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Synthesis, characterization and application of poly(acrylamide-co-methylenbisacrylamide) nanocomposite as a colorimetric chemosensor for visual detection of trace levels of Hg and Pb ions

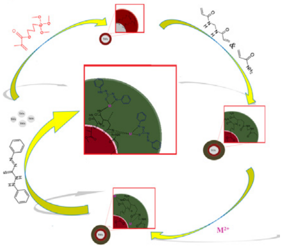
Roya Sedghi*, Bahareh Heidari, Mohammad Behbahani

Department of Polymer, Faculty of Chemistry, Shahid Beheshti University, G.C., 1983969411 Tehran, Iran

HIGHLIGHTS

- Poly(acrylamide-co-methylenbisacrylamide) nanocomposite.
- Colorimetric chemosensor.
- Determination of trace levels of Hg and Pb ions.
- Environmental samples.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a new colorimetric chemosensor based on TiO_2/poly(acrylamide-co-methylenbisacrylamide) nanocomposites was designed for determination of mercury and lead ions at trace levels in environmental samples. The removal and preconcentration of lead and mercury ions on the sorbent was achieved due to sharing an electron pair of N and O groups of polymer chains with the mentioned heavy metal ions. The hydrogel sensor was designed by surface modification of a synthesized TiO_2 nanoparticles using methacryloxypropyltrimethoxysilan (MAPTMS), which provided a reactive C=C bond that polymerized the acrylamide and methylenbisacrylamide. The sorbent was characterized using X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscope (SEM), EDS analysis and Fourier transform in frared (FT-IR) spectrometer. This nanostructured composite with polymer shell was developed as a sensitive and selective sorbent for adsorption of mercury and lead ions from aqueous solution at optimized condition. This method involves two-steps: (1) preconcentration of mercury and lead ions by the synthesized sorbent and (2) its selective monitoring of the target ions by complexation with dithizone (DZ). The color of the sorbent in the absence and presence of mercury and lead ions shifts from white to violet and red, respectively. The detection limit of the synthesized nanochemosensor for mercury and lead ions was 1 and 10 $\mu g L^{-1}$, respectively. The method was successfully applied for trace detection of mercury and lead ions in tap, river, and sea water samples.

1. Introduction

Environmental pollution of toxic heavy metal ions can lead poisoning and death [1], and have been reported that Hg ion could

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* Corresponding author. Tel.: +98 2129902890; fax: +98 2122431661.
E-mail address: r_sedghi@sbu.ac.ir (R. Sedghi).

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cause perennial damaging effects in living organisms, such as memory loss, nephritic damage, decrease in the rate of fecundity, also birth defects in offspring [2]. The World Health Organization recommends the standard water quality to be less than 10 $\mu g\,L^{-1}$ for Hg, Pb, and other toxic metal ions. In spite of the increasing demands for simple and rapid monitoring of water quality, the sensitivities of commercial methods are inadequate to meet the recommended concentration guidelines. There are urgent necessities for simple, inexpensive and sensitive detection of toxic metal ions for a wide range of applications, such as: industrial process management, environmental monitoring, chemical threat detection and food quality control.

Therefore, it should be developed specific sensors for the quick detection of Hg and Pb ions. Many common methods have been used for detection and measuring of Hg and Pb concentration in aqueous solution. These methods are atomic spectrometry [3–5], voltammetric methods [6–8], and molecular spectrophotometry [9–13]. Compared to conventional methods, the application of chemical sensor based on colorimetric detection is simpler and more sensitive and moreover eliminates the request of sophisticated instruments because of results can be detected by "naked-eye". Unfortunately, toxic metals are persistent agents in the ecosystem; so detection of them is important in the aquatic environments.

Chemical sensor technology is a specific method for ions detection based on chemical recognition. Optical sensors are based upon diagnosis of analyte-induced color changes in the sensor compounds [14–16]. Dithizone (DTZ) is well recognized as a nitrogen and sulfur donor atoms containing chelating compound with heavy metals [17]. Therefore, dithizone is a common employed indicator that is a highly sensitive and selective reagent which applies for heavy metal ions [18]. The concentration of heavy metals is usually below detection limits, so the trace heavy metals should be preconcentrate before the measurement.

Moreover, many nanotubes materials have been synthesised such as: titanium dioxide (TiO_2), zirconium dioxide, silica, V_2O_5, MoO_3 [19]. It is reported that TiO_2 nanotubes have larger surface area than the starting titanium, and contain more ion-exchangeable OH groups in the interlayer and surface [20]. TiO_2 nanotubes has also gained great interests in analytical chemistry because of its high chemical stability, durability, corrosion resistance, non-toxicity and cost effectiveness.

