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Reusable fluorescent photocrosslinked polymeric sensor for determining lead ions in aqueous media

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ABSTRACT

In this study, 1-vinylimidazole units bearing photocured films were prepared as fluorescent sensors towards Pb^{2+} in aqueous solutions. The influence of experimental parameters such as pH, time and foreign ion concentrations were investigated. Sensor response was linear over a concentration range of 4.83×10^{-8} to $4.83 \times 10^{-7} \text{ mol L}^{-1}$. The sensor was highly sensitive with a detection limit as low as $1.87 \times 10^{-8} \text{ mol L}^{-1}$, and having a selectivity of over four thousand fold. The response time of the sensor was found to be 5 min. When stored in a desiccator at room temperature the sensor showed good stability after a 5 month period. The fluorescence sensors were successful in the determination of Pb^{2+} in water samples as well as in the determination of the quantitative amount of lead and the results were satisfying. Compared with previously reported literature, the prepared new sensor is highly sensitive and selective.

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1. Introduction

Heavy metal ions such as lead (II) have long been identified as major toxic environmental pollutants [1]. Lead contamination of the environment, especially of drinking water and the food chain, leads to serious problems due to its high toxicity and non-biodegradability. It is well known that low levels of lead exposure cause severe risks to human health such as convulsions, central brain damages, miscarriages, kidney damages, and even death [2,3]. Basic sources of these ions are natural sources, mining and industrial applications which include pigments, anticorrosion coatings, batteries, and alloys [4]. The maximum concentration of lead (II) is strictly regulated by the European Union which is 1 mg L^{-1} for food and the level of Pb^{2+} in drinking water should be below 10 mg L^{-1} according to the World Health Organization [5]. Because of these regulations and risks, detection of lead (II) in environmental or biological samples has become a crucial matter for researchers.

Atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), fluorescence spectrometry and electrochemical techniques (such as ion-selective potentiometry and anodic stripping voltammetry) have been widely used methods for the determination of trace amounts of metal ions [6]. However, the need of sufficient chemistry knowledge, the difficulty in learning the instruments, complicated pretreatment procedures, the high costs of the instruments and the long analysis times can be counted among the drawbacks for

these methods. Therefore, there is a great demand for molecular recognition and sensing systems for the detection of small amounts of metal ions.

Among these systems, fluorescent chemical sensors have attracted considerable attention for the detection of metal cations because of their good selectivity and high sensitivity [7]. For this reason, the fluorescent polymers have become very attractive. These polymers usually contain covalently bonded fluorophore units such as indole and imidazole groups on their backbone which behave similar to their monomeric sensor units [8,9].

Hereby, we report the preparation and analytical properties of imidazole groups bearing UV cured polymeric film, designed to act as a fluorescence chemo sensor for lead (II) analysis. The influence of pH value and time on the fluorescence intensity of the sensor have also been investigated and discussed.

2. Experimental

2.1. Materials

1-Vinylimidazole (VIM), poly(ethylene glycol) diacrylate (PEGDA) ($M_n = 575 \text{ g mol}^{-1}$) and trimethylolpropane triacrylate (TMPTA) were purchased from Sigma Aldrich. The photoinitiator, DMPA (2,2-dimethoxy-2-phenylacetophenone) was obtained from Across. All other reagents were purchased from Merck and were used without further purification. The water used in the experiments was purified by using a Milli Q-water purification system (Millipore, Incekaralar-Turkey). The resulting purified water has a resistivity of $18.2 \text{ M}\Omega \text{ cm}$.

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2.2. Preparation of lead sensitive fluorescence sensor

A polymeric fluorescence sensor was prepared by photopolymerization method. While poly(ethylene glycol) diacrylate was used as a base resin, trimethylolpropane triacrylate was used as a crosslinker. Due to the photopolymerizable vinylic group on the molecule, 1-vinylimidazole was used as a reactive fluorophore. Besides, DMPA was used as a photoinitiator. 10% VIM, 70% PEGDA, 20% TMPTA and the photoinitiator (3% of whole formulation) were mixed in a small beaker. To eliminate the dissolved oxygen, nitrogen gas was purged with the formulation for about 15 min. Then, the formulation was poured into Teflon® molds ($W \times L \times D$: 12 mm \times 50 mm \times 1 mm) and cured under a high pressure UV lamp (OSRAM 300 W, $\lambda_{\text{max}} = 365$ nm) for 3 min and then UV cured films were removed from the molds. In order to remove the unreacted monomers, cross-linked films were kept inside deionized water for 24 h, then dried in a vacuum oven at 30 °C to a constant weight.

2.3. Characterization

FT-IR spectrum was performed on a Perkin Elmer Spectrum100 ATR-FTIR spectrophotometer in the range of 4000–650 cm^{-1} at room temperature with the 4 cm^{-1} resolution mode and 20 scans. Morphology of the polymeric films was investigated by scanning electron microscopy (SEM). Prior to the SEM analysis, a dried sample was coated with platinum having a thickness of approximately 300 Å using an Edwards S 150 B sputter coater and the surface was observed by using a Philips XL30 ESEM-FEG/EDAX system. Fluorescence measurements were carried out by using a Varian Cary Eclipse Spectrofluorometer. The pH values of the solutions were checked using a digital pH meter (WTW) calibrated with standard buffer solutions from Merck. All the experiments were carried out at room temperature: 25 ± 1 °C.

