Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1121839

57 (2016) 21627–21633
September

Study on lead ion wastewater treatment of self-assembled film

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Received 3 January 2015; Accepted 7 November 2015

ABSTRACT

The cetyl-trimethyl ammonium bromide (CTAB) and glycine betaine self-assembly formed film on the quartz glass and glass slides were prepared, respectively. The microstructure of self-assembled film was observed by the optical microscope and SEM. It was found that the self-assembled film of CTAB on quartz glass slide exhibits good film-forming effect, and the best processes of self-assembled film are that the quartz glass slide immersed in 30 mmol/L CTAB for 180 min at 40°C and pH 8. The adsorption property was evaluated through UV spectrophotometer. The removal ratio of lead ions in wastewater is up to 80%.

Keywords: Self-assembled film; Lead ion wastewater; Wastewater treatment

1. Introduction

With the development of industrialization, the water pollution is more serious, especially the lead ion wastewater. It also poses a huge threat and destruction for the environment, ecology, and human health. The total content for lead ion of national emission standard is below 1 mg/L in water [1]. If your daily intake of lead is from 0.3 to 1.0 mg, it will cause health diseases such as anemia and neuritis [2]. In the process of industrialization, the wastewater emissions of lead-acid battery production, metallurgical wastewater containing lead ion, lead wastewater, and electroplating industry producing coating wastewater containing lead ion are the sources of lead pollution [3–6]. So it is an important research on scientifically dealing with wastewater containing lead in the industrialization and modernization.

At present, there are many deficiencies in the traditional treating process of lead pollution. However, more strict environmental standards put forward higher requirements on lead pollution treatment. So higher technology is urgently required to reduce lead pollution. Self-assembled film is a highly dense, stable, two-dimensional orderly organic ultrathin membrane system, has unique physical properties, chemical properties, optical properties, and electron transport properties [7]. The basic assembly process for self-assembled film is: activated substrate is soaked in a surfactant solution, and the matrix is removed after a certain reaction time and thoroughly washed and dried; at last active molecules form a dense ordered self-assembled film [8]. Active molecules are grafted onto the substrate by the reactive group. By choosing the outer groups, the self-assembled film exhibits

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different interface physicochemical properties, e.g. acidity or alkalinity, hydrophilic or hydrophobic, polar or non-polar, etc. [9]. So, the outer groups and molecular chain can be designed according to the requirement for the adsorption of metal ions in water to guaranteeing purification quality of wastewater. In addition, its preparation is simple and the process is a popular green chemistry to treat wastewater [10]. Yu et al. prepared NH_2-self-assembled film on the SiO_2 substrate and found that the removal rate of residual insecticide simazine can reach up to 76.5% [11]. Song et al. obtained alternating assembled sodium dodecyl sulfate monomolecular film and titanium dioxide nanoparticles film on the surface of silica ball using layer-by-layer self-assembly method.

The composite multilayer film further calcined at high temperature to obtain a core – shell nanostructure TiO_2/SiO_2 composite particles which can be used in organic wastewater treatment [12]. In this experiment, we obtained the self-assembled film formed by surfactant cetyl-trimethyl ammonium bromide (CTAB) and glycine betaine and explored its ability to absorb lead ion wastewater.

2. Experimental sections

2.1. Materials

CTAB used in this study was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd; Organic glycine betaine and Lead nitrate were purchased from Sinopharm Chemical Reagent Co., Ltd. Sulfuric acid, hydrogen peroxide, anhydrous ethanol, and ammonia water were produced by Xi'an Chemistry Reagent Company. Disulfide hydrazone was provided by Tianjin hedong district red crag reagent factory. Unless otherwise stated, all solvents were of analytical grade.

2.2. The preparation of self-assembled film

In order to obtain clean and activated substrates, the glass slides and quartz glass slides were pretreated as follows: the substrates were soaked in H_2O_2/H_2SO_4-mixed solution (volume ratio = 1:1) for 6 h. The substrates were rinsed repeatedly by redistilled water. Then substrates were immersed in $H_2O/H_2O_2/NH_3{\cdot}H_2O$ solution (volume ratio 5:1:1) for 6 h. Then substrates were sonicated in ethanol for 20 min. Redistilled water was further used to rinse removal etching agent and solvent. The substrates were re-suspended in water. Before use, it is necessary to blow dry substrates.

