

Removal of Cu(II) by Polypyrrole Deposits on Stainless Steel Mesh

Tian Ying,¹ Yang Weishen,² Yang Fenglin²

¹School of Environmental and Chemical Engineering, Dalian Jiaotong University, China

²Department of Environmental Science and Technology, Dalian University of Technology, China

Received 10 April 2006; accepted 13 September 2006

DOI 10.1002/app.25632

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The reduction of Cu(II) in aqueous media by polypyrrole deposits on stainless steel mesh is examined in this work. The kinetics of Cu(II) reduction, the influence of temperature, and the possibility of the regeneration and reuse of polypyrrole for Cu(II) reduction have been investigated. The morphology of stainless steel mesh/polypyrrole electrodes has been monitored with

scanning electron microscopy. The X-ray diffraction technique has been used to detect the formation of metallic copper deposits on the surface of polypyrrole films. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 629–633, 2007

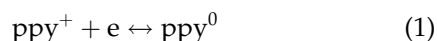
Key words: electrochemistry; kinetics (polym.); polypyrroles

INTRODUCTION

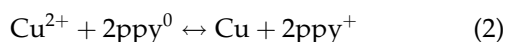
Copper is used in a variety of applications, including electrodeposition, metal fining, and electroplating. Wastewater containing Cu(II) must be treated to restrict its concentration before discharge. Treatment strategies include ion exchange, active carbon adsorption, and chemical treatments. The former two methods can remove Cu(II) effectively but at a comparatively high price. Chemical treatments can produce hydroxide precipitation at high pHs, which prevents water recycling because of the high salt content.

A novel application of conducting polymers has been proposed for environmental remediation. In particular, polypyrrole (ppy) is being considered for the reduction of heavy metals because of its good reversible redox properties.^{1–5}

ppy can be reduced from an oxidized state to a reduced state (ppy⁰) as follows:



ppy⁰ can reduce Cu²⁺ to Cu⁰ and can itself be oxidized:



Oxidized ppy can be reduced again for regeneration and reused for another reaction cycle between ppy⁰ and Cu²⁺.

Stainless steel mesh (SSM) was chosen as a substrate to generate ppy deposits in our work. The objective of this study was to evaluate the efficiency of the Cu(II) removal procedure from a sulfuric acid medium by ppy-modified electrodes.

EXPERIMENTAL

Before electropolymerization, SSM (80 pores per inch) as a working electrode with dimensions of 18 × 12 mm² was rinsed with acetone and distilled water. A stainless steel plate with dimensions of 18 × 30 mm² was employed as a counter electrode and also rinsed before use. A saturated calomel electrode (SCE) was used as a reference electrode.

The preparation of the ppy films was carried out in a one-compartment glass cell. The ppy film was grown potentiostatically at 0.8 V for 10 min on the SSM electrode from an aqueous solution containing 0.21M pyrrole and 0.14M *para*-toluenesulfonic sodium (PTS) in a three-electrode cell. After growth, the SSM-ppy composite was rinsed with distilled water and reduced in a 0.21M PTS solution at –0.8 V for 10 min. Then, the reduced-ppy-coated electrode was rinsed in distilled water and transferred to an acidified CuSO₄ solution (10 mL, 4.3 × 10^{–4}M concentration, pH 1.6). After a reaction with Cu(II), the metallic copper that was deposited during the reaction process on the surface of the ppy film was cleaned up by immersion in a 8M H₂SO₄ solution for 10 min. After that, the ppy film was in its oxidized state and then was regenerated with the conditions for reduction specified previously for further use.

Correspondence to: Y. Fenglin (sweethusk@126.com).

After each contact cycle, a small part of the ppy film was peeled off the electrode to determine the conductivity by the four-point method.

Cyclic voltammetry was performed to investigate the electroactivity of the ppy film at a scanning rate of 50 mV/s and in the potential range of -0.2 to 0.8 V in a $0.1M$ Na_2SO_4 solution. All electrode potential values are reported with respect to SCE, and all experiments were carried out at room temperature.

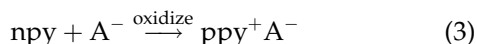
Samples containing Cu(II) were monitored with a Perkin model AA-646 flame atomic adsorption spectrophotometer (Japan). The synthesis and cyclic voltammetry of ppy were accomplished on a model 263A potentiostat/galvanostat from Princeton Applied Research. The scanning electron microscopy (SEM) was performed with a JSM 5600LV microscope (Japan). The X-ray diffraction (XRD) pattern of the sample was studied with a Perkin model 6000 diffractometer (Japan) with Cu $K\alpha$ radiation.

ppy was freshly distilled before use; otherwise, all reagents were acquired from commercial sources and were used as received. The solutions were prepared with distilled water.

