เมมเบรนที่มีไดเมทิลไกลออกซีมสำหรับตรวจวัดไอออนนิกเกิล

Membranes Containing Dimethylglyoxime as Optical Sensors for Nickel Ion Detection

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บทคัดย่อ

ในการเตรียมเมมเบรนพอลิไวนิลคลอไรด์ที่มีไดเมทิลไกลออกซีมสำหรับใช้เป็นเซนเซอร์ในการตรวจวัดไอออนของนิกเกิล โดยอาศัยหลักการเกิดสารประกอบเชิงซ้อนสีชมพู $Ni(DMG)_2$ ซึ่งสามารถยืนยันได้ด้วยเทคนิคฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปกโตรสโคปีและเทคนิคยูวี-วิสิเบิลสเปกโตรสโคปี พบว่าความสามารถในการตรวจวัดเพิ่มขึ้นเมื่อเพิ่มปริมาณไดเมทิลไกลออกซีม อย่างไรก็ตามพบว่าค่าการสะท้อนแสงมีค่าแตกต่างกันมากสำหรับเมมเบรนพอลิไวนิลคลอไรด์ที่มีปริมาณไดเมทิลไกลออกซีม 20% ทั้งนี้อาจเป็นเพราะความไม่สม่ำเสมอบนพื้นผิวของเมมเบรน เมื่อใช้พอลิ(สไตรีน-โค-เมทิลเมทาคริเลต)เป็นเมทริกซ์ พบว่าให้ค่าการสะท้อนแสงสูงกว่าเมมเบรนพอลิไวนิลคลอไรด์เล็กน้อย เมื่อศึกษาผลของ pH และความเข้มข้นของสารละลายนิกเกิลต่อการตรวจวัดของเมมเบรนพอลิ(สไตรีน-โค-เมทิลเมทาคริเลต)ที่มีไดเมทิลไกลออกซีม 20% พบว่าค่า pH ที่เหมาะสมอยู่ในช่วง 9.0 - 10.0 และพบค่าการสะท้อนแสงสูงสุดที่ความเข้มข้น 0.8 mM เป็นต้นไป เมื่อศึกษาความจำเพาะเจาะจงของเมมเบรน พบว่าเมมเบรนมีความจำเพาะเจาะจงต่อไอออนของนิกเกิลเท่านั้น อย่างไรก็ตามประสิทธิภาพในการตรวจวัดลดลงในสภาวะที่มีไอออนของโลหะอื่น

ABSTRACT

Polyvinyl chloride containing dimethylglyoxime (DMG) membranes were prepared as optical sensors for detection of nickel ions based on the formation of $Ni(DMG)_2$ complex. The resulting pink complex was confirmed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and Ultraviolet-Visible spectroscopy (UV-Vis). Sensing performance was found to increase with increasing DMG content; however a high deviation was observed in PVC with 20%DMG membrane due to the inhomogeneous surface. The use of poly(styrene-*co*-methyl methacrylate) (PS-*co*-PMMA) as a polymer matrix provided a slightly higher sensing ability compared to that of PVC membranes. The optimized pH range for Ni^{2+} detection of PS-*co*-PMMA containing 20% DMG membrane was 9.0 - 10.0. The maximum reflectance occurred to Ni^{2+} concentrations above 0.8 mM. The membrane was capable of determining Ni^{2+} with a high selectivity over other selected metal ions. However, the performance decreased in the presence of both Ni^{2+} and other metal ions.

คำสำคัญ: สารประกอบเชิงซ้อนนิกเกิล สมบัติทางแสง เซนเซอร์

Keywords: Nickel complex, Optical properties, Sensors

1. INTRODUCTION

The detection of trace metals in environment has gained much attention due to a potential harzard to human and animal organisms. According to EPA's drinking water regulations, nickel level is set below 0.6 ppm for human consumption. At higher nickel concentrations, it has been shown to be lethal to several aquatic species. Various methods have been developed for the detection of nickel, including atomic absorption spectroscopy, mass spectrometry (Kato et al., 2012; Mochizuki et al., 1990), spectrophotometry (Tôel et al., 1975), electrochemical method (Baldwin et al., 1986), colorimetric analysis and ion exchange.

Recently, electrospun poly(caprolactone) fibers containing dimethylglyoxime (DMG) were used as dipping optical sensors for Ni^{2+} detection based on the complex formation between nickel and DMG (Poltue et al., 2011). The resulting red $Ni(DMG)_2$ complex showed an absorbance peak at 547 nm. Ponnuswamy and Chyan (2002) also developed a DMG probe using attenuated total reflectance infrared spectroscopy (ATR-IR) for the detection of nickel ions. It was found that sensing performance depended on the solution pH, and the suitable pH operation range was 6 - 8.

