Coprecipitated Removal of Cu²⁺ Using Dextran in Cationic Porphyrin Aqueous Solution

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Removal of copper ion (Cu²⁺) using water-soluble porphyrin and dextran was investigated. Cu²⁺ can be removed using dextran very rapidly in the form of a [(TMPyP)Cu]⁴⁺ complex, and the extent of removal can reach almost 100% with the addition of acetone. Electron paramagnetic resonance (EPR) results confirm the existence of Cu²⁺ in precipitates. The order in which dextran and acetone are added strongly influences the removal of Cu²⁺. This work suggests an efficient method to remove Cu²⁺ ions from waste water.

1. Introduction

Copper is an important trace element for living organisms, because it is involved in several biological processes.[1,2] However, the intake of an excess amount of copper is toxic for humans. Therefore, the determination and removal of trace amounts of copper in waste water are meaningful and essential for human life. Much effort has been made to remove copper from waste water. Previous methods, such as liquid–liquid extraction (LLE),[3] cloud point extraction (CPE),[4] and solid phase extraction (SPE),[5] have been widely used to remove copper from water.

Porphyrins are macrocyclic compounds that contain four pyrrole rings. Porphyrins can coordinate with medium-sized metals, such as Cu, Zn, and Ni, to form metalloporphyrins.[6,7] *meso*-Tetrakis(*N*-methylpyridinium-4-yl)-porphine (TMPyPH2) (Fig. 1) is a water-soluble porphyrin, which can selectively coordinate with Cu²⁺. The complex [(TMPyP)Cu]⁴⁺ can be easily detected by UV-vis absorption spectroscopy. Thus, TMPyPH2 can be used as a chelating agent to interact with Cu²⁺, and the concentration can be determined from UV-vis spectra without the use of some other

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Fig. 1.   Structure of TMPyPH2 and dextran.

methods requiring high-cost equipment, such as atomic absorption spectroscopy and inductively coupled plasma mass spectrometry.

Dextran is a bacterial polysaccharide, which has been used in food, pharmaceutical, and chemical industries.[8] There are many OH groups in the structure of dextran (Fig. 1) with which dextran can interact with water molecules in an aqueous solution. Moreover, Yokoi *et al*.[9] reported a hydrophobic interaction between $Cu(OH)_2$ and poly(vinyl alcohol) (PVA). In their study, $Cu(OH)_2$ was covered with a PVA polymer chain to form a complex [Fig. 2(a)]. Dextran also contains a hydrophilic OH group and is similar to PVA. Dextran experiences the same type of interaction with the complex [(TMPyP)Cu]$^{4+}$. Thus, dextran and the complex [(TMPyP)Cu]$^{4+}$ could be coprecipitated [Fig. 2(b)]. Dextran was used in this study to investigate its effect on the removal of Cu^{2+} from an aqueous solution. In this study, the removal of Cu^{2+} using TMPyPH2 and dextran was investigated. This study may provide a useful method for heavy metal absorption.

2.   Materials and Methods

2.1   *Materials*

All reagents were used directly after purchasing without any further purification except as noted.   5.10.15.20-Tetrakis(*N*-methylpyridinium-4-yl)-21H, 23H-porphine, tetrakis(*p*-toluenesulfonate) (TMPyPH2) was purchased from Dojindo Molecular Technolgies (Japan).   Sulfuric acid (97%), acetone, standard copper solution (1000 ppm), acetic acid, and sodium acetate were purchased from Nacalai Tesque, Inc. (Japan). Hydroxylamine hydrochloride (>97%) was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Two dextran polymerswith molecular weights of 40000 and 2000000 (Dex-4 and Dex-200, respectively) were purchased from Pharmacia (Sweden).

2.2   *Methods and measurement*

Buffer solution: A buffer solution with a pH of 4.5 was obtained by mixing acetic acid and sodium acetate.

