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Removal of Ni(II) in aqueous solutions by foam fractionation

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ABSTRACT

The electroplating industry uses a lot of water in many of its processes. Because of the rapidly decreasing availability of water in many areas and the need of pollution control, efficient and economical methods for treating electroplating wastewater are urgently studied. Foam fractionation was used to remove divalent ions Ni(II) from its aqueous solutions with two surfactants. The optimum values influencing the separation effect of these ions were studied. The optimum separation conditions for Ni(II) were initial Ni(II) concentration 5 mg/L, liquid loading volume 200 mL, gas velocity 70 mL/min, the initial pH and temperature 30℃, providing an enrichment ratio 12, and a recovery 98%. Enrichment ratio was found to increase with an increase in the feed flow rate. With a concentration decrease in the bulk solution, the separation factor was found to increase. The study indicates the foam separation is a feasible and promising way for treating electroplating effluents.

Keywords: Foam fractionation; Heavy metal; Nickel removal; Surfactant

1. Introduction

The electroplating waste water discharged from electroplating industry causes serious threats to the environment and due to the presence of a large number of heavy metals, which are toxic even at low concentrations [1,2]. In view of the human health impacts, different metals cause different symptoms, such as the case of minor zinc exposure, irritability, muscular stiffness, loss of appetite and nausea [3]. The presence of nickel exceeding its critical level, on the other hand, might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis [4]. Therefore, it is necessary to remove heavy metals from wastewaters before discharging into the environment. To achieve this aim, further processing of water to discharge is required and selective separation processes should be considered to achieve metals recovery [5].

In recent years, a variety of methods have been reported in the literature for their separation effects of Ni^{2+} from aqueous solutions [6–8], including reduction followed by absorption on miscellaneous adsorbents [9,10], membrane separation [11], chemical precipitation, ion exchange [12]. Among them, the most effective and versatile technique for heavy metal removal, even at low concentrations, is adsorption. However, the high cost of adsorbents is regarded as the major obstacle for industrial application [13].

Nowadays, special attention has been given to searching for low cost, easily available, efficient and environmentally friendly methods for the removal of heavy metal ions from wastewaters. Foam fractionation

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[14–17] presents high selectivity and efficiency, low space requirements, flexibility, production of small volume of sludge and moderate costs. It is an adsorptive bubble separation process in which a surface active agent and its counter ions adsorb specifically at the air–water interface or bubble surface of the foam, leading to the sequential separation of both surface active agent and counter ions from the bulk liquid at the foam exit of the process [18]. The aim of the present study is to establish the optimum flotation conditions in term of several parameters, including the airflow rate, initial pH, initial solute concentration, type of surfactant, initial liquid volume and operation time on foam fractionation performances.

2. Materials and methods

2.1. Materials and reagents

Sodium dodecyl sulphate (SDS) and dodecyl benzene sulphonic acid (DBSA) were used as surfactants. Nickel sulphate hexahydrate ($NiSO_4 \cdot 6H_2O$) was used to carry out the experiments. Nitric acid and standard solution of nickel ion were used for analysis by atomic absorption spectrophotometer. All chemicals were used as received without further purification. Deionized water was used in all experiments.

2.2. Equipment set-up

The experimental set-up was consisted of a bubble column, a nitrogen gas cylinder, humidifier, a gas flow meter, a pressure gauge, a gas distributor, a foam collector and a stirrer. A schematic diagram of an experimental set-up for batch foam fractionation used in this study is shown in Fig. 1. The column was made of polymethyl methacrylate tube with a length of 70 mm and an inner diameter of 30 mm. Sintered glass filter with a height of 10 mm and a diameter of 15 mm, which had pores of 10×10^{-6}–15×10^{-6} m mean diameter, was installed as a gas distributor at the bottom of the column. A rotameter was used to control the superficial airflow rate. A Eutech PH700 pH meter and a Thermo M6 spectrophotometer were used for adjusting pH of the solution and determining concentration of metal ions at a recommended wave length.

The foaming process column was operated in a batch mode at room temperature. Metal ion solution was loaded into the column at the beginning of each experiment to a typical height from the bottom of the column and foam was then generated by adjusting the flow rate of air. The experiments were run until foam ceased to exit the outlet.

