

DEVELOPMENT OF Ni(II) DETERMINATION IN WASTEWATER BASE ON COMPLEXATION BY DIMETHYLGLYOXIME

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ABSTRACT

Complexation of Ni(II) and dimethylglyoxime (DMG), solid particles of reddish-pink complex used to determine Ni(II) ion in wastewater sample, was developed. Increasing of the reddish-pink particles color depended on the Ni(II) concentration increased. Ni(II) ions in water can be determined by comparing to the color chart of known concentrations of Ni(II) ion after detection process. Effect of pH on size and shape of the Ni(II)-DMG complex particles, was studied by scanning electron microscope (SEM). Linearity response for Ni(II) concentrations ranging from 0.5 to 5.0 mg/L. Limit of detection and limit of quantitation were 0.40 and 0.90 mg/L, respectively. The relative standard deviation was less than 5. The developed method showed high recovery. The percentage of recovery was range from 77 to 115. Effect of interference ions were studied by spiked with difference concentration of Mg²⁺, Ca²⁺, Pb²⁺, Hg²⁺, Co²⁺, Cu²⁺, Mn²⁺, Zn²⁺, Fe²⁺, Al³⁺, Cr³⁺, Cl⁻, SO₄²⁻, PO₄³⁻ and CO₃²⁻ in Ni(II) 2 mg/L solution. Al³⁺ and Cr³⁺ ions could be interfere the Ni(II) determination.

KEYWORDS: Ni(II) ion; complexation; dimethylglyoxime

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INTRODUCTION

Nickel occurs naturally in the environment at low levels. Nickel dermatitis, consisting of itching of the fingers, hands, and forearms, is the most common effect in humans from chronic (longterm) skin contact with nickel [1–2]. Human and animal studies have reported an increased risk of lung and nasal cancers from exposure to nickel refinery dusts and nickel subsulfide. Animal studies of soluble nickel compounds (i.e., nickel carbonyl) have reported lung tumors [2]. Limit of nickel in discharged waste water was less than 1.0 mg/L [2].

Colorimetric method is a method of determining the concentration of an element or compound in a solution with the aid of a color reagent. The method is widely used in medical laboratories and industrial purposes, including the analysis of water samples in connection with industrial water treatment. The Ni(II) determinations are base on the nickel dimethylglyoxime complex using colorimetric solid phase extraction [1], Nickel(II) ions sensing properties of dimethylglyoxime/poly(caprolactone)

electrospun fibers [2], colorimetric sensor using coumarin derivatives [3], Fabrication of paper-based devices by lacquer spraying method [4]. Thus, this study was developed the method for measure the Ni (II) in the wastewater before discharge. Ni(II)-DMG complexation reaction was showed in figure 1.

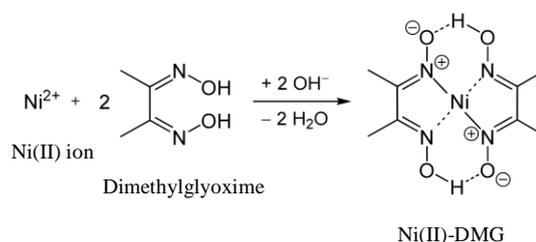


Fig. 1 The reaction of Ni(II) and DMG formed to Ni(II)-DMG complex.

MATERIALS AND METHODS

Chemical and apparatus

Fe, Hg and Co standard solutions, analytical grade, were purchased from Perkin Elmer, U.S.A. Ni, Cr, Al, Cu, and Mg standard solutions, analytical grade, were purchased from Merck, Germany. Methanol, citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) and nitric acid, analytical grade, were purchased from J.T. Baker, U.S.A. Tri-sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), analytical grade, was purchased from QReC, New Zealand. Di-sodium hydrogen orthophosphate (Na_2HPO_4) and potassium hydrogen phthalate ($KHC_8H_4O_4$), analytical grade, were purchased from APS Finechem, Australia. Sodium tetraborate ($Na_2B_4O_7$), sodium tetraborate ($Na_2B_4O_7$), and potassium dihydrogen orthophosphate (KH_2PO_4), analytical grade, were purchased from Ajax Finechem, Australia. Dimethyl glyoxime ($C_4H_8N_2O_2$) and sodium sulphate (Na_2SO_4), A.C.S. grade, were purchased from SIGMA-ALDRICH, Germany. Sodium Carbonate (Na_2CO_3), analytical grade, was purchased from fluka, Switzerland. Deionized water was obtained from a Milli-Q water purification system.