In this work, DMG-doped membranes were prepared as dipping optical sensors for

Ni^{2+} detection. The effects of DMG content and polymer matrix on sensing performance were studied. Complex formation between Ni^{2+} and DMG was confirmed using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and Ultraviolet-Visible spectroscopy (UV-Vis). The influences of pH and Ni^{2+}concentration on sensing ability were investigated along with the selectivity and interference of other metal ions.

2. MATERIALS AND METHODS

2.1 Materials

Polyvinyl chloride (PVC, M_W 43,000, M_n 22,000), poly(styrene-*co*-methyl methacrylate) (PS-*co*-PMMA, ~40 mol% styrene, M_w 100,000 - 150,000) and dimethylglyoxime (DMG, ≥ 99%) were purchased from Sigma-Aldrich (U.S.A.). Tetrahydrofuran was supplied from Fluka Chemical (U.S.A). Nickel (II) sulfate hexahydrate and cobalt (II) nitrate hexahydrate were purchased from Guangdong Guanghua Chemical Factory Co. Ltd (China). Iron (III) nitrate nonahydrate was obtained from Merck. Zinc (II) chloride, silver (I) nitrate, lead (II) nitrate and 30% ammonia solution were supplied by Carlo Erba Reagents (Thailand). Copper (II) nitrate hemipentahydrate and manganese (II) sulfate monohydrate were obtained from Ajax Finechem (Thailand). All chemicals were used as received.

2.2 Membrane preparation

A 5 wt.% polymer solution was prepared by dissolving polymer (PVC or PS-*co*-PMMA) and DMG (10% or 20% by weight of polymer) in tetrahydrofuran (THF). The solution was stirred for 24 h prior to casting on a petri dish. The membrane was dried at room temperature, and later peeled off. PVC membrane and PS-*co*-PMMA membrane in the absence of DMG were prepared similarly, and used as blank samples.

2.3 Characterization

Membranes were gold-coated prior to imaging by a Scanning Electron Microscope (SEM, SEC Co., Ltd., SNE-4500M). Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were measured on a Bruker FTIR spectrometer (Tensor 27) with Opus 7.0 software. Reflectance was measured using UV-VIS-NIR scanning spectrophotometer (Shimadzu, UV-3101PC) with a slit width of 30 nm. The membranes were cut into 1 cm x 1 cm pieces. Membrane thickness was measured with vernier caliper, and the reported value was the mean of four 1 cm x 1 cm samples.

2.4 Detection of Ni^{2+}

Response performance of membranes toward Ni^{2+} was carried out as follows. The membranes were cut into 1 cm x 1 cm pieces. Aqueous nickel (II) sulfate hexahydrate solution (1.0 mM) was prepared, and pH was adjusted to 9.0 using ammonia solution (30%). The cut membrane was then immersed in 25.00 mL of Ni^{2+} solution for 15 minutes. The membrane was gently blotted dried with paper towel prior to reflectance measurements. Reflectance peak height was calculated from the difference between the reflectance at 600 nm and the reflectance at 548 nm. The mean of two measurements was used for each sample. Error bars represented ± 1 Standard Deviation (SD) from the mean.

3. RESULTS AND DISCUSSION

3.1 Membrane preparation

Free standing membranes were obtained via solvent-cast method. The thicknesses of PVC/10%DMG, PVC/20%DMG, PS-*co*-PMMA/10%DMG, and PS-*co*-PMMA/20%DMG were 0.11, 0.23, 0.14, and 0.16, respectively. SEM images of these four membranes were shown in Figure 1. Smooth surfaces were observed for DMG-doped PS-*co*-PMMA membranes, while rough surfaces were shown for DMG-doped PVC membranes. The higher membrane thickness of PVC/20%DMG membrane could be resulted from its heterogeneous surface.

3.2 Sensing performance

Effects of DMG content and polymer matrix

Sensing performance of the prepared membranes toward Ni^{2+} was studied. Upon immersion in 1.0 mM Ni^{2+} solution for 15 min, a pink complex of Ni^{2+} and DMG could be observed by naked eye. The complex formation was also confirmed by FTIR. Band corresponding to carbonyl group of methyl methacrylate in PS-*co*-PMMA was shown at 1727 cm^{-1} (Figure 2) (Wang et al., 2013). Bands at 2948 and 2869 cm^{-1} were assigned to stretching vibrations of methyl and methylene groups, respectively. Deformation vibration of C-H in phenyl ring appeared at 696 cm^{-1}. N-O vibration and O-H stretching bands of DMG were shown at 979 cm^{-1}, and 3196 cm^{-1}, respectively (Panja et al., 1991). Upon immersion in Ni^{2+} solution, an additional band at 1572 cm^{-1} relating to the C=N stretching in $Ni(DMG)_2$ complex was observed along with the disappearance of the band at 3196 cm^{-1} due to the strong hydrogen bonding between DMG and nickel (Poltue et al., 2011). Furthermore, the formation of the complex was also confirmed through the appearance of reflectance signal at 548 nm.