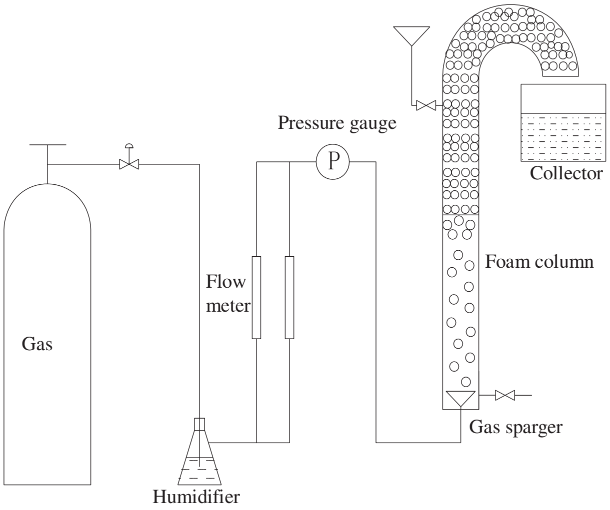

Fig. 1. Schematic diagram of the foam fractionation system.

2.3. Performance parameters of foam fractionation

Performance indicators used for the foaming process are the enrichment ratio (*E*) and recovery percentage (*R*). *E* is the ratio of the concentration of metal ions in the final foam sample, compared to the concentration of metal ions in the initial liquid sample. *R* is the percentage of metal ions by mass recovered in the foam from the initial liquid sample. The two indicators are showed as follows, which was defined according to Eqs. (1) and (2):

$$E_r = C_f / C_0 \tag{1}$$

$$R_p = C_f V_f / C_0 V_0 \times 100\% \tag{2}$$

where C_0 and C_f are metal ions concentration (mg/mL) of initial solution and the foamate, and V_0 and V_f are volume (mL) of initial solution and the foamate, respectively.

3. Results and discussion

3.1. The effect of type of surfactant and Ni^{2+} concentration on separation

Effects of type of surfactant and Ni^{2+} concentration at different airflow rates on separation efficiency, enrichment ratio and recovery percentage of metal ions were carried out under the concentration of surfactant, conditions of temperature, initial pH and loading liquid volume fixed at 0.1 g/L, 30.0℃, 5.68 and 200 mL, respectively, and superficial airflow rate was ranged from 40 to 100 mL/min. The results are shown in Table 1.

As shown in Table 1, with an increase in the superficial airflow rate, both residual liquid concentration and enrichment ratio of Ni^{2+} concentration decreased and recovery percentage kept in a small range of values. As the initial concentration was constant at 25 mg/L, the recovery percentage was slightly higher, when DBSA was used as the surfactant than SDS was used. Besides, while SDS was used as the surfactant, the recovery percentage was relatively high at low Ni^{2+} concentration. The recovery percentage reached 100% when the initial Ni^{2+} concentration was 5 mg/L. However, it was only 50–60% when the initial Ni^{2+} concentration was 25 mg/L.

As the Ni^{2+} concentration became higher and the surfactant concentration was constant, only a certain amount of surfactant molecules could bond with Ni^{2+} and then contribute surfactant to foaming becomes smaller. According to Table 1, it is predicted that, when the amount of surfactant is less than the chemical equivalent value for the bond between metal and surfactant, the foam flow disappears. As a result, more Ni^{2+} ions were left in the initial solution when the Ni^{2+} concentration was higher and the recovery percentage became lower.

3.2. Effects of airflow rate on separation

Effects of airflow rate on separation efficiency, foam volume, enrichment ratio and recovery percentage of Ni^{2+} were carried out under the concentration of surfactant, concentration of initial Ni^{2+} concentration, conditions of temperature, initial pH and loading liquid volume fixed at 0.1 g/L, 15 mg/L, 30.0°C, 5.68 and 200 mL, respectively, and superficial airflow rate was ranged from 70 to 150 mL/min. The results are shown in Figs. 2 and 3.

As shown in Figs. 2 and 3, with an increase in the gas flow rate, the concentration of nickel ion in residual liquid decreased gradually, the recovery percentage increased gradually, the enrichment ratio decreased significantly and the foam volume increased.