The reddish-pink Ni-DMG particles was filtered using whatman NO. 1, diameter 25 mm, and analysis at 540 nm by UV-VIS-NIR Spectrophotometer. The size and shape were detected by scanning electron microscope (SEM). Ni concentrations were analysed by ICP-OES.

Test pH

The 2 mg/L and 8-ml of Ni(II) was mixed with the 2-mL of buffer solution (pH 3–11). Then, the dimethylglyoxime solution (0.022M, 0.1 mL) was added into the mixed solution, stirred and incubated for 10 min for the Ni-DMG formation reaction complete. The reddish-pink Ni-DMG particles was filtered using whatman NO. 1, diameter 25 mm, and analysis at 540 nm by UV-Vis-NIR spectrophotometer. The size and shape were detected by scanning electron microscope (SEM).

-pH 3 was prepared from $Na_3C_6H_5O_7 \cdot 2H_2O$ 0.05 M, dissolved $Na_3C_6H_5O_7 \cdot 2H_2O$ 1.47 g with deionized water, then adjust pH by 0.05 mol/L of citric acid solution and adjust volume of solution to 100 mL by deionized water.

-pH 5 was prepared from $C_8H_5O_4K$ 0.05 M, dissolved $C_8H_5O_4K$ 1.02 g with deionized water, then adjust pH by 0.10 mol/L of sodium hydroxide solution and adjust volume of solution to 100 mL by deionized water.

-pH 7 was prepared from KH_2PO_4 0.1 M, dissolved KH_2PO_4 1.36 g with deionized water, then adjust pH by 0.10 mol/L of sodium hydroxide solution and adjust volume of solution to 100 mL by deionized water.

-pH 8–10 were prepared from $Na_2B_4O_7 \cdot 10H_2O$ 0.013 M, dissolved $Na_2B_4O_7 \cdot 10H_2O$ 0.495 g with deionized water, then adjust pH by 0.10 mol/L of sodium hydroxide or hydrochloric acid solution, and adjust volume of solution to 100 mL by deionized water.

-pH 11 was prepared from Na_2HPO_4 0.05 M, dissolved Na_2HPO_4 1.46 g with deionized water, then adjust pH by 0.10 mol/L of sodium hydroxide solution, and adjust volume of solution to 100 mL by deionized water.

Study of cation and anion interferences

Cation (Fe^{2+} , Hg^{2+} , Co^{2+} , Cr^{3+} , Al^{3+} , Cu^{2+} , Mg^{2+} 2 and 5 mg/L) and anion (PO_4^{3-} , SO_4^{2-} , CO_3^{2-} 100 mg/L) interferences were determined in the same of test pH method. The test method used the sodium tetraborate buffer (pH 9) for the further experiments.

Test method

The linearity range, limit of detection (LOD), limit of quantitation (LOQ) repeatability, accuracy and ion interference were determined in the same of test pH method. The Test method used the sodium tetraborate buffer (pH 9) for the further experiments.

RESULTS AND DISCUSSION

Effect of pH

The pH in the range of 3 to 10 on a shape and particle size of Ni(II)-DMG were determined. The pH of 3 and 5 did not complexation between Ni(II) and DMG while the pH was between 7 and 11 appeared. The SEM microstructure of Ni(II)-DMG indicated the particle shape was hollow square, the complex was distributed and wide in the range of 0.11 to 0.68 μm , small and big size was combined at pH 7–11 (Fig. 2). Sodium tetraborate buffer (pH9) showed the uniform particle shape, size and color of Ni(II)-DMG. The shape of Ni(II)-DMG particles was a hollow square shape and the size of Ni(II)-DMG particles was 0.43 μm . Thus, pH 9 was selected for the further experiments.