RESULTS AND DISCUSSION

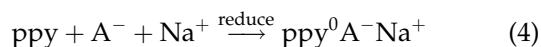
Kinetics of Cu(II) reduction by SSM-ppy⁰ electrodes

After polymerization, ppy is in oxidative state. The polymerization of ppy can be depicted as follows:



where py is pyrrole.

To maintain the charge neutrality, A^- counteranions are incorporated into the polymer structure. PTS is used as a dopant to form a ppy film in our experiment. The counteranion, *p*-toluene sulfonate, is large and immobile. Therefore, during the polymer reduction process in a PTS medium, cations (Na^+) in the solution are incorporated into the polymer structure as follows:



Then, ppy⁰ is immersed in a solution containing Cu(II). The kinetics of Cu(II) reduction as a function of contact time is shown in Figure 1. The removal efficiency is 37% at only 1 min and increases to reach a peak value of 90% at 20 min, which indicates that the reduction process is very fast. The charge consumed for the preparation of the ppy film at a constant potential of 0.8 V is 10 C, and the charge is 1.4 C during the reduction process by -0.8 V for 10 min. Obviously, the charge in the reduction process is considerably lower than that in the ppy preparation process, and this indicates that the film cannot be reduced completely and

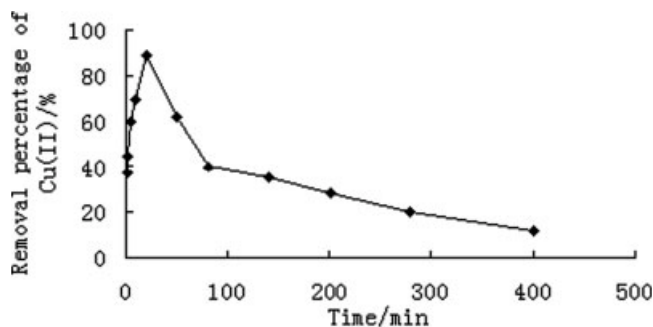
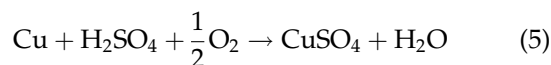


Figure 1 Removal percentage of Cu(II) as a function of time.

that part of the ppy film is still in its oxidative state or even loses its redox reversibility because of the nucleophilic attack by H_2O or O_2 causing conductivity decay in the ppy film.⁶ However, the theoretical charge needed to reduce the $4.3 \times 10^{-4}M$ $CuSO_4$ solution (10 mL) is only about 0.4 C; therefore, the stored charge in ppy⁰ is enough to react with Cu(II) according to eq. (2).

Figure 1 shows that the removal efficiency declines after 20 min, with only 10% at 400 min. This is ascribed to metallic copper dissolving in the sulfuric medium in the presence of oxygen. The reaction is



This result indicates that the contact time should be controlled strictly for the recovery of copper to avoid its dissolution in an acidified solution.

Influence of the temperature on the removal of Cu(II)

SSM-ppy⁰ electrodes were immersed in solutions with different temperatures and different rotation speeds in solutions containing Cu(II) for 10 min. The solutions were stirred by a rotor. The removal percentage as a function of the solution temperature is shown in Figure 2. The reduction efficiencies increase with the temperature, up to 100% at $65^\circ C$, but then decrease drastically to 10% at $90^\circ C$ and 3% at $100^\circ C$ at a rotation speed of 0 rpm. The removal efficiencies at a rotation speed of 600 rpm are much higher than that at 0 rpm.

The polymer electroactivity is controlled by both electron transfer and ionic transport between the solution and the polymer. The Cu(II) reduction process includes two primary rate-controlling steps: (1) Cu^{2+} ion diffusion from the bulk solution to the polymer/solution boundary or within the polymer and (2) charge transfer between Cu^{2+} and ppy⁰ A^-Na^+ . As we know, a high rotation speed can accelerate ion transport in a solution, whereas the process of elec-