When the airflow rate was low, foam liquid rose slowly, the nickel ion could fully contact with the surfactant and combined with rising bubbles. Then the amount of liquid entrained between bubbles returned to the initial solution became lager which made the enrichment ratio increase and the residual concentration decrease. When the airflow rate increased, the foam rose rapidly and the entrained liquid was difficult to return to the initial solution, which made the recovery rate increased the foam volume increased.

3.3. Effect of loading liquid volume on separation

Effects of loading liquid volume on separation efficiency, foam volume, enrichment ratio and recovery percentage of Ni^{2+} ions were carried out under the concentration of surfactant, concentration of initial Ni^{2+} concentration, conditions of temperature, initial pH and airflow rate fixed at 0.1 g/L, 5–25 mg/L, 30.0°C, 5.68 and 70 mL/min, respectively, and loading liquid volume was ranged from 150 to 250 mL. The results are shown in Fig. 4.

Fig. 4 shows that as the loading liquid volume increased from 150 to 250 mL, the residue concentration of Ni^{2+} and recovery percentage did not change significantly. However, as the concentration of the nickel ion increased from 15 to 25 mg/L, the enrichment ratio decreased slightly and the highest value was 12 when the concentration of Ni^{2+} was 5 mg/L. It can also be seen that when the initial Ni^{2+} concentration was lower, the residual ion concentration was close to 0 mg/L and the recovery percentage was

Table 1
Effect of Ni^{2+} concentration on the process of foam fractionation

Type of surfactant	Initial Ni^{2+} concentration (mg/L)	Airflow rate (mL/min)	Residual Ni^{2+} concentration (mg/L)	Residual volume (mg/L)	Enrichment ratio (E)	Recovery percentage (R)
SDS	25	70	13.375	187	7.69	49.98
SDS	25	85	13.28	169	3.56	55.11
SDS	25	100	12.915	156	2.71	59.71
DBSA	25	40	12.34	190	10.62	53.11
DBSA	25	70	11.78	187	8.61	55.94
DBSA	25	100	11.665	157	2.95	63.37
SDS	5	70	0.407	184	11.56	92.51
SDS	5	85	0.389	135	2.92	94.75
SDS	5	100	0.135	80	1.65	98.92

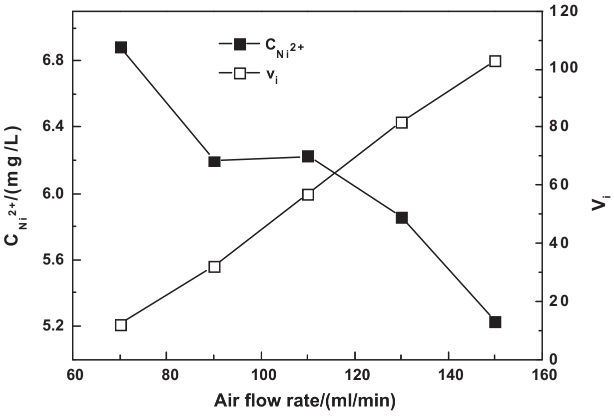

Fig. 2. Effect of airflow rate on Ni^{2+} separation efficiency and foam volume.

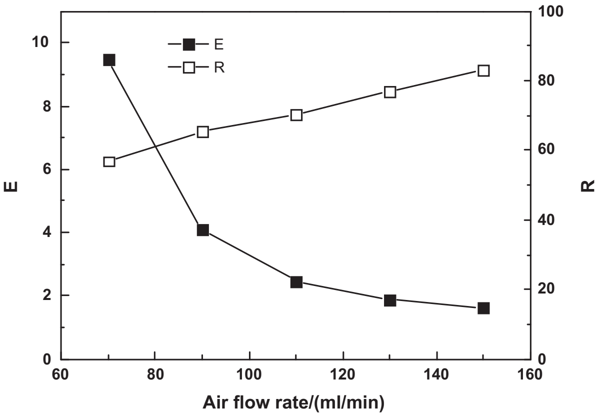

Fig. 3. Effect of airflow rate on Ni^{2+} enrichment and recovery percentage.

almost 100%. When the loading liquid volume was 200 mL, the enrichment ratio was up to 12. Considering the results mentioned above, the optimum condition for separation was reached when the nickel ion concentration was 5 mg/L and the carrier fluid volume was 200 mL.

