Novel multifunctional membrane technology for visual detection and enhanced adsorptive removal of lead ions in water and wastewater

Linzi Zhang and Renbi Bai

ABSTRACT

A multifunctional membrane for visual detection and enhanced adsorptive removal of lead ions in aqueous solution was prepared by immobilizing lead sensitive ligand, dithizone (DZ), on chitosan (CS)/cellulose acetate (CA) blend membrane. The prepared membrane can display visible color change (from yellow to red) as a response to lead ions in solutions; and at the same time, lead ions can be adsorptively removed by the amine groups on the membrane surface. Thus, the development provides a truly multifunctional membrane technology that can achieve optical warning as well as removal of lead ions simultaneously. Experimental results showed that the prepared membrane exhibited the advantages of quick response, easy naked-eye recognition and improved lead uptake capacity.

Key words | adsorptive removal, lead ions, ligand immobilization, multifunctional membrane, visual detection

INTRODUCTION

Anthropogenic activities have generated large amounts of industrial and domestic wastes that may contain pollutants with detrimental and even lethal effects to the environment and human beings. Lead pollution in water or wastewater, for example, has been one of the problems that cause a great concern to the living lives (Dias et al. 2005). Lead-containing pollutants are often introduced into the environment through the effluents discharged from industries such as electroplating, metal furnishing and mining. It is well known that lead ions do not degrade into harmless end products in the metabolic pathway in the environment. Consequently, lead can accumulate in human body and may cause dysfunction of the kidneys, liver, brain and central nervous systems, etc. (Eiden et al. 1980; Jin & Bai 2002). Therefore, it is essential to develop high-performance technologies that can effectively warn the presence of lead ions in as well as remove them from the contaminated water.

In recent years, sensing technology for heavy metal ions has attracted a great attention. Among the many sensing techniques, optical sensor that provides instant visual indication is considered as one of the most advantageous techniques. The method is simple and gives on-site naked-eye recognition with less labor demands and lower analysis cost, compared to other methods such as atomic absorption spectrometry, fluorescent sensors and electrochemical techniques (Chatterjee et al. 2002; Hashem 2002; Yaman & Dilgin 2002). In order to make optical sensors more applicable, the chromophore receptors (e.g., indicator dyes) are usually immobilized on or entrapped into a suitable solid matrix (Che et al. 2003; Choi et al. 2006). El-Safty et al. have reported the immobilization of dithizone (DZ), diphenylcarbazide (DPC), tetraphenylporphine tetrasulfonic acid (TPPS) and 5, 10, 15, 20-tetrakis(1-methyl-4-pyridinio) porphyrin tetra (p-toluenesulfonate) (TMPyP), on porous silica monolithic
cage matrix for the detection of Pb$^{2+}$, Cr$^{6+}$, Hg$^{2+}$ and Cd$^{2+}$ ions, respectively (Balaji et al. 2006; El-Safty et al. 2008).

Porous membrane could also be an ideal pedestal for carrying chromophore receptors as heavy metal sensor. Adsorptive membrane has been a relatively new membrane technology that can adsorptively remove heavy metal ions from water or wastewater during the filtration process. Adsorptive membranes are usually a type of porous microfiltration (MF) or ultrafiltration (UF) membranes bearing functional groups on their external and internal surfaces. These functional groups, such as $-\text{COOH}$, $-\text{SO}_3\text{H}$ or $-\text{NH}_2$, can bond with heavy metal ions through the complexation or ion exchange mechanism. Therefore, heavy metal ions can be removed when they are passing through the membrane matrix, even though their dimensions may be much smaller than the pore sizes of the membrane. Thus, adsorptive membranes can remove heavy metal ions with less energy consumption and higher permeate flux (Liu & Bai 2006).

Among various types of adsorptive membranes, chitosan-based adsorptive membranes have attracted a considerable attention. Chitosan (CS) is a biopolymer that can be easily obtained from the shells of crustaceans such as shrimps, crabs and lobsters. The presence of a large percentage of free amine and hydroxyl groups on chitosan structure renders it a good capability in the sorption of heavy metal ions (Guibal 2004).