Sulfuric acid solution [H_2SO_4 (aq)]: 50 mL of 97% sulfuric acid and 50 mL of distilled water were mixed together and cooled.
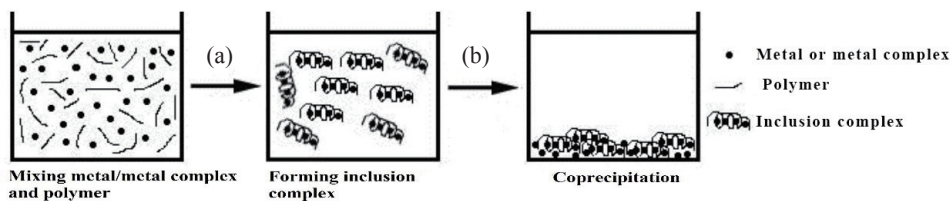
Fig. 2.   Illustration of the interaction between a polymer and a metal.

Cu-TMPyPH2 solution with 10 ppm Cu^{2+}: 0.25 mL of 1000 ppm standard copper solution and 0.0107 g of TMPyPH2 were mixed and poured into a 25 mL volumetric flask. Then, 1 mL of buffer solution (pH = 4.5) and 1 mL of 0.5% hydroxylamine hydrochloride aqueous solution were added, and the solution was diluted to a volume of 25 mL with distilled water.

Dextran solution: Aqueous Dex-200 solutions with concentrations of 4.86 g/100 mL and 1.62 g/100 mL were prepared by dissolving the polymer in 100 mL of distilled water at 40 °C and cooling to room temperature. An aqueous Dex-4 solution with a concentration of 4.86 g/100 mL was prepared by stirring the polymer in 100 mL of distilled water at room temperature.

UV-vis absorption spectra were recorded with a JASCO V-570 UV/VIS/NIR spectrophotometer. Electron paramagnetic resonance (EPR) spectra were measured with a JEOL-JES-310 EPR spectrometer at room temperature.

3.   Results and Discussion

3.1   *UV-vis spectra*

UV-vis spectra of Cu-TMPyPH2 solutions with and without Dex-200 are shown in Fig. 3. The Cu-TMPyPH2 solution showed two Soret bands with λ_{max} = 423 nm and λ_{max} = 449 nm. Peaks at 423 and 449 nm were assigned to the complexes of $[(TMPyP)Cu]^{4+}$ and $[(TMPyP)H4]^{6+}$.[10] Under these conditions, the amount of TMPyPH2 is in excess for binding all of Cu^{2+} ions. By comparing the absorbance values of the Soret bands of Cu-TMPyPH2 solutions with and without Dex-200, the absorbance was determined to obviously decrease after the addition of Dex-200. Moreover, in these experiments, a brown precipitate was observed after adding acetone in the solution containing Dex-200, while the pure dextran polymer precipitated by acetone was white. This indicates that $[(TMPyP)Cu]^{4+}$ was bound to dextran. The existence of Soret bands after adding Dex-200 also showed that there was some $[(TMPyP)Cu]^{4+}$ in the solution. More acetone was added to the solution, and a very small additional precipitate was observed, indicating that the amount of acetone was sufficient to precipitate Dex-200 under these conditions (shown in Fig. 3). Then, the concentration of Dex-200 was increased from 1.62 to 4.86 g/100 mL to determine whether dextran can remove Cu^{2+} at a higher efficiency. In addition, Dex-4 with a molecular weight of 40000 was also investigated for comparison.
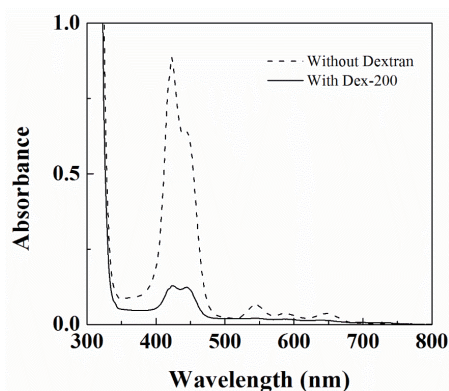
Fig. 3.   UV-vis spectra of the Cu-TMPyPH2 solutions with and without Dex-200. Conditions: 2 mL of solution (1 mL of Cu-TMPyPH2 solution + 2 mL of H_2SO_4 aq + 8 mL of 1.62 g/100 mL Dex-200 solution) + 8 mL of acetone.