The self-assembled films were made in a simple process. Firstly, CTAB or glycine betaine was dissolved in anhydrous ethanol to obtain a certain concentration solution. The pH value was adjusted by 2 mol/L sodium hydroxide. Then, substrates were immersed in CTAB solution or glycine betaine solution for a certain time at a certain temperature. At last, the substrates were taken out and air-dried under nitrogen protection to obtain self-assembled films.

2.3. The treatment of lead ion in wastewater

Lead ion wastewater was copied by configuring lead nitrate (0.5 mol/L) aqueous solution. Above self-assembled films were put into 50 mL of lead ion wastewater for a certain time. At last, the substrates were taken out and air-dried under nitrogen protection.

2.4. Characterization

Fourier transform infrared spectrometer (Nicolet (5700), American Nicolet Company) was used to investigate the structure of self-assembled films with KBr tablet method. The self-assembled film was dissolved in ethanol and coated on the KBr tablets. The solvent was evaporated before the test. The microstructure morphology of self-assembled films was observed by BX-51Optical microscope (Olympus Company) and JSM 6390A Search Engine Marketing (SEM, JEOL Company).

The concentrations of lead ion wastewater were tested by UV 3300PC Ultraviolet–visible spectrophotometer (APADA Company). The wavelength range was 200–800 nm under the standard curve method. Firstly, the maximum absorbance peak value of test solution was at 510 nm. Lambert–Beers' law is obeyed in the range of Pb^{2+}. Weakly alkaline condition, bivalent lead ions (Pb^{2+}) and disulfide hydrazone generated purple complex. Then, in order to acquire different concentrations of lead ion solution, we took a reasonable amount of the prepared 50 mmol/L lead standard solution (1, 2, 4, 6, 8, 10, 15, 18, 20 mL) in 50-mL volumetric flask, diluted with water to 50 mL and shook well. The linear calibration curve was drew up through gradient experiments (see Fig. 1). We scanned the solution before and after lead ion treatment, and then obtained their concentration through absorbance to calculate the removal ratio of lead ion. The removal ratio of lead ion was calculated by the following formula:

$$R = \frac{C_0 - C_1}{C_0} \times 100\%$$

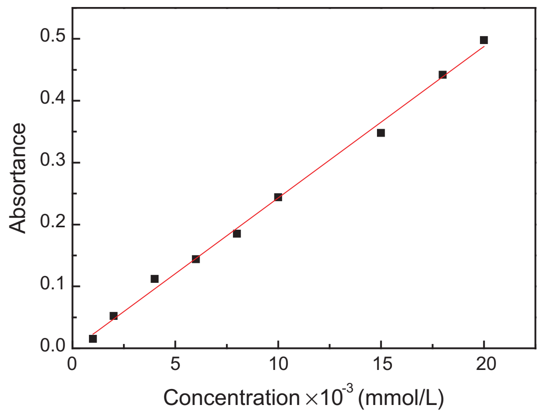

Fig. 1. The linear calibration curve of lead ion wastewater at 510 nm.

where R is the removal ratio of lead ion, C_0 and C_1 are the lead ion concentrations before and after adsorption, respectively.

3. Results and discussion

3.1. The relationship of self-assembled film morphology and surfactant types

The morphology of self-assembled film was observed by optical microscope. It could be seen from Fig. 2 that the surface of self-assembled film by CTAB was compact and smooth.