Over the years, optical sensors and adsorptive membranes have been developed as two parallel technologies. There is a logical desire to combine the two functions together so as to improve the overall treatment efficiency, simplify the treatment system and reduce the environmental footprint. In this study, a novel multifunctional membrane was designed to achieve both visual detection and adsorptive removal of heavy metal ions, with a particular interest in lead ions. A lead-sensitive optical ligand, dithizone (DZ), was immobilized onto the CS/CA blend membrane through a simple solution reaction. The prepared membrane was tested for its optical response as well as adsorption behavior towards lead ions. Unlike other developments that focused either on adsorbing or sensing heavy metal ions, the membrane obtained in this work can achieve both functions by a single membrane system. To the best of our knowledge, this is the first kind of such multifunctional membrane prepared for on-site naked-eye detection as well as adsorptive removal of lead ions in aqueous solutions.

**METHODS**

**Materials**

CS flakes (85% deacetylated) were supplied by Sigma-Aldrich. CA, with acetyl content of 40%, was purchased from Fluka. Formic acid (98–100%) from Fluka was used as the co-solvent for both the CS and CA polymers. NaOH solution (2 wt.%) was used as the nonsolvent to coagulate the CS/CA blend membrane. DZ (> 85%), from Sanland-Chem International Inc., was used as the optical indicator for lead ions. Pb(NO$_3$)$_2$ standard solutions (1000 mg/L) from Merck was used in the adsorption experiments. Deionized (DI) water was used to prepare all test solutions as needed.

**Preparation of porous CS/CA blend membrane**

The general method for the preparation of CS/CA blend membrane was the same as described elsewhere (Liu & Bai 2006). In this study, the CS/CA membrane was prepared similarly but in a different ratio of 2:16 in terms of CS:CA. The casted membrane was dried and stored in a vacuum desiccator at room temperature (22–23°C) prior to further use for characterizations or performance tests.

**Immobilization of DZ on CS/CA membrane**

Firstly, 0.1 g DZ was dissolved in 50 mL ethanol in a flask. Then, 2 g dry CS/CA membrane was added into the solution. The mixture in the flask was stirred at room temperature for 30 min, followed by a gentle evaporation of ethanol with a rotavapor (BUCHI Rotavapor R-210) at 40°C. The prepared membrane was finally washed thoroughly with DI water until no elution of DZ was detected by a UV/Vis spectrometer. The membrane was then vacuum-dried at room temperature and stored in a vacuum desiccators for further uses. The obtained membrane is denoted as CS/CA-DZ in this paper.

**Experiments on chromatic response of the membranes in detection of lead ions in solutions**

The tests were first done for lead solutions with different pH values. Lead solutions with an initial concentration of 5 mg/L were prepared by diluting the 1000 mg/L standard lead
solution with DI water and then adjusted to a desired pH value in the range of 2 to 11 with dilute HCl or NaOH solutions. Membrane samples, cut into pieces, with a weight of around 0.06 g were added into a 50 mL flask containing 20 mL of a lead solution at a specific pH value. The contents in the flasks were shaken in an orbital shaker at 150 rpm and room temperature for 20 min. The membrane samples were then taken out from the flasks, rinsed with DI water and used for the color assessments.

Next, the prepared functional membrane was investigated for its color change at different contact times. A specific type of membrane, cut into pieces, with a weight of about 0.06 g was added into the lead solution with an initial concentration:5 mg/L, solution volume:20 mL and pH 5. The mixture was shaken on a shaker at 150 rpm under room temperature. Membrane samples at various reaction contact times were taken out for the color assessments.

The chromatic response of the functional membrane to lead solutions with different concentrations was also examined. The experiments were similarly conducted as above but at a different initial lead concentration ranging from 0 to 200 mg/L with a contact time of 10 min (pH 5, 22–23°C).

