Extraction of Nickel(II) and Zink(II) by Using A Solvent Impregnated Resin Containing 1-Nitrophenyl-3-methyl-4-octylbenzoyl-5-pyrazolone

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Abstract

The study on the equilibrium distribution of nickel(II) and zink(II) between aqueous solution and macromolecular resin impregnated with 1-nitrophenyl-3-methyl-4-octylbenzoyl-5-pyrazolone (HNPMOBP, HL) have been conducted. In this research, the effects of pH values, and metal ion concentration on the yield were investigated. Analysis of the results shows that the extraction of the two metal ions can be explained assuming the formation of metal complexes in the resin phase with a general composition ML_2. An extraction reaction is proposed and the equilibrium constants of the complexes were determined to be -6.15 and -3.45. The efficiency of the resin in the separation of nickel (II) and zink(II) is provided according to the separation factors. Under the experimental conditions employed, pH_{50} values for zink (II) and nickel(II) were respectively found to be at 2.76 and 4.95.

Key words: Extraction, Zink, Nickel, Solvent impregnated resin, 1-nitrophenyl-3-methyl-4-octylbenzoyl-5-pyrazolone

Introduction

Solvent extraction and ion exchange techniques have been widely used as a basic technique for the separation of metal ions from aqueous solutions. However, recovery and separation by solvent extraction requires multiuse extraction and back-extraction in order to attain the sufficient separation. Also, ion exchange resins have lower extraction selectivity for transition metals with respect to alkali metals. As an alternative approach, solvent impregnated resins (SIR) have been proposed by Warshawsky (Warshawsky, 1981) for selective separation of metal ions by direct adsorption of the extractant into macroporous polymeric supports.

In the last decades, the study of SIR has been a major field of research in separation science, and they could be considered as a link between solvent extraction and ion-exchange technologies (Cortina and Warshawski, 1997). The SIR concept is based on the incorporation of a solvent extraction reagent into a porous polymer by a physical impregnation technique.

Recently, solvent impregnated resins have been used in the extraction of metals from a multicomponent mixture in various analytical applications. The impregnated extractants include acidic organophosphorus compounds such as di(2-ethyl-hexyl)phosphoric acid, and 2-ethylhexylphosphonic acid mono-2-ethylhexylester, bifunctional organophosphorus compound. Some other extractants such as tri-n-octylamine, quaternary alkylammonium

salts, tri-n-dodecylammonium chloride, 1-(2-pyridylazo)-2-naphthol and crown ethers have also been used (Mu et al., 2008).

Since the separation of nickel and zink are of great importance and some SIR containing organophosphorus acids and pyrazolone derivative have been proved to be effective, the sorption and separation of these two metals with various SIR containing organophosphorus acids are very attractive. The investigation of nickel and zink extraction by solvent-impregnated resins containing 1-nitrophenyl-3-methyl-4-octylbenzoyl-5-pyrazolone (HNPMOBP, HL) is the subject of this study. The extracted complexes are suggested and the equilibrium constants of the extracted complexes are calculated and The Freundlich isotherm have also been determined.

Materials and Methods

Procedure

The extractant, 1-nitrophenyl-3-methyl-4-octylbenzoyl-5-pyrazolone (HNPMOBP) was sintesized (Khaldun et al., 2014). The resins of Amberlite XAD-16 was supplied by Rohm & Haas. The resins was washed with 2 mol.L^{-1} HNO_3, 2 mol.L^{-1} NaOH, pure water and acetone, successively, and then were dried in vacuo before use.

The impregnation of HNPMOBP into the resins (50/ 50 wt.%) is carried out in the following way: a 10-g portion of HNPMOBP was diluted with 50 cm of acetone. To this solution was added 10 g of the resin. The mixture was stirred under the reduced pressure followed by evaporation of the acetone. The products were dried in vacuo at 50^{0}C.

The content of HNPMOBP in the resin is determined to be 1.25 mmol/g by titrating with standard NaOH after shaking the resin in ethanol for 5 h.

Stock solutions of MCl_2 (M = nickel, zink) were prepared with AR Chemicals (Merck). The pH values of aqueous solutions were adjusted by the addition of a small amount of HCl or NaOH solution. All extraction experiments were performed at constant ionic strength (0.2 mol/L NaCl). The concentrations of Ni(II) and Zn(II) in aqueous phase were determined by atomic absorption spectroscopy method (AAS, AA-6300 Shimadzu). All the other reagents used in this study were of analytical reagent grade.