However, the surface of self-assembled film by glycine betaine possessed loose hole. CTAB was more easily spread on the substrate due to more charge than glycine betaine. In addition, Fig. 2(c) and (d) shows the surface of self-assembled film by CTAB was more smooth and orderly on quartz glass slide than glass slide. This is because the quartz glass slide has more silicon atoms than glass slide, after pretreatment, it exhibits better compatibility with the surfactant and its electrostatic adsorption force is stronger, which is more favorable to self-assembled formed film. So in subsequent experiments, we choose the

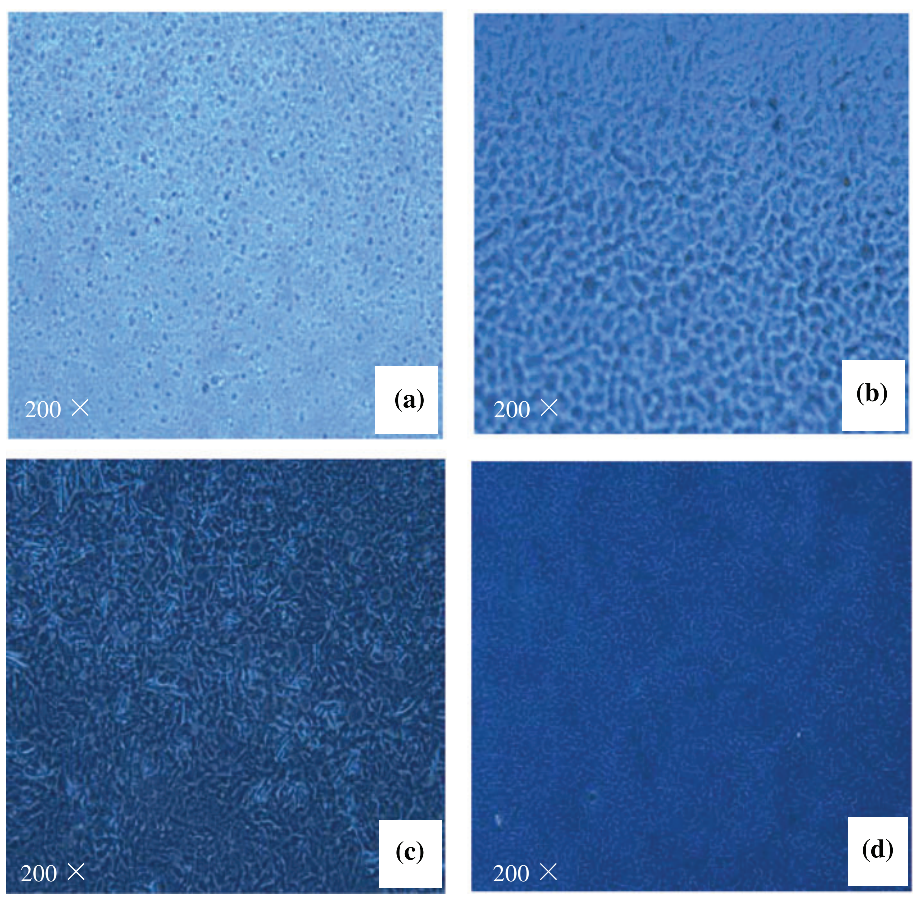

Fig. 2. The optical microscope images of the self-assembled products from: (a) glycine betaine on glass slide, (b) glycine betaine on quartz glass slide, (c) CTAB on glass slide, and (d) CTAB on quartz glass slide.

self-assembled film by CTAB on the quartz glass slide to study the wastewater treatment.

The influences of CTAB concentration, the preparation time, and temperature of self-assembled film on the forming film are studied in Tables 1 and 2. Table 1 indicates that the self-assembled film is smooth and compact, when concentrations of CTAB were 30 and 40 mmol/L. But CTAB emerged precipitate from the solution for 40 mmol/L solution. So 30 mmol/L of CTAB is adopted to study the film variation by adjusting the preparation time and temperature in Table 2. Table 2 shows that the self-assembled film is obvious, when the preparation time are 60, 120, 180 min and the temperature are 30, 40, and 50℃. But, in order to cut cost and enhance efficiency, 180 min and 40℃ are selected. So the best processes of forming self-assembled film are 30 mmol/L of CTAB for 180 min at 40℃. After assembling the film, the time of the film absorbing lead ion is 180 min, for which temperature is 40℃.