In this work, the polymeric nanocomposite applied as a highly selective and sensitive colorimetric sensor for ultra-trace levels detection of hazardous (mercury and lead) ions from aqueous solution. At first, we used acrylamide as a monomer and methylenbisacrylamide as a cross-linker to obtain the polymer on TiO_2 nanoparticles surface. Cross-linker has been used to acquire a three-dimensional structure to make more interaction between the polymer and the heavy metals. Then, ions detection accomplished by secondary interaction of dithizone with adsorbed target ions on the synthesized hydrogel (Scheme 1). In this process when chemosensor interact with Hg(II), its color changes from white to violet and in interaction to Pb(II), changes to red. The high sensitivity of the sensor makes it capable to detect trace levels of Hg(II) and Pb(II). The detection limit of the sensor for mercury and lead ions was 1 and 10 ppb, respectively.

2. Experimental

2.1. Reagents and materials

Ammonium(II) sulfate, titanium(IV) chloride, ammonium hydroxide (25–30%), methacryloxypropyltrimethoxysilane (MAPTMS), acrylamide, methylenbisacrylamide, azobisisobutyronitrile (AIBN), dithizone, HCl, NaOH, dimetylsulfoxide, 1-heptanol, and other solvents obtained from Merck company (White-house Station, NJ).

2.2. Synthesis of TiO_2 nanoparticle

For the synthesis of TiO_2 nanoparticle, ammonium sulfate solution (1.5 $mol\,L^{-1}$) and titanium(IV) chloride (0.75 $mol\,L^{-1}$) was used. The solution was heated at 75 °C and remained at this temperature for 90 min. In the next step, ammonium hydroxide (2.5 $mol\,L^{-1}$) was added under high speed stirring to the above solution (at pH 7). Then, the precipitated production was collected and washed with water/ethanol mixture and dried at 60 °C. The sample was calcined at 350 °C for 4 h and then was slowly cooled at ambient temperature.

2.3. Grafting of MAPTMS onto TiO_2 nanoparticles

To decrease the agglomeration and increasing the stability of the nanoparticles in the casting solution, the surface modification of TiO_2 nanoparticles was carried out by grafting reaction of MAPTMS as silane coupling agent, according to the given procedure [21]. After dispersing 1 g of TiO_2 nanoparticles in 20 mL toluene, 1.5 mL MPTMS was added, and then this solution was placed under N_2 atmosphere for 24 h at room temperature. The surface-modified TiO_2 nanoparticles were isolated by centrifugation and washed two times with toluene; then it was dried under vacuum at 30 °C for 24 h.

2.4. Polymerization

For the polymerization of monomers on the surface of nanoparticles, acrylamide (1.0 g), methylenbisacrylamide (4.31 g) and modified TiO_2 (0.8 g) were dissolved in 12 mL of dimetylsulfoxide/1-heptanol with 2.5/1 ratio at 50 °C. Then, the solution was refluxed under N_2 atmosphere for 15 min followed by the addition of AIBN (0.053 g), and the polymerization accomplished at 60 °C for 5 h. The synthesis polymer was exposed to solvent, and then washed 3 times with ethanol and water. Finally, it was dried at 50 °C for 24 h.

2.5. Instruments

The reflection spectra of the chemosensor were collected using a solid state 2100-UV–vis Shimadzu spectrophotometer. This means uses light in the adjacent visible ranges. The reflectance in the visible range directly affects the perceived color of the involved chemicals. The morphology of the sorbent was characterized using SEM (Philips XL-30). X-ray diffraction patterns were measured using Siemens D5000 diffractometer, and 2θ scan were recorded with monochromatic CuKα ($\lambda = 1.54060$ A) in the range of $2\theta = 10–80$. FT-IR absorption spectra of samples were carried out using a BOMEM MB-series FT-IR spectrometer in the form of KBr pellets. Thermogravimetric analysis was performed by a thermal analyzer instrument (TGA/DTA BAHR: STA 503) from 25 to 1000 °C at a heating rate of 10 °C/min under air. All the pH measurements were carried out with a digital pH meter Metrohm 827 equipped with a combined glass calomel electrode at 25 ± 1 °C temperatures.

3. Results and discussion

3.1. Characterization of the chemosensor

3.1.1. X-ray diffraction analysis

X-ray powder diffraction (XRD) is a rapid analytical technique that primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. Also