**Lead adsorption experiments**

Adsorption kinetic study was carried out to characterize the uptake rates of lead ions and also the adsorption equilibrium time. The experiments were conducted by adding 0.21 g membrane in pieces to 200 mL lead solution with the initial concentration of 10 mg/L, at pH 5 (22–23°C). The mixture was shaken on an orbit shaker at 150 rpm for up to 600 min. A 10 mL amount of the solution was taken at each desired time interval, filtered through a 0.45 μm Waterman membrane filter and then analyzed with an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima 3000DV) for determining the lead concentrations. The adsorbed amount of lead ion on the membrane at time t_i, q(t_i) (mg/g), was calculated from the mass balance equation as:

\[ q(t_i) = \frac{\sum (C(t_{i-1}) - C(t_i)) V(t_{i-1})}{m} \]

where \( C_0 \) (= \( C_0 \)) is the initial lead concentration, \( C(t_i) \) (mg/L) is the lead concentration at time \( t_i \); \( V(t_i) \) (L) is the volume of the solution at time \( t_i \), and \( m \) (g) is the dry weight of the membrane pieces added.

Adsorption isotherm study was conducted to determine the adsorbed lead amounts versus lead concentrations in the solutions. The experiments were conducted by adding about 0.06 g membrane pieces to a number of 50 mL flasks containing 20 mL lead solution with different initial concentrations (in the range of 0–200 mg/L) at pH 5, 22–23°C. The contents in the flasks were shaken on an orbital shaker at 150 rpm for a contact time of 300 min (above the adsorption equilibrium time of about 200 min). As predicted by the MINEQL+ software analysis, no lead precipitation would occur under the experimental conditions. The adsorbed amount at adsorption equilibrium, \( q_e \) (mg/g), was calculated by the following equation:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]

where \( C_0 \) (mg/L) and \( C_e \) (mg/L) are the initial and final lead ion concentrations in the solution in each flask, respectively, \( V \) (L) is the volume of the solution in each flask, and \( m \) (g) is the dry weight of the membrane pieces added. For comparison, the same type of experiment was also conducted with the CS/CA base membrane.

**Experiments on interference study**

The interference of other metal ions in the solution on the response and uptake of lead ions by the functional membrane was examined. The experiment was conducted by equilibrating the membrane pieces with solutions containing a fixed concentration of lead ions (1 mg/L) at pH 5, 22–23°C with the presence of other metal ions including K⁺, Na⁺, Ca²⁺, Mg²⁺, Cd²⁺, Zn²⁺ and Ni²⁺.

**RESULTS AND DISCUSSION**

**Immobilization of DZ molecules**

DZ has been reported as a spectrophotometric reagent for lead ions in the literatures (Deoliveira & Narayanaswamy 1992; Zaporozhets et al. 1999). It can change color in response to the interaction with lead ions in solutions. As reported, DZ...
can be immobilized onto different types of solid matrix such as silicas and Amberlite XAD-4 resin through van der Waals force or H-bonding interactions (El-Safty et al. 2008). However, the immobilization of DZ on chitosan based membrane for visual detection and adsorptive removal of lead ions was never reported. In this study, DZ was immobilized on CS/CA membrane through a simple solution reaction. The mechanism of DZ immobilization and the binding event of lead ions on the obtained membrane were proposed in Figure 1. The obtained CS/CA-DZ membrane has a pure water flux of 8 - 20 L/m²·hr·bar and it can be considered as a typical ultrafiltration membrane in water and wastewater treatment. When lead ions are present in the water to be treated, they would interact with DZ molecules as well as –NH₂ groups on chitosan when the water passes through the membrane matrix, which would lead to a color change of the membrane and the adsorptive removal of lead ions.

**Effect of solution pH**

The solution pH is often an important parameter affecting the detection performance of heavy metal ions by sensitive materials, because solution pH not only affects the form of metal species in solution but also influence the surface properties of the sensitive materials in terms of dissociation of functional groups and surface charges. It was found that the optimum pH range for lead detection is from pH 5 to pH 7. At pH < 4, DZ would leach out because of the protonation of DZ molecules. In the lead solution with higher alkalinity (pH > 8), the color changes were not obvious because the metal hydroxide formation limited the interaction between lead ions and the DZ probes.