3. Results and discussion

3.1. Characterization

3.1.1. FTIR spectroscopy

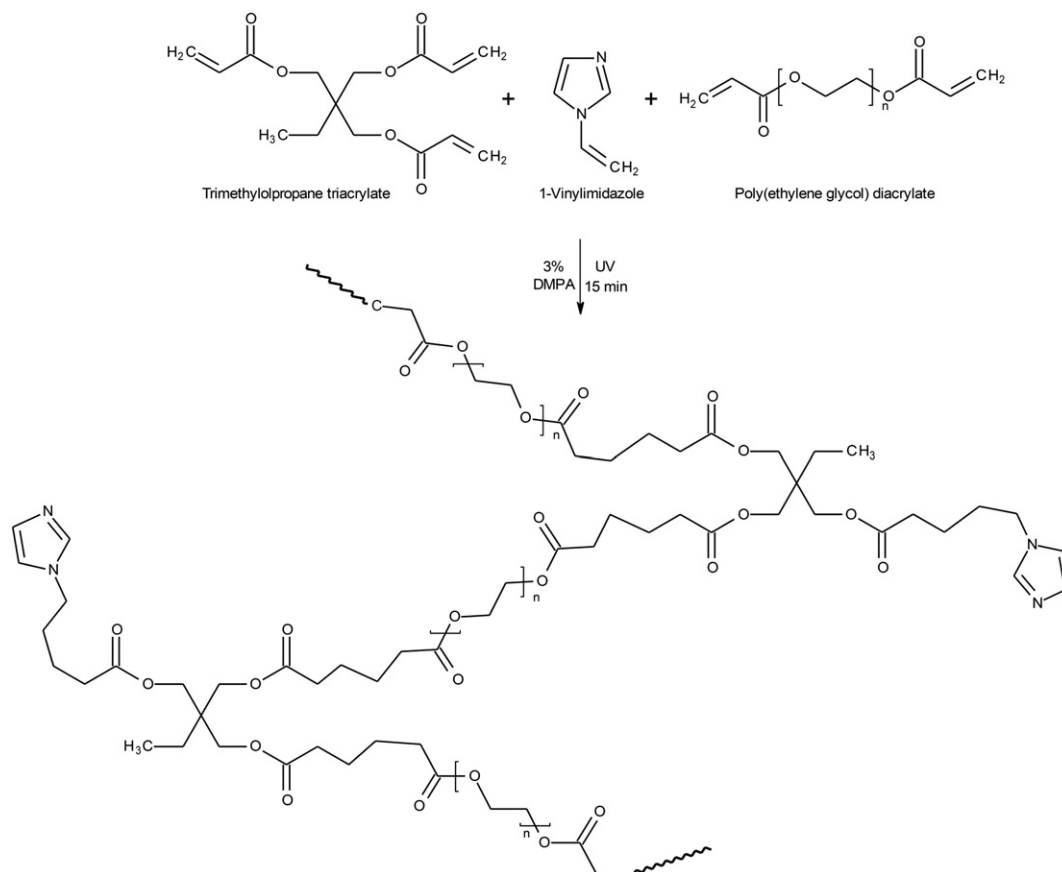
1-Vinylimidazole (VIM), poly(ethylene glycol) diacrylate and trimethylolpropane triacrylate were cross-linked in the presence of the photoinitiator by using a UV lamp. Scheme 1 demonstrates the preparation and structure of the polymeric film. The structure of the obtained polymeric films was investigated by ATR-FTIR spectrometer. The ATR-FTIR spectrum of the film is given in Fig. 1. The absorption peak at 1720 cm^{-1} is attributed to the stretching vibration of the carbonyl groups of PEGDA and TMPTA. The disappearance of the vinyl stretching at 1040 cm^{-1} was taken as an indication of successful crosslinking of VIM. The peak around 1635 cm^{-1} can be attributed to the CC double bonds of acrylates, stating that not all of the acrylate groups have participated in the crosslinking process [10].

3.1.2. SEM measurements

The surface morphology of the polymeric film is an important factor for the design of an efficient sensor. Homogeneity, porosity and surface conditions are the most important parameters, which influence the fluorescence efficiency. After the UV curing process, a macroscopically uniform semi-transparent film was obtained. Fig. 2 demonstrates the SEM images of the Pb^{2+} sensing film. SEM images showed a smooth surface without any phase separation, indicating the formation of good structural integrity.

3.2. Spectral characterization

Fluorimetric experiments were carried out on a Varian Eclipse spectrofluorometer. The excitation and emission bandwidth slits were set at



Scheme 1. Chemical structure of the polymeric sensor.

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