3.2. *The lead ion adsorption of self-assembled film by CTAB on quartz glass slide*

Fig. 3 shows the FTIR of CTAB, self-assembled film by CTAB before and after adsorption of lead ion. For CTAB, the anti symmetric stretching vibration peak of CH_3–(N^+) are from 2,942 to 3,065 cm^{-1}. The 1,487 cm^{-1} peak is attributed to the anti symmetric angular vibration of CH_3–(N^+). The 1,473 cm^{-1} peak is caused by scissoring vibration of CH_2–(N^+). And when $n \geq 4$, the C–C and C–N stretching vibrations can be found at the scope of 719–730 cm^{-1} and 1,056 cm^{-1}, respectively. Fig. 3 also displayed that the shift of three curves has no obvious difference. It implied that self-assembled film by CTAB can be formed through static adsorption, Van der Wals forces or hydrogen bonds on the quartz glass slide. Similarly, lead ion wastewater also can be absorbed into self-assembled film [13]. So we concluded that the film forming mechanism of CTAB and adsorption mechanism as shown in Fig. 4. CTAB with positively charged nitrogen adsorbed on hydrophilic-treated quartz substrates by silicon oxygen bond, good wetting, so as to form a uniform film on the surface of the substrate. Due to a combination of silicon oxygen bond of the substrate and the CTAB film, when self-assembled film with negative oxygen ion was immersed in the Pb^{2+} solution, positive and negative ions attract each other to form self-assembled multilayers.

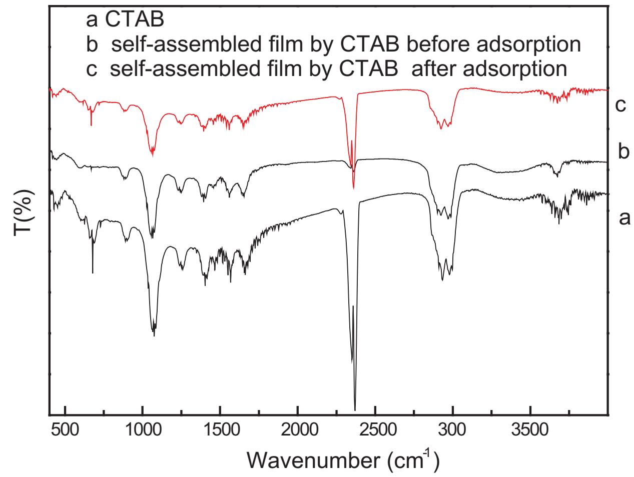

Fig. 3. FTIR of self-assembled film by CTAB.

Table 1
Influence of CTAB concentration on the forming film

Concentration (mol/L)	Before lead ion treatment
25	No obvious film
30	Smooth and compact film
40	Smooth and compact film, but CTAB precipitation from the solution

Table 2
Time and temperature of assembling film

	Temperature (℃)		
Time (min)	30	40	50
60	No obvious film	Irregular film	Obvious film
120	No obvious film	Obvious film	Obvious film
180	Irregular film	Obvious film and compact	Obvious film

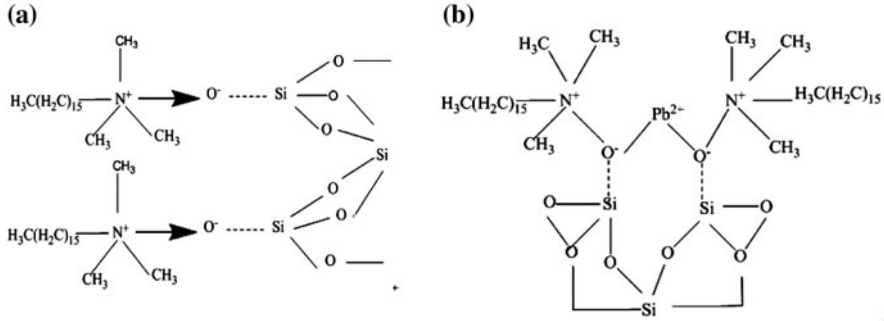

Fig. 4. The film forming mechanism of CTAB (a) and adsorption mechanism (b).

