Hydrometallurgy 180 (2018) 246–253

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Adsorption of trace Iron from nickel sulfate solutions using Monophos resin

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ARTICLE INFO

Keywords:
Adsorption
Kinetic
Thermodynamics
Monophos resin
Nickel sulfate solution

ABSTRACT

This paper deals with the removal of trace iron from nickel sulfate solution using Monophos resin. Kinetics, thermodynamics and adsorption mechanism of iron adsorption were studied. Kinetic and thermodynamic parameters as well as equilibrium constants were calculated based on various equilibrium models. Liquid film diffusion, particle diffusion and chemical reaction models were used to fit the experimental data. It was shown that the adsorption mechanism was well represented by particle diffusion model. And pseudo-second-order and intra-particle diffusion model were more consistent with the adsorption process and clearly predicted the intra-particle distribution of iron concentration. Langmuir isotherm well described the adsorption data. Thermodynamic parameters indicated that the adsorption process was spontaneous and endothermic. An iron adsorption rate of 89% was reached with iron concentration being reduced from 1.92 mg/L to 0.21 mg/L.

1. Introduction

High purity nickel has good ductility, high temperature properties, excellent corrosion resistance, and good linearity of resistance temperature characteristics as well as good thermal neutron capture performance. Therefore, it is widely used in high temperature structural materials, aero engines, nuclear reactor protection materials, biomaterials and low expansion alloys. In particular, high purity nickel with a purity of 99.999% (5 N) or higher is applied to large scale integrated circuit as contact layer and wiring materials, magnetic thin film materials, and special packaging materials (Palumbo and Aust, 1990). It is normally produced via a hydrometallurgical process with nickel sulfate solution as the process liquor. Because the aqueous chemical properties of iron and nickel are very similar, one of the challenges for producing 5 N nickel is to lower iron in the process liquor to a milligram per liter level.

It is known that precipitation method is often used to deal with high concentration of iron. However, the precipitation method is not a good ideal for removing the iron concentration of the milligram level (Tekerlekopoulou et al., 2013). The extraction process (Liu and Zhou, 2005; Pospiech et al., 2005) needs to further remove the diluents such as kerosene, which is more complex compared with ion exchange method. Among the three methods, ion exchange method is believed to be the method of choice for lowering iron in the process liquor to milligram per liter level (Fan and Sun, 2012).

A relatively new macroporous chelating resin nemed Monophos has been reported to be quite effective for removing trace iron from copper sulfate (Mckevitt and Dreisinger, 2009) and cobalt sulfate solutions (Wang et al., 2018). It seems very promising for lowering iron in our nickel sulfate liquor. Therefore, we decided to test this resin as part of our effort to develop a high purity nickel production process. This paper reports the results obtained from our test with emphasis being placed on thermodynamics and kinetics of trace iron adsorption.

2. Experimental

In order to study the adsorption kinetics, a 150 mL nickel sulfate solution with a nickel concentration of [Ni] = 90 g/L and an iron concentration of [Fe] = 1.92 mg/L was added into a conical bottle, which was placed in a 60 °C hot water. Duo to the acidity of the solutions, Fe in this study is believed to be mainly in the form of Fe(III). Then, 25 g wet resin was added into the solution. Sampling was done every 5 min in the first 10 min, every 10 min in the time range from 10 min to 60 min, and every 30 min afterwards till the total adsorption time reached 240 min. Each time, a 2.5 mL sample was taken.

For studying the adsorption thermodynamics, 5 wet resins (12.5 g each) and 5 solutions (150 mL each) with different concentrations ([Ni] = 50 g/L,60 g/L,70 g/L,80 g/L,and 90 g/L) were added into 5 conical bottles, respectively. The bottles were placed in a thermostatic oscillator with a constant temperature and an oscillation frequency of 110 r/min. For 300 min to achieve an adsorption equilibrium state. A 5 mL sample was then taken from each bottle. These tests were done for 3 different temperatures of 20 °C, 35 °C and 70 °C.

Iron concentrations of all samples were analyzed using an ICP-OES

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https://doi.org/10.1016/j.hydromet.2018.08.003
Received 19 April 2018; Received in revised form 29 July 2018; Accepted 10 August 2018
Available online 11 August 2018
0304-386X/

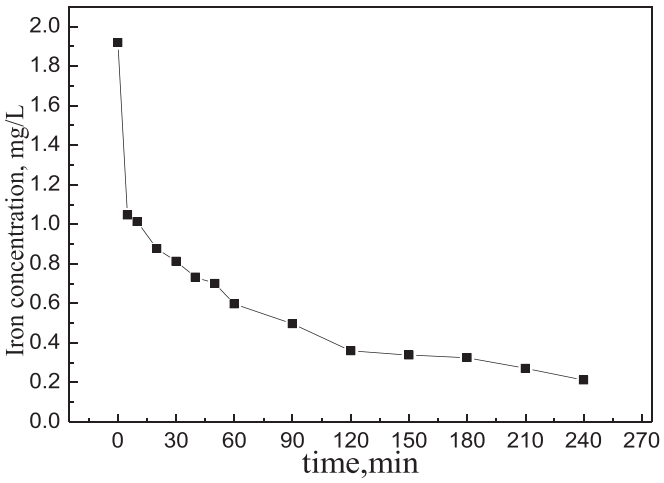

Fig. 1. Change of Fe concentration in nickel sulfate solution.