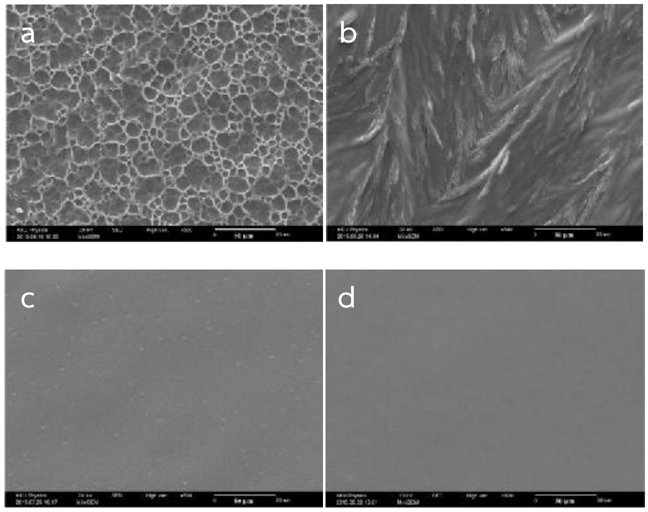

Figure 1 SEM images (500 magnification) of PVC/10%DMG (a), PVC/20%DMG (b), PS-*co*-PMMA/10%DMG (c), and PS-*co*-PMMA/20%DMG (d). Scale bar is 50 μm.

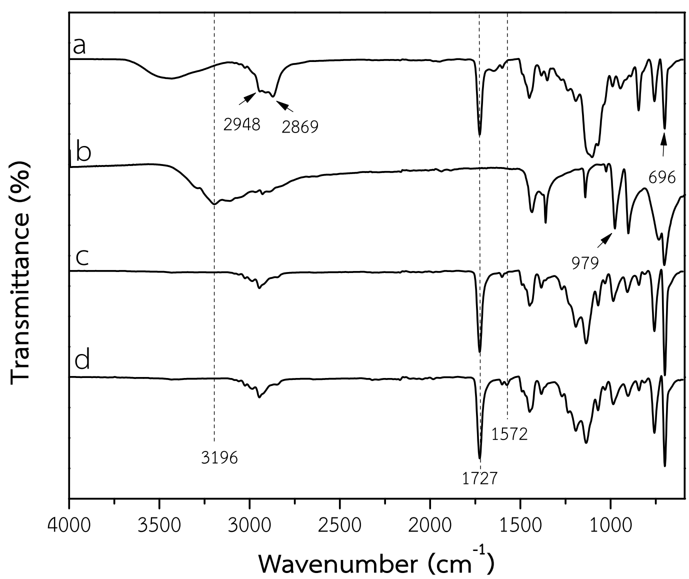

Figure 2 ATR-FTIR spectra of PS-*co*-PMMA (a), DMG (b), PS-*co*-PMMA/20%DMG membrane before (c) and after immersion in 1.0 mM Ni^{2+} solution (d).

Sensing abilities of the four membranes and two blank samples toward 1.0 mM Ni^{2+} solution were compared. As expected, reflectance signal at 548 nm was observed for the membranes containing DMG, while no signal was shown for the blank samples. Refer to Figure 3, membranes with larger amount of DMG provided higher reflectance signals. The use of different polymer matrix did not significantly affect the sensing performance. Membranes prepared from PS-*co*-PMMA provided slightly higher reflectance signals, while a high deviation was observed in PVC with 20%DMG membrane due to the heterogeneous surface resulting from the inhomogeneity between the hydrophobic nature of PVC and DMG. PS-*co*-PMMA containing 20%DMG membrane was selected for the subsequent work.