The results are shown in Figs. 4 and 5.   The photograph of the three solutions in Fig. 4 shows that the solution turned from yellow to colorless and a brown solid was precipitated.   This indicates that dextran is very effective for removing Cu^{2+} from the solution.   Figure 5 shows that the absorbance was almost 0 for the solution with these two dextran polymers.   Dex-200 demonstrated better removal of Cu^{2+}.   The calculated removal ratios for Dex-4 and Dex-200 are 98 and 99%, respectively.   Here, the removal ratio is defined as $R = (A-A_{dex})/A \times 100\%$.   The term A is the absorbance of a solution without dextran at 423 nm, and A_{dex} is the absorbance of a solution with dextran at 423 nm.

3.2   *EPR spectra*

EPR spectra were recorded at room temperature.   The results (Fig. 6) showed that the EPR spectra of the two precipitates were almost the same; the parameters are $g_{\parallel} = 2.19$, $g_{\perp} = 2.02$, and $A_{\parallel}(Cu) = 2.06 \times 10^{-2}$ cm^{-1}.   These values are similar to those of copper (II) porphyrin complexes reported previously.[11]   This indicates that, in the precipitates, Cu^{2+} interacted with TMPyPH2 as a complex $[(TMPyP)Cu]^{4+}$.   Therefore, the complex $[(TMPyP)Cu]^{4+}$ retained its structure during the inclusion process and moved from water to the dextran phase in these processes.

3.3   *Influence of acetone volume*

In this study, acetone served as a precipitating reagent for dextran.   Thus, the amount of acetone added is an important factor that influences the removal efficiency.   The removal efficiency of dextran using different volumes of acetone was investigated.   Figure 7 shows the change in removal ratio using Dex-4 and Dex-200 with the addition of acetone in 1 mL increments.   The efficiencies were estimated by measuring the
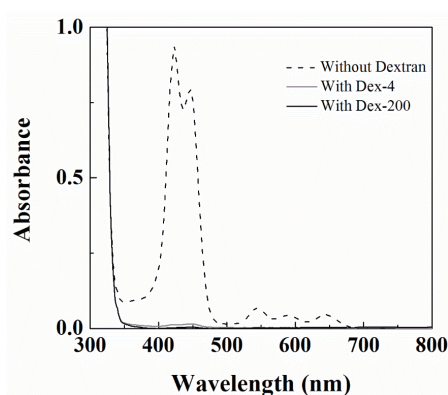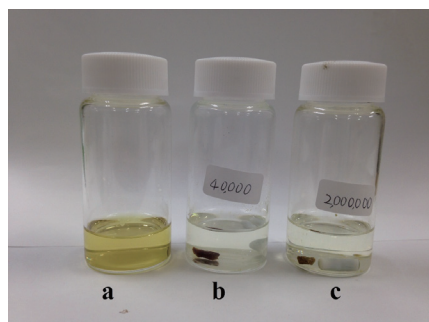
Fig. 4 (left). (Color online) Picture of the aqueous Cu-TMPyPH2 solution (a) without dextran, (b) with Dex-4, and (c) with Dex-200.

Fig. 5 (right). UV-vis spectra of Cu-TMPyPH2 solutions with and without dextran. Conditions: 1 mL of Cu-TMPyPH2 solution + 2 mL of H_2SO_4 aq + 8 mL of 4.86 g/100 mL Dex-200 solution + 8 mL of acetone.
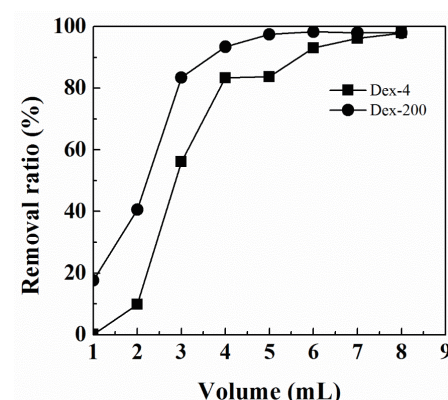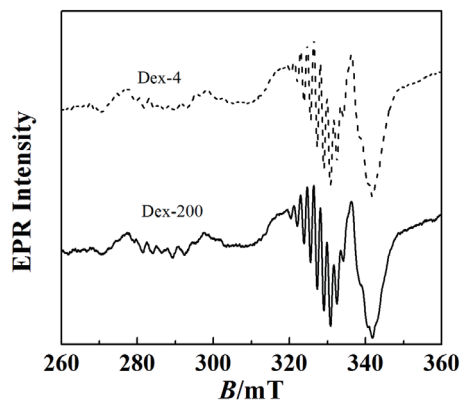

Fig. 6 (left). EPR spectra of precipitates at room temperature.