As we know, pH is a critical factor in the process of self-assembled film which can change the interaction between the molecules. Therefore, firstly we watched the self-assembled film by adjusting pH at fixed 30 mmol/L CTAB, 180 min and 40℃. It was found that self-assembled films were smooth and compact at the range of pH 2–8. The self-assembled films were obvious at pH 10 and 12. Then the removal ratio of lead ion in wastewater was investigated (see Fig. 5). On increasing the pH, the removal ratio gradually increased at the range of pH 2–8. However, the removal ratio slightly decreased when pH > 8. The removal ratio of lead ion is best, increased up to 80% at pH 8. Under alkaline conditions, CTAB in solution easily forms negatively charged micelles, which more easily absorbed lead ions in solution. But under strong alkaline conditions, it is difficult to obtain smooth and compact large-area films, so the removal ratio decreased. Under acidic conditions, the removal protonic acid in the film decreased the lead ion adsorption ability of film.

Then, we discussed the influence of the time of treating wastewater on the removal ratio of lead ion. As shown in Fig. 6, as the treating time increased from 0 to 120 min. the removal ratio gradually increased from 77 to 80%. When the extension of processing time increased from 120 to 180 min, the removal ratio tended to equilibrium in the self-assembled film.

Fig. 7 gave the morphology of self-assembled film by CTAB before and after lead ion treatment. The optical and SEM images indicated that the film was smooth, compact, and ordered before lead ion treatment (see Fig. 7(a) and (c)). As shown in Fig. 7(b) and (d), after the adsorption of lead ions, tiny holes appeared on the film , but it was still a closely packed whole film. After pretreatment of quartz slides, the surface contained more charge, so CTAB is more beneficial for electrostatic adsorption, and firmly attaching to the substrate. Therefore, the structure of the self-assembled film is relatively stable, it does not fall off even after immersion of lead ions in wastewater.

At last, the distribution of the element was confirmed by the energy disperse spectrometric (EDS) from Fig. 8. As shown in Fig. 8(a), the contents of C and O element were higher, which imply CTAB

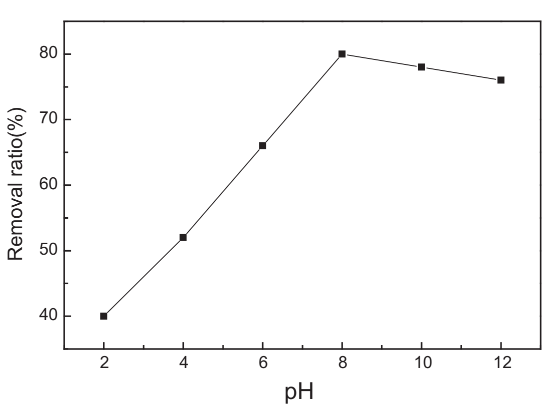

Fig. 5. The effect of pH value on removal ratio of lead ion in wastewater.

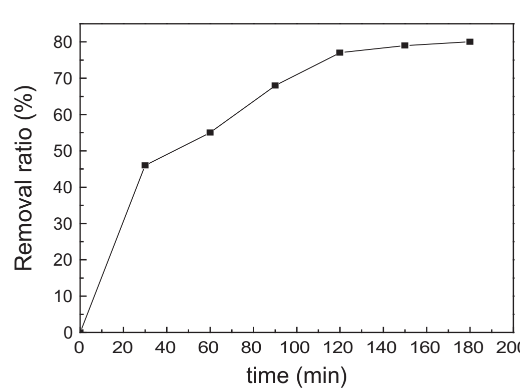

Fig. 6. The effect of the time of treating wastewater on the removal ratio of lead ion in wastewater.