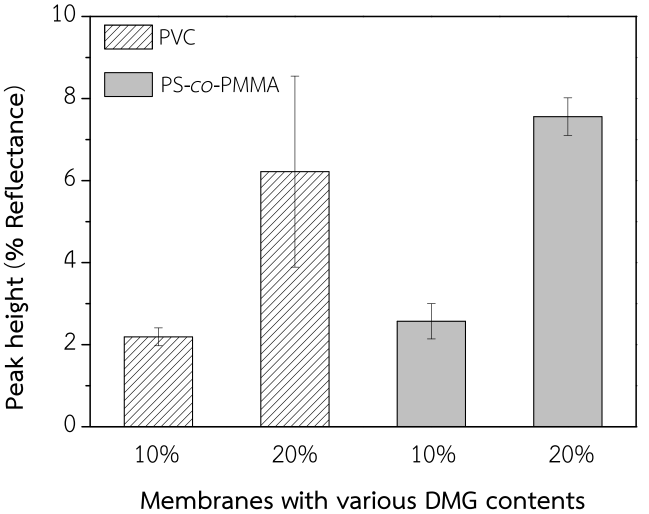

Figure 3 Effects of DMG content and polymer matrix on Ni^{2+} detection.

Effect of pH

The effect of pH on sensing performance was investigated by adjusting the pH of Ni^{2+} solution from 6.4 to 11.0 using ammonia solution. The result was shown in Figure 4. The maximum reflectance was observed between pH 9.0 – 10.0. The reduction in reflectance at lower pH values was due to the protonation of coordination group of ligand (Hashemi-Moghaddam, 2011). The leaching of $Ni(DMG)_2$ complex out of polymer matrix could possibly be accounted for a drop in reflectance signal at higher pH value (Ponnuswamy and Chyan, 2002). Gazda et al. (2004) have similarly shown that the most rapid precipitation of Ni^{2+} and DMG occurred at pH 9.0. Therefore, pH 9.0 was chosen for further investigations.

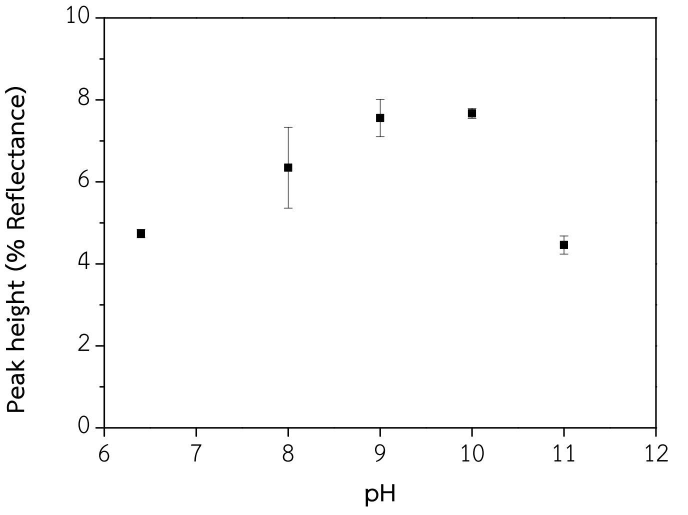

Figure 4 Effect of solution pH on Ni^{2+} detection.

Effect of Ni^{2+} concentration

The effect of Ni^{2+} concentration on detection was explored over the concentration range of 0.2 – 1.0 mM. As shown in Figure 5, reflectance signal increased with increasing Ni^{2+} concentration, and began to approach a maximum value at 0.8 mM. This limiting concentration agreed with the calculated concentration required to form a 1:2 stoichiometric Ni-DMG complex within experimental error. Though the prepared membrane was able to detect Ni^{2+}, it should be noted that the sensitivity was still lower than that of DMG-doped electrospun poly(caprolactone) fibers, which could be used to determine Ni^{2+} over the concentration range of 1 – 10 ppm (Poltue et al., 2011).

3.3 Selectivity and interference studies

The selectivity of PS-*co*-PMMA with 20%DMG membrane was evaluated by immersing the membrane in 0.8 mM aqueous solutions of Ag^{+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+}, and Fe^{3+} for 15 min. As shown in Figure 6, no reflectance peak at 548 nm was observed for other metal ions, illustrating that the membrane was capable of determining Ni^{2+} with a high selectivity. The sensing performance of the membrane toward Ni^{2+} in the presence of other metal ions was also investigated. Figure 7 revealed that the sensing ability toward Ni^{2+} of the membrane decreased in the presence of additional metal ions. This observation suggested that these selected ions could compete with Ni^{2+} to occupy the binding sites of DMG. The interference of Co^{2+}, Mn^{2+}, Pb^{2+} and Zn^{2+} was also previously reported in solid phase extraction of Ni^{2+} using DMG as a complexing agent (Ali et al., 1999). In addition, the presence of Cu^{2+} was shown to interrupt the detection of Ni^{2+} using ATR technique (Ponnuswamy and Chyan, 2002). It is worth noting that although the interference of other metal ions was observed in our study, relatively good reflectance signal of $Ni(DMG)_2$ complex could still be obtained.