Fig. 7 (right). Change in the removal ratio of the two dextran polymers with change in acetone volume. Conditions: 2 mL of the solution (1 mL of Cu-TMPyPH2 solution + 2 mL of H_2SO_4 aq + 8 mL of 4.68 g/100 mL dextran solution) + acetone.

absorbance at 423 nm {the Soret band of $[(TMPyP)Cu]^{4+}$}. From the graph, we observe that the removal ratio increased as the amount of acetone added increased, and that 8 mL of acetone could precipitate almost all of $[(TMPyP)Cu]^{4+}$ (Fig. 7). Dex-200 yielded better results than Dex-4 when compared with the same acetone volume. For these two dextran polymers, the removal ratio reached almost 100%. That the dextran with higher molecular weight was more efficient may be caused by the less relaxed polymer chains of Dex-200.

3.4   *Influence of dextran mass*

The influence of dextran was investigated by adding a dextran solution to Cu^{2+} solution (0.5 mL of Cu-TMPyPH2 solution + 2 mL of H_2SO_4 aq + 22 mL of acetone). The volume ratio of Cu-TMPyPH2: H_2SO_4: acetone was kept the same as the conditions in the caption of Fig. 5.   The UV-vis spectrum (Fig. 8, 0 mL) of the solution before adding dextran showed the Soret band at a slightly different wavelength compared with spectra in earlier discussion.   The Soret band had 4 peaks at λ_{max} = 396, 423, 449, and 477 nm. The peaks at the wavelengths of 423 and 449 nm belong to $[(TMPyP)Cu]^{4+}$ and $[(TMPyP)H4]^{6+}$, while the origin of the other two peaks is not clear yet.   The absorbances of peaks at 423 and 449 nm increased when the solutions were diluted with water, indicating that the concentration of $[(TMPyP)Cu]^{4+}$ and $[(TMPyP)H4]^{6+}$ complexes increased with dilution.   The absorbances of peaks at 396 and 477 nm decreased with dilution.   Finally, the absorbance of the peak at 423 nm reached its highest value when 12 mL of water was added to the solution. At the same time, the peaks at 396 and 477 nm disappeared.   The change in absorbance in Soret band suggests that TMPyPH2 interacts with acetone and Cu^{2+}.   The interaction between TMPyPH2 and acetone could be disrupted by adding water.

To precisely determine the effect of dextran mass, the Cu^{2+} solution (0.5 mL of Cu-TMPyPH2 solution + 2 mL of H_2SO_4 aq + 22 mL of acetone) was diluted with 12 mL of water.   The experimental conditions were slightly different from the conditions shown in Fig. 5, because the absorbance of peak at 423 nm was highest after the addition of 12 mL of water.   As shown in Fig. 9, the removal ratio increased as the dextran mass was increased.   Compared with the conditions shown in Fig. 5, the removal ratio was smaller in Fig. 9 than in Fig. 5, even if the reagent ratio was higher in Fig. 9.   Thus, we
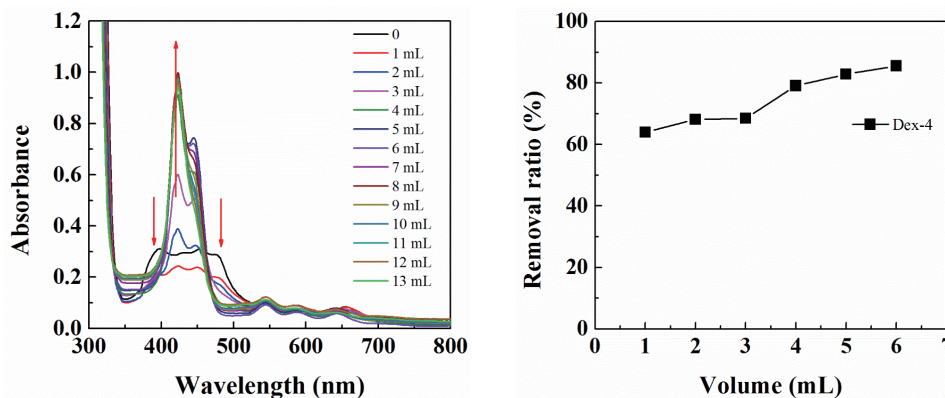