If the height of foam fractionation column is fixed, the variation of loading liquid volume changes the ratio of foam layer height and bulk liquid layer height, and then affected adsorption of target molecules on the gas–liquid interface, foam drainage and foam fractionation performances. In relatively high foam layer, a lot of liquid entrained between bubbles flowed downward by gravity. It has been reported that the liquid hold-up is higher in the lower part than in the upper part of the foam layer [19].

3.4. Effect of surfactant concentration on separation

Effects of surfactant concentration on separation efficiency, foam volume, enrichment ratio and recovery percentage of Ni^{2+} were carried out under the concentration of initial Ni^{2+} concentration, conditions of temperature, initial pH, airflow rate and loading liquid volume fixed at 25 mg/L, 30.0℃, 5.68, 70 mL/min and 200 mL, respectively, and the concentration of Ni^{2+} was ranged from 0.05 to 0.25 g/L. The results are shown in Figs. 5 and 6.

Figs. 5 and 6 show that the recovery percentage of nickel ions increased significantly when SDS concentration increased. The residual concentration of nickel ions and enrichment ratio decreased as SDS concentration increased. When SDS concentration was 0.25 g/L,

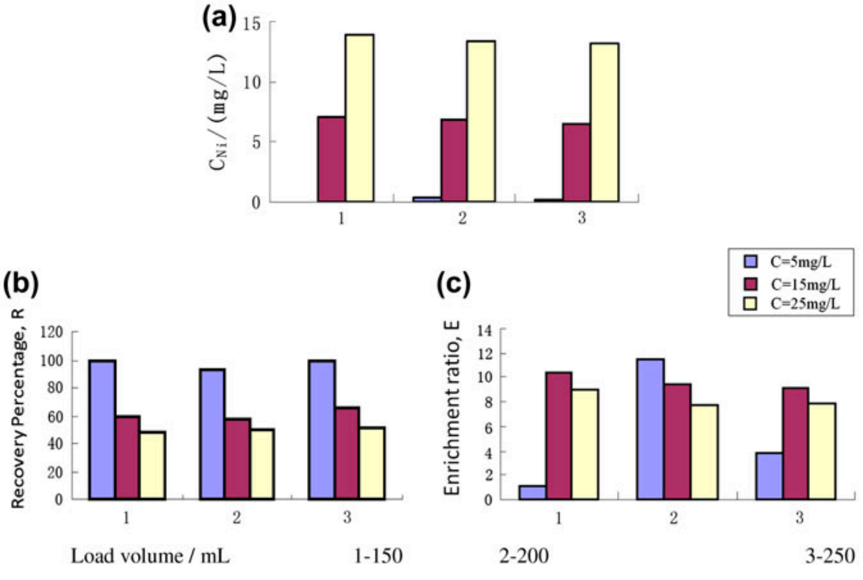

Fig. 4. Effect of loading volume on the process of foam fractionation: (a) effect on the residue concentration, (b) effect on recovery percentage and (c) effect on enrichment ratio.

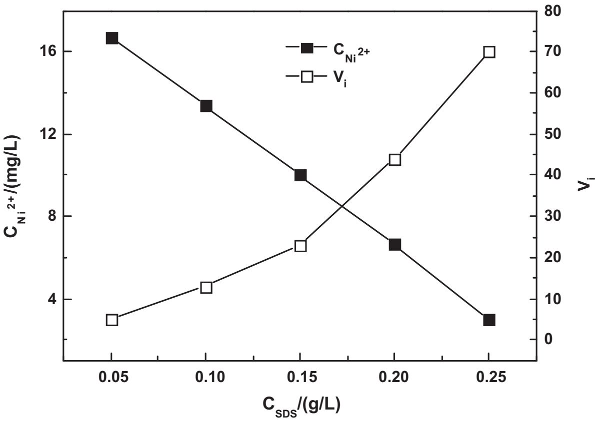

Fig. 5. Effect of surfactant concentration on Ni^{2+} separation efficiency and foam volume.