**Optical response to lead ions**

The response of CS/CA-DZ membrane to lead ions at different contact times was characterized by a UV/Vis spectrophotometer and the color evolution was recorded. It can be seen from the UV/Vis spectra [Figure 2(a)] that there is an obvious decrease in the absorbance at 490 nm within the first 2 min. UV/Vis spectra also exhibited a hypsochromic shift for the absorbance peak, λ_max, from 490 nm to 440 nm with the increase of the contact time. These changes in UV/Vis spectra indicate an overall color change of the membrane surface from yellow to red. The rapid visual detection to Pb²⁺ recognized by naked-eyes demonstrated a great potential for practical and on-site application of the membrane sensor in water and wastewater treatment process.

**Figure 2(b)** illustrates the color-change pattern and the difference in absorbance intensity at 490 nm (i.e., the amount of the adsorption) in response to lead ions with different concentrations. As can be seen, the intensity difference at 490 nm (A₀-A) showed a significant increase from 0 to 5 mg/L.
Then, a saturation stage was gradually approached when the lead concentration was at higher than 10 mg/L. The result is consistent with the color-change pattern that significant color changes from yellow to red were observed when the lead concentration increased from 0 to 5 mg/L. Further increase of lead concentration would not contribute much further to the developed color. The results in Figure 2(b) indicate that the color change is related to the amount of lead ions interacted with the immobilized DZ probes on the membrane surface.

Adsorption study of lead ions

Adsorption kinetic study was conducted to evaluate the uptake rate of lead ions on the prepared membrane. As shown in Figure 5(a), the CS/CA-DZ membrane had both higher adsorption uptakes and shorter equilibrium time than the CS/CA base membrane. It was found that the uptake of lead ions on the CS/CA-DZ membrane reached the adsorption equilibrium in around 100 min with an adsorption amount up to 2.3 mg/g in this case. In contrast, lead ion adsorption on the CS/CA base membrane underwent a slower process with a lower uptake amount (up to 0.5 mg/g at around 300 min). The enhanced performance of the CS/CA-DZ membrane can be attributed to the immobilized DZ probes that provide more functional groups (-NH$_2$, -NH$^-$, -N$^-$) on the prepared membrane surface which could also bond with lead ions, thus providing a higher adsorption capacity and shorter equilibrium time than those of the CS/CA base membrane.

The experimental adsorption isotherm data of the CS/CA base and the prepared CS/CA-DZ membranes were obtained, as shown in Figure 3(b). To well understand the adsorption behaviors, the Langmuir and Freundlich isotherm models are applied to fit the experimental data respectively. The Langmuir equation can be expressed as:

\[ q_e = \frac{q_m c_e}{K_L + c_e} \]
where $q_e$ is the amount of adsorption uptake (mg/g) at adsorption equilibrium, $q_m$ is the maximum uptake capacity (mg/g), $c_e$ is the equilibrium concentration of lead ions in the solution (mg/L), and $K_L$ is the Langmuir adsorption constant (L/mg), reflecting the affinity of the absorbate for the absorbent.

The Freundlich equation, which is an empirical equation used to describe heterogeneous adsorption systems, can be represented as follows:

$$q_e = K_F c_e^{1/n}$$

where $q_e$ and $c_e$ have the same definitions as before and $K_F$ is the Freundlich constant [((mg/g)/(L/mg))$^{1/n}$] which has a positive correlation with the adsorption capacity, and $n$ is an empirical parameter, in general larger than 1. It will increase with the increasing degree of the heterogeneity.

