational limitations of the thermostatic bath used. For the pH parameter, the maximum value was set at the natural pH of the metal salt solution at room temperature, which is 4.5. We did not use values higher than 4.5 because the addition of NaOH to the copper solution promoted the precipitation of metal hydroxides at pH values greater than 6. The minimum pH was set at 2.5 because this approximates the values obtained from copper leaching experiments [28]. The maximum metal/surfactant ratio was defined based on the stoichiometric concentration of the surfactant, taking into account the hypothetical complete reaction of the copper ions. The experiments were performed in random order and were conducted in duplicate. The effect of each factor was analyzed through the generation of response surfaces by the STATISTICA 7.0 program.

2.2.4. Determination of the solubility of the copper surfactant flocs as a function of temperature

A more detailed study of the effect of temperature on the solubilization of the copper surfactant flocs was carried out between 30 and 109.2 °C (the value defined as the Krafft point of the copper hexadecanoate) to analyze the temperature influence on the metal removal process. The concentration of surfactant and pH of the metal solution

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