Synthesis and Characterization of Colorimetric Chemosensors Using New Direct Dyes

Eunyeong Heo, Sung-Hoon Kim, Jin-Seok Bae*

Department of Textile System Engineering, Kyungpook National University 1370 Sangyeok-dong, Buk-gu, Daegu, 702-701, Korea E-mail: jbae@knu.ac.kr

1. ABSTRACT

Colorimetric chemosensors are now considered as one of the most effective analytical method used in the environmental monitoring. In this study, 10 new direct dyes were synthesized to be used as colorimetric chemosensor. When metal ions such as Al^{3+} , Ca^{2+} , Cd^{2+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , Li^+ , Mg^{2+} , Na^+ , Ni^{2+} , Pb^{2+} and Zn^{2+} were added to the solutions of new dyes, the colors of the solutions were changed and can be easily detected by eyes without any expensive equipments. Some metal ions were coordinated to the new direct dyes forming complex. The experimental data and conclusions were rationalized by UV-VIS spectroscopy.

2. ITRODUCTUCTION

Colorimetric chemosensors are now recognized as the valid analytical method used in the process control, environmental and biomedical monitoring. The detection of heavy metal ions is of particular significance due to the toxic impact on the environment. Heavy metal ion pollution poses severe risks for human health and the environment. Once absorbed into the body, heavy metal is piled up in our body binding with protein and causes severe side effects for a long time. For example, lead (Pb) anesthetizes muscle and the nerve system of our body. Cadmium (Cd) causes lung cancer and weakens the bone. Manganese (Mn) affects growth and reproduction system.

The equipments such as atomic absorption spectrometer (AAS) and inductively coupled plasma – mass spectrometer (ICP-MS) have been used to detect heavy metals. The design and synthesis of heavy metal selective colorimetric chemosensor is popular due to their capability for naked-eye detection without restoring to such expensive instruments. In this study, new direct dyes were synthesized to detect heavy metals easily with eyes instead of equipments which need high cost and time. The basic structure of new direct dye synthesized is shown in Figure 1.

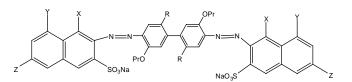


Fig. 1 Basic structure of new direct dye

Total 10 new direct dyes were synthesized using J-acid, H-acid, Chromotropic acid, Nevill-winther acid and gamma acid as coupler were used as couplers.

3. EXPERIMENTAL AND RESULTS

1. The synthesis of new direct dyes

2,2'-dimethyl-5,5'-dipropoxybenzidine and 5,5'dipropoxybenzidine were diazotized in presence of HCl and NaNO2 and coupled with J-acid, H-acid, Chromotropic acid, Nevill-winther acid and gamma acid to make new direct dyes as shown in Figure 2..

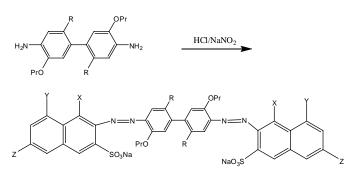


Fig. 2 Synthesis of the new direct dye (R=CH₃ or H)

2. Metal Sensing

The color of the dye (R-CH₃, chromotropic acid) solution has changed when several metal ions were added as shown in Figure 3.



Fig. 3 color changes of dye solutions with various metal ions

In this case, it is clearly shown that the color of new direct dye (R-CH₃, chromotropic acid) was changed by Al^{3+} , Cu^{2+} , Fe^{3+} , and Ni^{2+} . It is also observed that the colors of new dye solutions were changed mostly with Al^{3+} , Cu^{2+} and Fe^{3+} and rarely with Hg^{2+} and Ni^{2+} for other dyes synthesized.

3. UV-VIS Spectroscopy

The UV-Vis spectroscopy was measured for the dye solutions by adding various concentrations of metal ions. From 0.25 to 2.25 mL of 10^{-4} M Al³⁺ solutions were added in 1 mL of dyes respectively and total volume of solutions were adjusted to 10 mL. Figure 4 shows the absorption spectral changes of a dye (R-CH₃, chromotropic acid) as a function of the Al³⁺ concentrations in water at room temperature. As the Al³⁺ concentrations increases, the absorbance of the dye decreased. It was also observed with other dyes that the result of UV-Vis spectrometer showed the same pattern with Figure 4.

0.8 0.25m 0.5ml 0 75ml 0.6 1ml 1.25ml 1.5ml 1.75ml Absorbance 0.4 2ml 2.25m 2.5ml 02 0.0 350 400 450 500 550 600 650 700 750 waevlength(nm)

Fig. 4 Absorbance changes of a new direct dye $(10^{-4}\text{molL}^{-1})$ in water with various concentrations of Al³⁺.

4. CONCLUSION

The new direct dyes were synthesized to be used as colorimetric chemosensor of heavy metals. The colors of synthesized dyes were changed by the addition of Al^{3+} , Cu^{2+} , Fe^{3+} , and rarely with Hg^{2+} and Ni^{2+} . It was also observed that increasing the amount of heavy metal ions reduced the absorbance of UV-Vis spectrometer. In conclusion, new direct dyes coordinated with certain heavy metals and formed complex changing its color. By using new synthesized dyes in this study, the existence of heavy metal can be easily detected without any other equipments.

5. REFERENCES

- [1] B. Valeur, I. Leary, Coord. Chem. Rev. 205, (2000) 3.
- [2] K. Rurack, Spectrochim. Acta., 57A,(2001)2161.
- [3] A. P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. Mc Coy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97,(1997)1515
- [4] S. Tatay, P. Gavina, E. Coronado, E. Palomares, Org. Lett., 8, (2006) 3957.
- [5] M. Yuan, Y. Li, J.Li, X. Liu, J. Lv, J. Xu, H. Liu, S. Wang, D. Zhu, Org. Lett., 9, (2007) 2313.
- [6] M.H. Lee, B. Cho, J. Yoon, J.S. Kim, org. lett., 7, (2007) 4515.
- [7] Miyuki Narita, Yutaka Higuchi, Fumio Hanmada, Hitoshi Kumagai, Tetrahedron lett. 39 (1998) 8687.