8000.

3. Results and discussion

3.1. Adsorption mechanism

Fig. 1 shows the change of Fe concentration in nickel sulfate solution with time during the adsorption process. It can be seen that iron concentration decreased from 1.92 mg/L to 0.21 mg/L. This corresponds to an iron adsorption rate of 89%. Such a low iron level is beneficial for producing 5 N nickel. The adsorption capacity Q_t at time t is calculated based on formula Eq. (1). The results is shown as follows in Fig. 2.

$$Q_t = (C_0 - C_t)V/m \tag{1}$$

where, C_0 is the concentration of initial iron ion in the nickel sulfate solution, mg/L. C_t is the concentration of iron ion at t time, mg/L. V is the volume of the solution, mL. m is the mass of the resin, g.

It can be seen from Fig. 2 that Fe adsorption capacity of Monophos resin as function of adsorption time. The adsorption reaction occurs mainly in the first 30 min and it reaches an equilibrium state after 120 min, with an equilibrium Fe adsorption capacity being about 8.30 mg/L.

An adsorption process of an ion exchange resin can be divided into three steps (Kocaoba and Akcin, 2008): liquid film diffusion (FDC), particle diffusion (PDC) and chemical reaction (CRC). Models for the three steps are as follows:

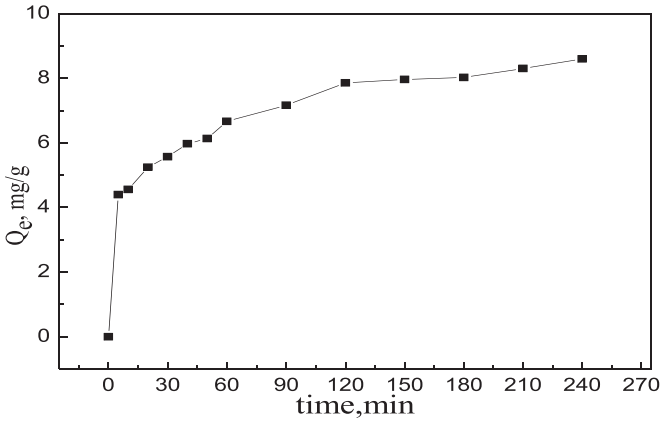

Fig. 2. Fe adsorption capacity of Monophos resin as function of adsorption time.

Liquid film diffusion model: $F = kt$ (2)

Particle diffusion model: $1 - 3(1 - F)^{2/3} + 2(1 - F) = kt$ (3)

Chemical reaction model: $1 - (1 - F)^{1/3} = kt$ (4)

Here, $F = Q_t/Q_e$ is conversion rate. Q_t and Q_e are adsorption capacity at time t and at equilibrium, respectively, mg/g. k is mass transfer coefficient.

In order to predict the adsorption mechanism of adsorption reaction, liquid film diffusion model, particle diffusion model, and chemical reaction model were used to fit the experimental data. Fig. 3 and (Table 1) show fitting plots for these three models. It can be seen from fitting results that liquid film diffusion ($R^2 = 0.87$) and chemical reaction ($R^2 = 0.88$) may not be the controlling step. The particle diffusion model ($R^2 = 0.98$) is more suitable for describing adsorption behaviour of Monophos resin than other two models.

3.2. Adsorption kinetics

In order to study the adsorption behavior of Monophos resin, five dynamic models such as pseudo-first-order equation, pseudo-second-order equation, Weber-Morris, Elovich and Bangham are used to fit the data (see Fig. 4 and Table 2).

Pseudo-first-order equation

The Lagergren equation is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase. The line form of pseudo-first-order expression of Lagergren is given as follows (Lagergren, 1898; Singh, 2015):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{5}$$

where, Q_e *and* Q_t are the amount of adsorbate adsorbed on adsorbent (mg/g) at equilibrium and at time t (min), respectively. k_1 is the constant of Lagergren.

Fig. 4a shows the plots of linearized form of Lagergren for the sorption. The constant of Lagergren (k_1) and Q_e values are determined for adsorbent from the slope and the intercept of corresponding plot Fig. 4a and are listed in Table 2. The correlation coefficient (R^2) of pseudo-first-order adsorption model is 0.97929. However, Q_e is not matched with experimental value. The reaction is not likely to be pseudo-first-order even if the plot has high correlation coefficient (R^2) with the experimental data. This indicates that the adsorption of iron using Monophos resin is not acceptable for this model.

Pseudo-second-order equation

Pseudo-second-order equation is often described by the McKay equation. It is based on the sorption capacity of the solid phase (Singh, 2015; Ho et al., 2000). Furthermore, it is in agreement with chemisorption being the rate-controlling step, which the rate-controlling step is a chemical reaction or through an electronic sharing or an electronic gain.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q^2_e} + \frac{t}{Q_e} t \tag{6}$$

where, Q_e *and* Q_t have the same meaning as mentioned above and k_2 is the constant for McKay equation. The plot of t/Q_t versus t for the adsorbents are shown in Fig. 4b.

The correlation coefficient value ($R^2 = 0.98466$) for pseudo-second-order adsorption model have high value. The R^2 value is higher as compared to that of pseudo-first- order model. Meanwhile, the equilibrium adsorption capacity Q_e is close to the experimental results. Those indicate the adsorption kinetics of iron using Monophos resin can be better described by pseudo-second-order model.