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Column separation of nickel and cobalt using a microencapsulated extractant

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ABSTRACT

The adsorption of nickel, cobalt, copper and zinc onto microcapsules containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) was investigated. Through scanning electron microscopy imaging of the microcapsule-surface and neutralization titration estimation of the amount of EHPNA extractant remaining in the microcapsule, the microencapsulated extractant was characterized. The equilibrium of adsorption for each of the metals was measured and applied to a Langmuir adsorption isotherm, and from this and the metal adsorption rates, it was estimated that both the formation of a metal complex and its diffusion through the pores of the microcapsule contribute to the overall adsorption rate of the metals. Furthermore, the separation ability of the metals was found to be enhanced by reducing the flow rate of the feed solution or increasing the height of the packed column. By repeating the adsorption–desorption of a Ni–Co mixture five times, the Ni and Co were effectively separated.

1. Introduction

There has been a recent increase in demand for a number of valuable metals such as nickel and cobalt that are commonly used in materials such as electronic devices and lithium ion battery electrodes, but which cannot be obtained as a raw material in Japan. This has therefore created a growing need to separate and recover such metals from waste water and recycled materials. In the case of industrial waste treatment, only very dilute aqueous solutions of valuable metals are obtained, which requires new technology to be developed.

Various methods already exist for the recovery of metals from aqueous solutions, with liquid–liquid extraction methods having been the most commonly employed so far (Hino et al., 1997; Kondo and Matsumoto, 1996; Lo et al., 1983; Mandar and Dhadke, 1999). In this, a solution containing an extractant is contacted with a metal-containing aqueous solution in order to form a metal complex, which is then extracted in an organic solution. However, despite the wide use of this method for the extraction and separation of metals, it requires a large amount of reagents and solvents. Furthermore, separation of the aqueous and organic solutions after metal extraction can tend to be difficult.

Over the last several decades, alternative techniques for the solvent extraction of metals from dilute solutions have been developed, with typical examples including: supported liquid membranes (Fu et al., 2004), emulsion liquid membranes (Kondo and Matsumoto, 1998), solvent impregnated resins (Cortina and Warshawsky, 1997) and microcapsules containing a metal extractant (Kamio and Kondo, 2002a, 2002b; Kamio et al., 2002, 2005; Kiyoyama et al., 2007; Kondo et al., 2007; Ngomsik et al., 2006; Nishihama et al., 2002; Singh and Srivastava, 2005). In the case of the latter, "microcapsule" refers to an extremely minute container (a diameter of about several μm), which is usually fabricated through a chemical technique that incorporates radical polymerization (Kondo, 1991). These microcapsules are usually packed in a column, and offer a number benefits over liquid–liquid extraction such as the ability to select a suitable extractant and monomer for a specific purpose (Kamio et al., 1999). In this study, we therefore explore the use of microcapsules as an alternative method for the recovery and separation of nickel and cobalt from a solution containing Ni, Co, Cu and Zn.

2. Experimental

2.1. Reagents

The metal extractant used in this study was 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (abbreviated as EHPNA hereafter), which was kindly supplied by Daihachi Chemical Industry Co. Ltd., Osaka, Japan and was used without further purification. The monomer used to make the polymer matrix of the microcapsules was divinylbenzene (DVB), with 2, 2′-Azobis(2, 4-dimethylvaleronitrile) (ADVN) used as the polymerization initiator and toluene employed as a DVB diluent. All chemicals used were JIS special grade reagents.

For the metal source, JIS special grade $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and $ZnCl_2$ powders were dissolved in aqueous solutions

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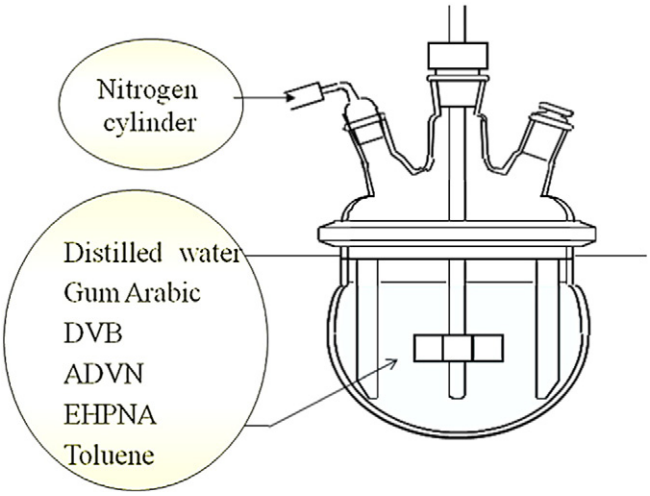

Fig. 1. Reactor for the preparation of microcapsule.

of 0.1 mol/dm^3 HCl–0.1 mol/dm^3 NH_3 to give the desired concentration of metal ions. The pH of each solution was adjusted using a pH meter (Horiba F-21).