Fig. 8 (left).   (Color online) UV-vis spectra of Cu-TMPyPH2 solutions diluted with water. Conditions: 0.5 mL of Cu-TMPyPH2 solution + 1 mL of H_2SO_4 aq + 22 mL of acetone.
Fig. 9 (right).   Change in removal ratio as the volume of Dex-4 was increased. Conditions: 0.5 mL of Cu-TMPyPH2 solution + 1 mL of H_2SO_4 aq + 22 mL of acetone + 12 mL of water.
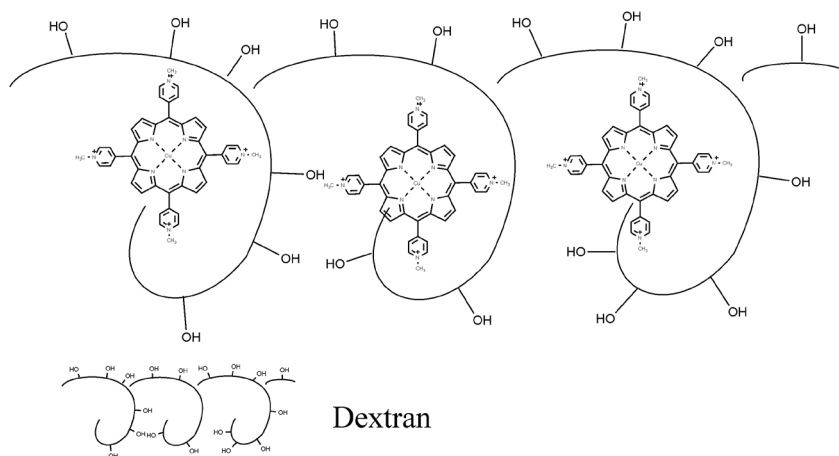
Fig. 10. Illustration of mechanism of the interaction between dextran and [(TMPyP)Cu]$^{4+}$.

can conclude that the reagent loading sequence influences the removal efficiency. For the Cu-TMPyPH2 solution (containing H$_2$SO$_4$), if dextran were added first, the dextran could mix with [(TMPyP)Cu]$^{4+}$ sufficiently and interact with [(TMPyP)Cu]$^{4+}$. Then, [(TMPyP)Cu]$^{4+}$ and dextran would be coprecipitated with acetone. However, if acetone were added first, dextran might be precipitated directly without [(TMPyP)Cu]$^{4+}$, because the acetone was in excess in the solution.

3.5   *Mechanism*

The result of changing the reagent loading sequence indicates that dextran interacts with [(TMPyP)Cu]$^{4+}$ in an aqueous solution. Additionally, there was no precipitate formed without dextran in the solution of Cu-TMPyPH2 and acetone. Therefore, dextran plays a main role in removing Cu^{2+}. EPR results showed that Cu^{2+} formed the complex [(TMPyP)Cu]$^{4+}$ in the precipitates, indicating that Cu^{2+} is removed by dextran in the form of [(TMPyP)Cu]$^{4+}$. From these results, we suggest that the mechanism for the interaction between dextran and [(TMPyP)Cu]$^{4+}$ is similar to the interaction mode described by Yokoi *et al.*[9] Figure 10 illustrates the interaction between dextran and [(TMPyP)Cu]$^{4+}$.

4.   Conclusions

Removal of Cu^{2+} using TMPyPH2 was investigated with the assistance of dextran. Cu^{2+} can be removed in the form of [(TMPyP)Cu]$^{4+}$ by dextran very rapidly, and the removal ratio can reach almost 100% by precipitation with acetone. EPR results confirm the presence of Cu^{2+} in precipitates. The loading sequence for dextran and acetone strongly influences the removal ratio. Dextran must be added to the solution first. This study presents an efficient method for the removal of Cu^{2+} from waste water.

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