All the experiments of metal ions extraction were carried out batchwise at 303 ± 1 K except for the temperature experiments. Samples of resin containing HNPMOBP and 5 mL aqueous solution of Ni(II) or Zn(II) were introduced into special glass-stoppered tubes and shaken to achieve equilibrium. After phase separation with a high-speed centrifuge the concentration of M(II) in the aqueous phase was analyzed by AAS. The amount of M(II) extracted on the resin was determined by material balance and distribution ratio (D) of metal ions was calculated by using the following formula:

$$D = \frac{V}{m} \cdot \frac{C_0 - C}{C} \quad (1)$$

where V represents the volume of the aqueous phase (mL), m stands for the mass of dry resin (g), C_0 and C denote the initial total concentration and the equilibrium concentration of metal ions in aqueous phase respectively.

Results and Discussion

Extraction stoichiometry

In preliminary experiments, it was determined that Cl^- ions are not co-extracted by the resin phase, the extraction of Ni(II) and Zn(II) with the resin can thus be expressed as the following general reaction (Cortina et al, 1996).

$$M^{2+} + (n+q)HL_{(r)} \leftrightarrow ML_n(HL)_{q(r)} + nH^+ \quad (2)$$

where r denotes the resin phase; q and n denote unknown coefficients. Figure 1 shows the metal distribution data from aqueous solutions of 0.2 mol/L (Na, H) Cl with HNPMOBP impregnated resin as log D versus pH. The distribution functions are straight lines with a slope of about 2 for both Ni(II) and Zn(II), indicating that 2 protons are released in the extraction reaction of metal ions by the resin phase. Equation (2) can thus be written as (3):

$$M^{2+} + (2+q)HL_{(r)} \leftrightarrow ML_2(HL)_{q(r)} + 2H^+ \quad (3)$$

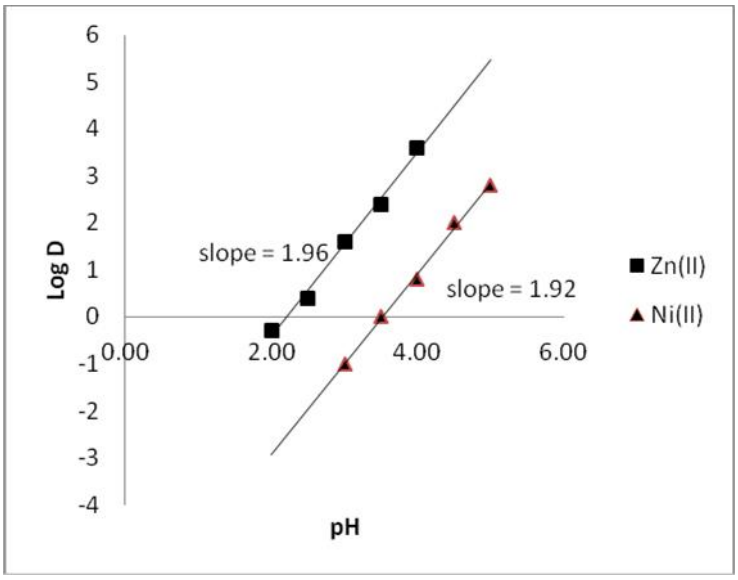

Figure 1. Effect of equilibrium pH on the extraction of Zn(II) and Ni(II) with HNPMOBP impregnated resin. m_{resin} = 0.05 g, cHNPMOBP = 1.25 mmol/g, $[M^{2+}]$ = 35.0 µg/mL, [(Na,H)Cl] = 0.20 mol/L

The stoichiometric equilibrium constant, K_{eq} , for the extraction can thus be expressed as:

$$K_{eq} = \frac{[ML_2(HL)_q]_{(r)}[H^+]^2}{[M^{2+}][HL]_{(r)}^{2+q}} \quad (4)$$

The distribution ratio for M^{2+} becomes:

$$D_c = K_{ex}[HL]_{(r)}^{2+q}[H^+]^{-2} \quad (5)$$

$$\log D_c - 2pH = (2+q)\log[HL]_{(r)} + \log K_{eq} \quad (6)$$

where $[HL]_{(r)}$ can be calculated according to $[HL]_{(r)} = [HL]_{(r),0} - (2+q)[M^{2+}]_{(r)}$; $[HL]_{(r),0}$ denotes the initial HNPMOBP content in the sorbent.

The data shown in Fig. 1 indicate that Zn(II) can be extracted at lower pH values than Ni(II), which is in accordance with previous results (Innocenzi and Veglio, 2012). However, it is difficult to compare the extraction by HNPMOBP impregnated resin with that by HNPMOBP in solvent extraction since the studies concerning extraction of Zn(II) and Ni(II) using HNPMOBP from chloride media are insufficient as mentioned above.