2.2. Preparation and characterization of the microcapsules

The reactor used for the preparation of the microcapsules is shown in Fig. 1. In this, distilled water containing 2 wt.% Arabic gum which is the continuous phase was stirred using a flat paddle. Once the temperature of this continuous phase reached 343 K, a dispersed phase consisting of DVB, ADVN, toluene and EHPNA was added. This mixture was then agitated at 300 rpm for 3 h at 343 K under a nitrogen atmosphere. The microcapsules obtained under the conditions listed in Table 1 were filtered from the solution and rinsed with distilled water, and then dried at room temperature. They were then sifted through several screens of increasing mesh size, with their particle size measured using a laser diffraction particle size analyzer (Shimadzu SALD-2000A). The surface of the microcapsules was also observed by a scanning electron microscopy (Hitachi SEM S2460N).

Table 1
Preparation condition of microcapsule.

	Materials	Weight [g]
Continuous phase	Distilled water	882
	Arabic gum	18.0
Dispersed phase	DVB	15.0
	ADVN	3.6
	EHPNA	18.8
	Toluene	18.8

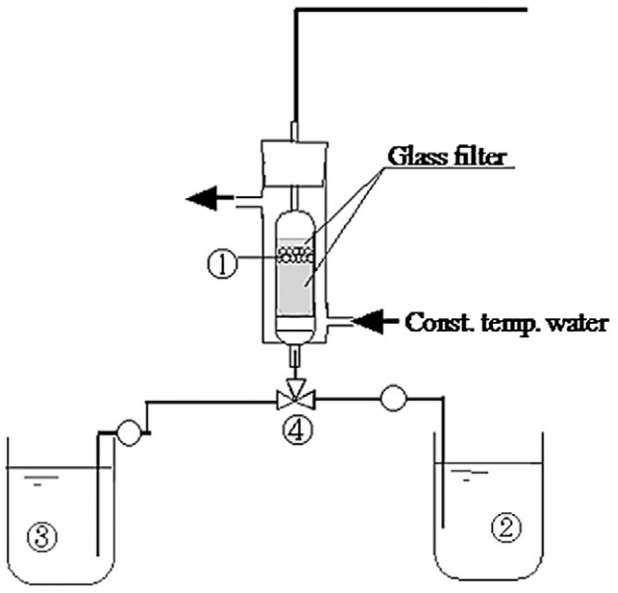

Fig. 2. Shallow bed reactor. ① Microcapsule; ② feed solution; ③scrubbing solution; ④ three-way cock.

The amount of extractant encapsulated in each of the microcapsules was measured as follows: First, 0.1 g of microcapsules was mixed with 50 cm^3 of methanol and left for 1 d, after which the microcapsules were separated out by filtration. The EHPNA content of the methanol solution was then determined by titration with a 0.05 mol/dm^3 NaOH solution using phenolphthalein as the indicator, from which the amount of extractant encapsulated in the microcapsules was determined.

2.3. Adsorption equilibrium of Ni, Co, Cu and Zn on the microcapsules

2.3.1. Adsorption behavior of a single metal system

A 10 cm^3 aliquot of each of the aforementioned metal salt solutions (the initial concentration of which varied from 0.001 to 0.03 mol/dm^3)

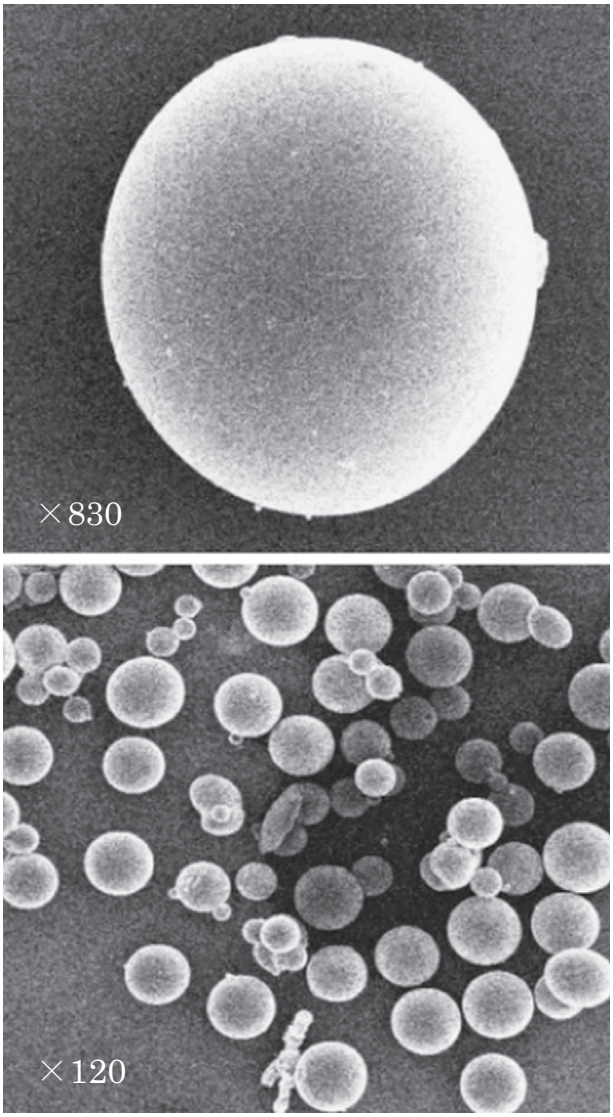

Fig. 3. SEM image of microcapsule.