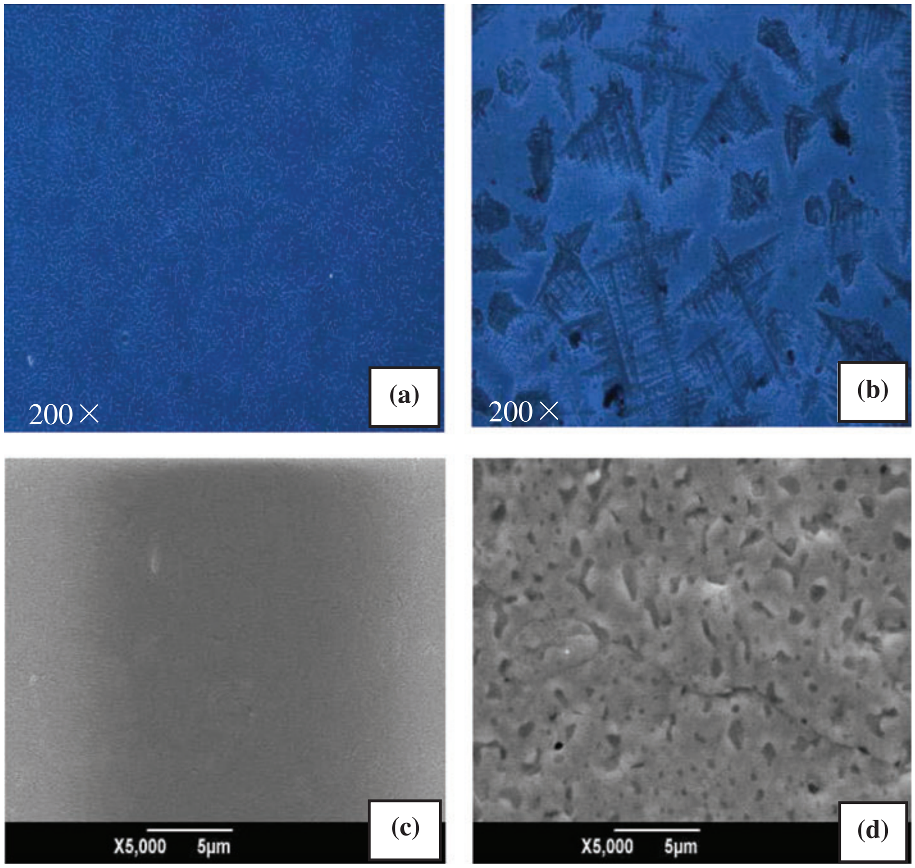

Fig. 7. The optical microscope images of the self-assembled film by CTAB ((a) before lead ion treatment and (b) after lead ion treatment), SEM images of the self-assembled film by CTAB ((a) before and (b) after lead ion treatment).

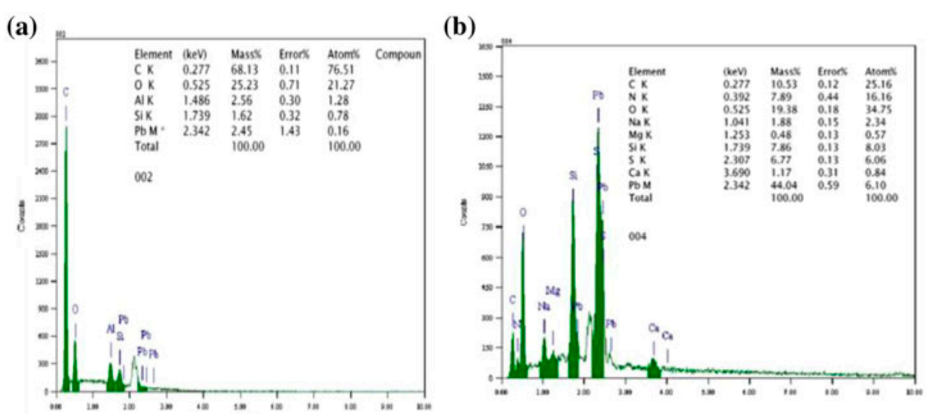

Fig. 8. EDS analysis of the self-assembled film by CTAB ((a) before and (b) after lead ion treatment).

absorbed onto the surface of quartz glass slide. The content of lead ion increased after lead ion treatment compared to before lead ion treatment. It further verified that lead ions are absorbed onto the self-assembled film.

4. Conclusion

In summary, self-assembled films were prepared in a simple process. The self-assembled film of CTAB on quartz glass is smooth, uniform, and compact. The best processes of forming self-assembled film are that quartz glass immersed in 30 mmol/L CTAB for 180 min at 40℃ and pH 8. The removal ratio of lead ions in wastewater is up to 80%.

Acknowledgments

We greatly acknowledge National Natural Science Fundation of China (No. 51402132), Jiangsu Provincial Natural Science Foundation of China (Grant No. BK2012279), Shaanxi Provincial Research Training Program (No. 201407051035).

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