The fitting of the Langmuir and Freundlich models to the adsorption data is also included in Figure 3(b) and the corresponding fitting parameters for the Langmuir and Freundlich isotherm models are obtained accordingly. From the results in Figure 3(b) and the correlation coefficients ($R^2$), it is found that the CS/CA base membrane is better fitted by the Langmuir isotherm models, giving the $R^2$ values of 0.9909; while the experiment data of the CS/CA-DZ membrane were better fitted by the Freundlich model ($R^2 = 0.9985$). The heterogeneity factor $n$ for the CS/CA-DZ adsorption system is calculated to be 1.65 which is greater than that for the CS/CA adsorption system (1.34). This may be attributed to the existence of more functional groups (-NH$_2$, -NH, -N-) on the CS/CA-DZ membrane from the immobilized DZ molecules which could exhibit different binding energies for the adsorption.

From the Langmuir model fitting, the maximum adsorption capacity of lead ions on the prepared CS/CA-DZ membrane is predicted to be about 25 mg/g, much higher than about 13 mg/g for the CS/CA base membrane. In other words, the functionalization of CS/CA by DZ also significantly enhanced the adsorption capacity of the prepared membrane for lead ions. The much higher lead adsorption capacity of CS/CA-DZ membrane is also supported by the much greater value of $K_F$ for CS/CA-DZ (0.702) than that for CS/CA (0.2866) from the Freundlich model fitting analysis.

### Interference study

The interference of other cations on the detection of the lead ions by CS/CA-DZ was investigated. An ion was considered as interference when its presence produced a different color change or resulted in a variation in the absorbance of the analytes at greater than 5% (Ensafi et al. 2008). Cations including Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Zn$^{2+}$, Ni$^{2+}$ and Cd$^{2+}$ were studied. The colormetric results indicate that species such as Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$ had little influence on both detection and adsorption of lead ions (1 mg/L) even when their concentrations were 20-fold higher than that of the lead ions. In other words, those cations do not show specific interactions with the functional groups on DZ and CS of the membrane. However, Ni$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ cations were found to exert interference. With these cations in presence, the membrane exhibited colors that were different from the one in the single lead ion system. Besides, adsorption of lead ions also decreased significantly. The reason was probably that those heavy metal cations could also bond with the amino groups on DZ and chitosan (Rinaudo 2006). However, a preliminary study has found that the influence could be mitigated by the addition of 2 mmol/L Na$_2$S$_2$O$_3$ in the analyst solution (see supplementary information). This is probably because sodium thiosulfate could form stable complexes with those interfering cations and reduce the availability of those cations to the membrane (Zaporozhets et al. 1999; Van Sprang & Janssen 2001).

Besides, the addition of 2 mmol/L Na$_2$S$_2$O$_3$ was found to have little influence on the detection and removal of lead ions as lead ions prefer to react with nitrogen containing chelating groups which exist in both DZ and CS of the membrane (Mahmoud et al. 2010).

### Desorption and reuse

The reusability of the prepared CS/CA-DZ membrane is also the interest of this study. EDTA (0.1%) has been found to effectively remove lead ions from the saturated membrane. However, some influence of the stripping agent on the sensing functionality was noticed with a gradually decreased sensitivity and delayed response-time during several cycles of the regeneration experiments. Experimental results showed that after three regeneration/reuse cycles, the absorbance intensity of the regenerated membrane at 490 nm was...
CONCLUSIONS

In this study, a simple and low cost multifunctional membrane for visual detection and adsorptive removal of Pb²⁺ was developed by immobilizing DZ on to the CS/CA blend base membrane. The obtained CS/CA-DZ membrane was able to show optical color changes when in contact with lead ions in solutions with a short response time (less than 5 min). Besides, the membrane also showed significantly enhanced adsorption performance towards lead ions. The DZ functionalized CS/CA membrane achieved truly multiple functions for easy on-site naked-eye detection and adsorptive removal of lead ions simultaneously. The developed multifunctional membrane would have a great potential in its applications in water and wastewater treatment to minimize the environmental and health effects of heavy metal pollutants.

ACKNOWLEDGEMENTS

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REFERENCES


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### Supplementary information:

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Color response of 1mg/L Pb²⁺ ions in presence of interfering cations in the solutions (pH 5, 22–23°C). Subscribers to the online version of Water Science and Technology: Water Supply can access the colour version of this table from http://www.iwaponline.com/ws