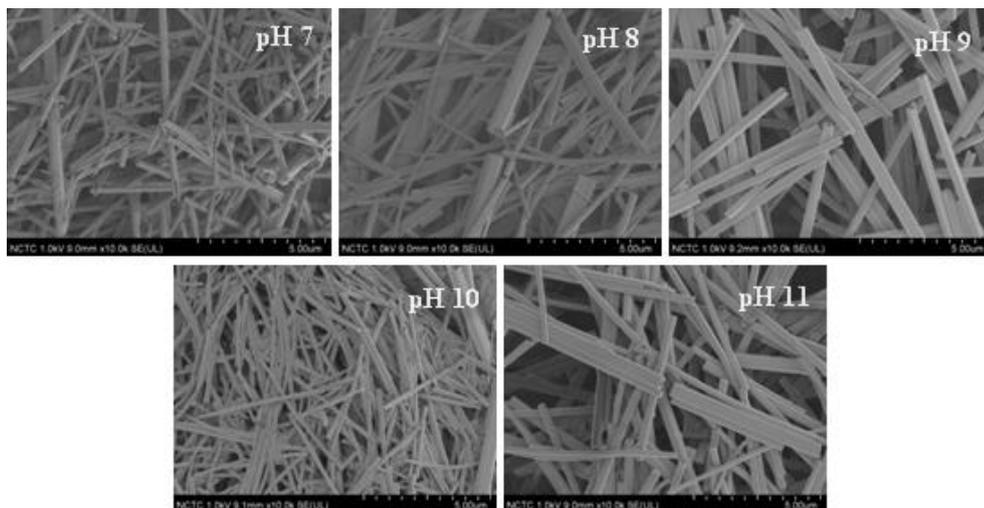


Fig. 2 SEM images of Ni(II)-DMG formed at different pH solution.

Linearity range

The chart color and standard graph were prepared by complexation of different Ni(II) concentration and DMG. The Ni(II)-DMG complex was detected at 540 nm. Absorbance was increased when Ni(II) concentration increased (Fig. 3). The standard graph was plotted between concentration of Ni(II) and absorbance at 540 nm. The graph was linear in the range of 0.5 to 5.0 mg/L. The linear regression was 0.9981.

The maximum concentration of Ni(II) formed the complex with 0.02 M of DMG was determined. The Ni(II) concentration varied from 0.5 to 50 mg/L and analysed by ICP-OES. Figure 4 indicated the Ni(II) concentration range from 0.5 and 12.5 mg/L was complete complexation but it was more than 12.5 mg/L be excess and had Ni(II) residue after complexation (Fig. 4).

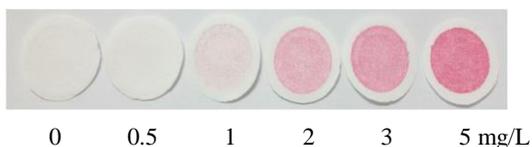


Fig. 3 The chart color was prepared by complexation of different Ni(II) concentration and DMG

Cations and anions interference

The ion interferences on Ni(II) determination were studied. The Mg^{2+} , Fe^{2+} , Co^{2+} and Cu^{2+} were affected a little by showed the recovery as 118, 83, 87 and 119%, respectively. Al^{3+} , Hg^{2+} and Cr^{3+} were interfered on the Ni(II) determination by showed the recovery was lower 28%. Hg^{2+} did not interfered on the Ni(II) determination at 2.0 mg/L by showed the recovery

was 98%. The SO_4^{2-} , PO_4^{3-} and CO_3^{2-} at 100 mg/L were not interfered on Ni(II) determination by showed the recovery as 91, 107 and 117%, respectively (Fig. 5).