Extraction isotherms

The concentration dependence of Zn(II) and Ni(II) extraction on HNPMOBP impregnated resin was studied at a fixed pH value and amount of adsorbent. The data for the extraction has been analyzed in terms of the Freundlich isotherm. It was found that this equation was capable of describing the data over the entire range of concentration studied. The Freundlich isotherm can be expressed as [7]:

$$q = kC^{1/n} \quad (7)$$

The validity of the Freundlich isotherm was further confirmed by the regression analysis of the equilibrium date and are represented in the form of simple straight-line equation as [8]:

$$\log q = \frac{1}{n}.logC_0 + logk \quad (8)$$

where C_0 is the initial concentration of M^{2+}, k and 1/n stand for Freundlich constants. The values of logk and 1/n for M^{2+} can be determined according to the slope and intercept values in Fig. 2.

For Zn(II): log q= 0.7667 logC_0 +2.71 (R^2 = 0.9981),
For Ni(II): log q= 0.5333 logC_0 +1.62 (R^2 = 0.9846).

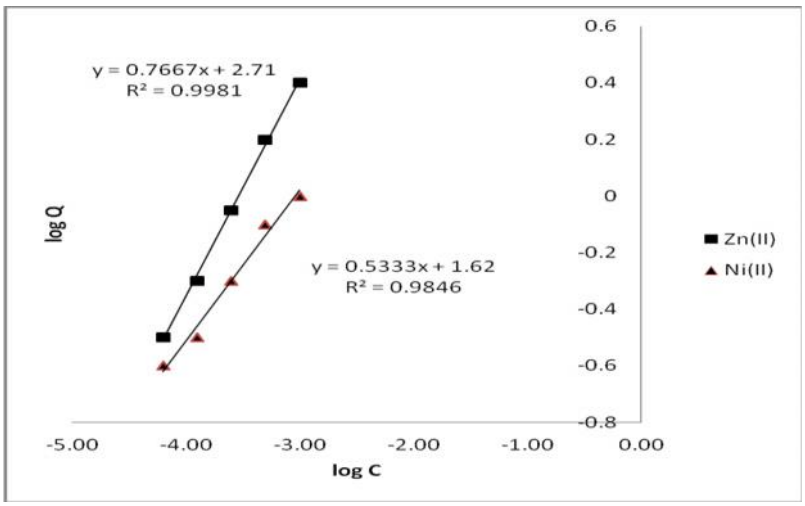

Figure 2. Effect of M^{2+} concentration on the extraction of Zn(II) and Ni(II) with HNPMOBP impregnated resin. mresin = 0.05 g, cHNPMOBP = 1.25 mmol/g, [(Na,H)Cl] = 0.20 mol/L

Freundlich isotherm model, does not have any restriction on the sorption capacity of the sorbent, and is more appropriate in situations where the sorption sites possess a heterogeneous nature.

Conclusions

Solvent impregnated resins containing HNPMOBP were used for the extraction and separation of zink(II) and nickel(II). The extraction stoichiometry is proposed and equilibrium constants of the extracted species are determined. A general composition, ML_2, is formed for both zink (II) and nickel (II). HNPMOBP contained in the resin behaves in the same extraction order as that in the organic diluents in solvent extraction, i.e. zink(II) is extracted at lower pH values than nickel (II). pH_{50} values for zink (II) and nickel (II) were

determined as 2.76, 4.95, respectively, which provides the possibility to separate these two metal ions. Freundlich's isothermal equations have also been obtained.

Acknowledgements

This research was supported by P2M DIKTI (Directorate of Higher Education) Ministry of Education, Indonesia through "Hibah Bersaing" Research Grand 2015 for the financial support.

References

Cortina, J.L., and Warshawsky, A. (1997). Ion Exchange and Solvent Extraction, p. 195. Dekker, New York.

Cortina, J.L.,Miralles, N., Aguilar, M., Sastre, A.M. (1996). Distribution studies of Zn(II), Cu(II) and Cd(II) with Levextrel resins containing di (2,4,4_trimethylpentyl) phosphinic acid (Lewatit TP807'84), Hydrometallurgy,40(1–2): 195–206.

Innocenzi, V., and Veglio F. (2012). Separation of mangan, zinc and nickel from leaching solution of nickel-metal hydride spent batteries by solvent extraction, Hydrometallurgy, 129-130: 50-58.

Khaldun, I., Rusman, and Amiruddin (2014). Ekstraksi nikel dan kobal dari bijih limonit dengan metode solvent impregnated resin menggunakan ekstraktan 1-nitrophenyl-3-methyl-4-octylbenzoyl-50pyrazolone hasil sintesis, Laporan Penelitian Hibah Bersaing, Universitas Syiah Kuala.

Mu, F.T., Jia, Q., Tian, Y.M., and Shang, Q.K. (2008). Extraction of Cobalt (II) and nickel (II) by solvent impregnated resin containing bis(2,4,4-trimethylpentyl)monothiophosphinic acid, Adsorption, 14: 31-36.

Warshawsky, A.(1981). Ion Exchange and Solvent Extraction, p. 229. Dekker, New York.