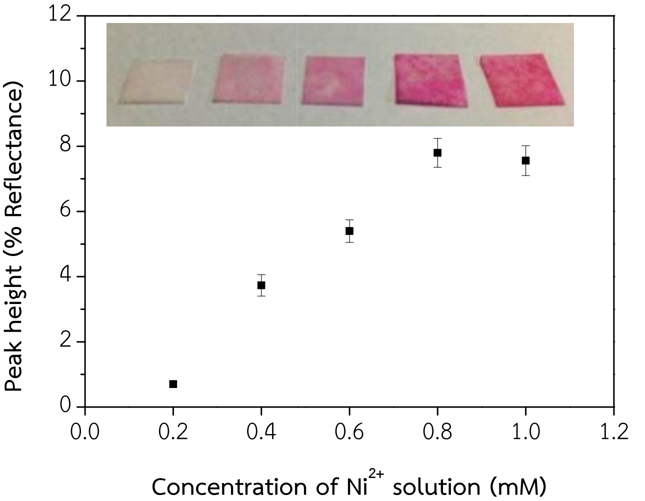

Figure 5 Reflectance signal as a function of Ni^{2+} concentration and corresponding membrane images.

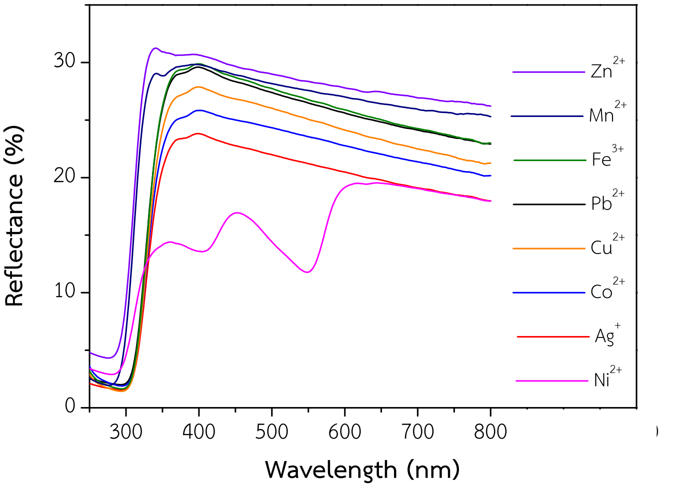

Figure 6 Reflectance spectra of PS-*co*-PMMA/20%DMG membrane after being immersed in 0.8 mM solution of selected metal ions.

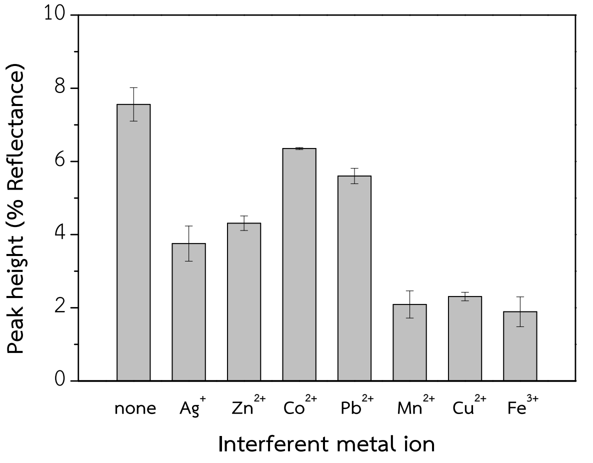

Figure 7 Responses of PS-*co*-PMMA/20%DMG membrane toward solutions containing both Ni^{2+} (0.8 mM) and other metal ion (0.8 mM).

4. CONCLUSION

A simple approach to fabricate optical sensor with good sensitivity toward Ni^{2+} was reported. Solvent-cast membranes of PVC or PS-*co*-PMMA and DMG were developed. PS-*co*-PMMA containing 20%DMG membrane showed the highest sensing performance and relatively low deviation. The formation of $Ni(DMG)_2$ complex was confirmed by the color change from white to pink, the additional band at 1572 cm^{-1} in FTIR, and the appearance of reflectance signal at 548 nm. Solution pH and Ni^{2+} concentration significantly affected Ni^{2+} detection of PS-*co*-PMMA/20% DMG membrane. The membrane exhibited highly selective response toward Ni^{2+} over other selected metal ions. However, the performance decreased in the presence of both Ni^{2+} and other metal ions due to the competition for DMG binding sites.

5. ACKNOWLEDGEMENTS

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