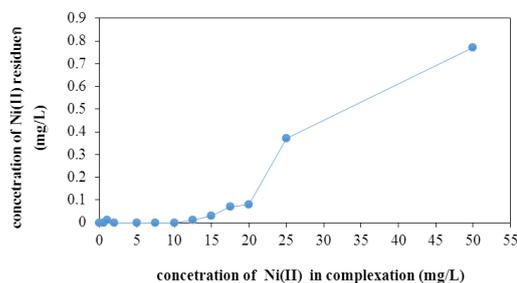
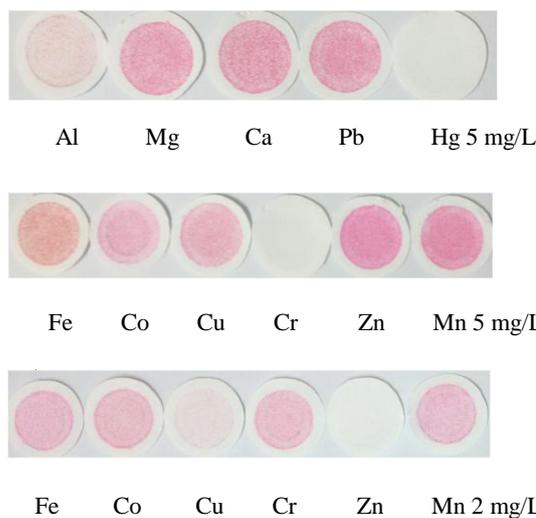


Fig. 4 The relation of Ni(II) concentration was added and residued after filter.



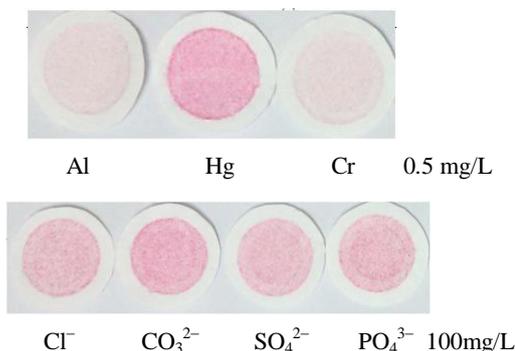


Fig. 5 The photographs of the color membrane obtained from the detection of 2 mg/L of Ni(II) in the presence of different anions at pH 9 and 10 mL of sample volume.

Method validation of Ni(II) determination

Limit of detection (LOD) and Limit of quantitation (LOQ) were determined by Ni(II) concentration analysis in blank solution for seven replicates. LOD and LOQ were 0.40 and 0.90 mg/L, respectively. The precision and accuracy were studied by spiked Ni(II) 2 mg/L and analysis for seven replicates. The developed method was high precision, repeatability and accuracy. The standard deviation was 0.1. The relative standard deviation was 3.9%. The percentage of recoveries of Ni(II) determination in blank solution, tap water and wastewater sample from textile factory treated before discharge was determined. The developed method showed high recovery. The percentage of recoveries were 115 for blank solution, 103 for tap water and 77 for wastewater. The recovery of blank solution and tap water were higher than the recovery of wastewater because they had less matrices while wastewater had high matrices as organic compounds and ion interference as Cr^{3+} and Al^{3+} .

CONCLUSION

It was found that the Ni(II) solution at pH 9 gave the most uniform Ni(II)-DMG particles in size and shape. This method had the linear range between 0.5 and 5.0 mg/L. LOD and LOQ were 0.40 and 0.90 mg/L, respectively. The repeatability and accuracy were good. Al^{3+} and Cr^{3+} were strongly interfered to the Ni(II) determination while Hg^{2+} , Mg^{2+} , Ca^{2+} , Pb^{2+} , Fe^{2+} , Cu^{2+} , Zn^{2+} , Mn^{2+} , Cu^{2+} , Cl^- , CO_3^{2-} , SO_4^{2-} and PO_4^{3-} were poor interfere.

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