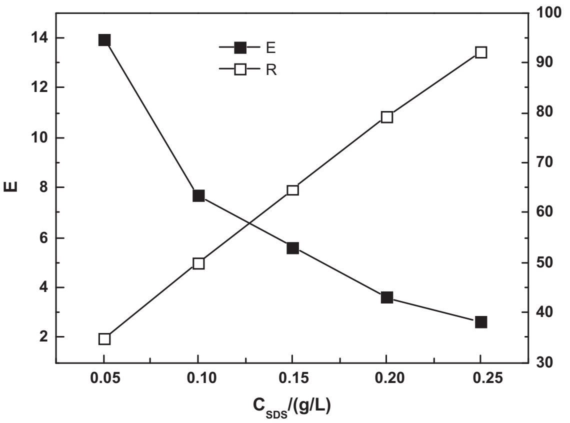

Fig. 6. Effect of surfactant concentration on Ni^{2+} enrichment and recovery percentage.

the residual concentration of nickel ions became 3.0 mg/L and the recovery percentage was 92.21%. When the concentration of SDS is 0.05 g/L, enrichment ratio approached to 14.0, while the recovery percentage was only 34.87%.

Fine and stable bubbles were easily acquired when the concentration of SDS reached a certain value, which was conductive to the separation of nickel ion. However, the increased concentration of SDS led foam volume increasing, resulted in the decrease in enrichment ratio. When the concentration of SDS was too high, all solution was formed to foam which made the separation meaningless.

3.5. Effect of time on separation

Effects of separation time on separation efficiency of Ni^{2+} ions were carried out under the concentration

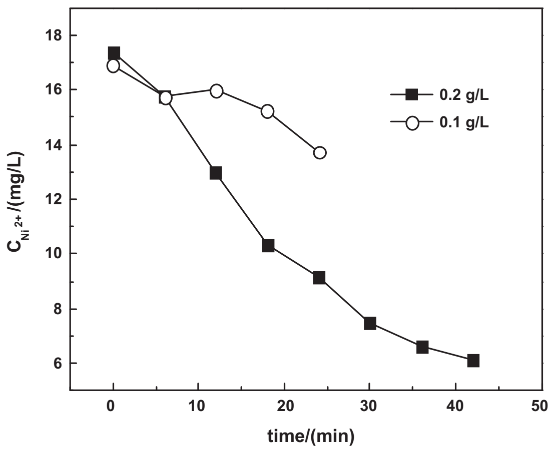

Fig. 7. Effect of separation time on Ni^{2+} separation efficiency.

of surfactant, concentration of initial Ni^{2+} concentration, conditions of temperature, initial pH, airflow rate and loading liquid volume fixed at 0.1 g/L, 25 mg/L, 30.0℃, 5.68, 70 mL/min and 200 mL, respectively. The results are shown in Fig. 7.

Fig. 7 shows that longer separation time led lower residual concentration of nickel ions. When the concentration of SDS was 0.1 g/L, the residual concentration of nickel ions decreased at the initial stage, followed with a stable period for 5–10 min, then decreased slowly. No foam was formed after 25 min. Explanation for this result was that little SDS molecules left in the solution made the contact time of SDS molecules and Ni^{2+} shorter and difficult to achieve 1:1 combination. Less SDS molecules to contact with nickel ions made that nickel ions left more in the residue solution. When the concentration of SDS was 0.2 g/L, the concentration of residue nickel ion decreased quickly and after 35 min, the concentration decreased slowly. Conclusion could be made that in condition of high nickel ion concentration, more surfactant was required to reach a higher recovery percentage. However, too much SDS would also produce a large amount of foam which made the separation process meaningless. These results indicated that foam separation could perform better at low metal ion concentration.

4. Conclusions

Non-surface active aqueous Ni^{2+} ions were made surface active with the aid of the well-known surfactant—SDS and DBSA. Ni^{2+} recovery from wastewater has been investigated via foam fractionation in a batch mode using anionic surfactant SDS and DBSA. At the initial stage of bubble production, stable foams were formed and rose up through the column to make the small foamate phase, in which Ni^{2+} was successfully concentrated with the surfactant. The recovery percentage of Ni^{2+} increased coordinated with an increase in the surfactant concentration and the airflow rate, and decreased with an increase in the Ni^{2+} concentration. The enrichment ratio of Ni^{2+} was improved by extending the drainage section of column, but deteriorated by increasing the concentrations of the surfactant and metal.

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