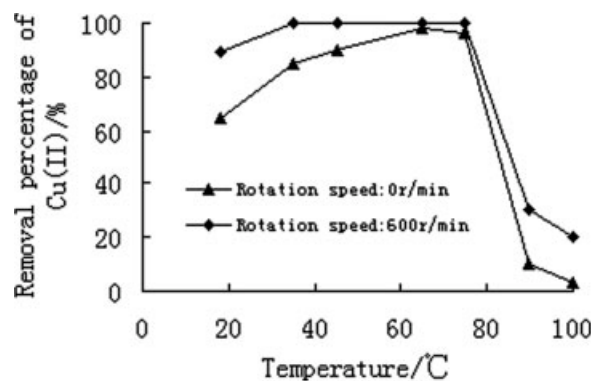


Figure 2 Removal percentage of Cu(II) as a function of temperature.

tron transfer is independent of the water flow speed. Data in Figure 2 demonstrate that a higher rotation speed results in higher reduction efficiencies. As a result, we can conclude that ionic transport is a rate-controlling step in this Cu(II) reduction process.

To investigate electroactivity at different temperatures for the prepared ppy film, cyclic voltammetry measurements in a 0.1M Na₂SO₄ solution were performed. Because the rate of ionic transport increases with the temperature, the magnitude of the current increases with the temperature, as shown in Figure 3, which means that the ppy film exhibits better electroactivity at higher temperatures. As a result, Figure 2 shows that the reduction efficiencies increase with the temperature; however, when the temperature is higher than 80°C, the Cu(II) reduction percentages decrease drastically. This abnormality is the result of two competing reactions. The ppy film shows higher electroactivity at higher temperatures, as mentioned previously, which can enhance the reaction between Cu(II) and the ppy⁰ film. However, the other reaction of the copper deposit dissolving in the presence of oxygen, expressed by eq. (5), is more competitive at a

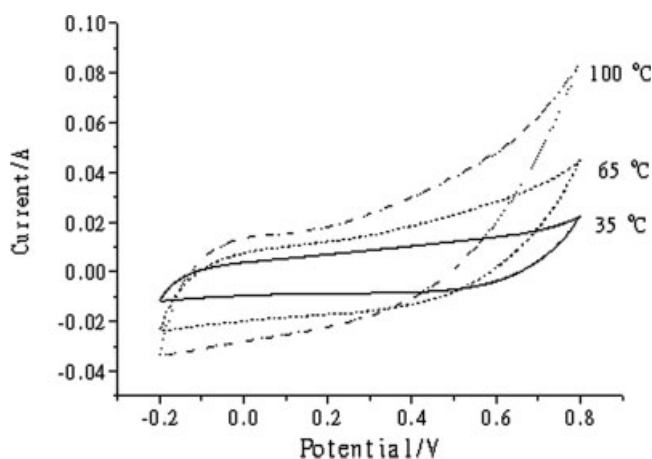


Figure 3 Cyclic voltammograms of ppy films in 0.1M Na₂SO₄ solutions at different temperatures.

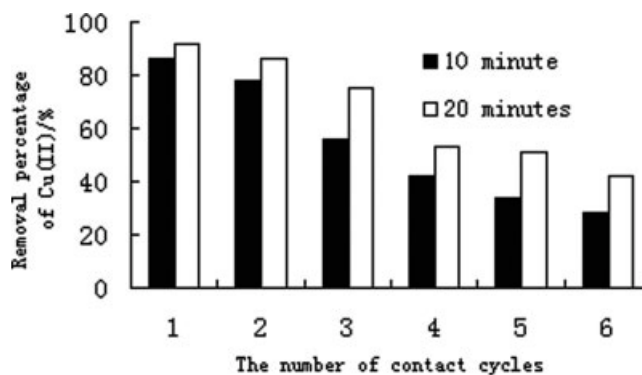


Figure 4 Removal percentage of Cu(II) as a function of the number of contact cycles.

higher temperature and dominates the whole process, thus resulting in low reduction efficiencies of Cu(II) at temperatures higher than 80°C.

Regeneration and reuse of the ppy film for the removal of Cu(II)

The removal percentages obtained with the SSM-ppy⁰ electrodes from the first to sixth contact cycles after regeneration are shown in Figure 4. Contact time of 20 min yields better results than 10 min. The reduction efficiencies in the first to sixth cycles vary from 86 to 28% for a contact time of 10 min and from 92 to 42% for a contact time of 20 min.

To investigate this efficiency decrease, the conductivity of the ppy film was determined. The conductivity of the freshly synthesized ppy film is 2 S/cm. However, it changes to 1 S/cm after the sixth contact cycle, and only 50% of the initial conductivity remains. Reference 6 suggests that the conductivity degradation occurs because of the attack of H₂O or oxygen on the conjugated double bonds within the polymer. The degradation of the ppy film exhibits reduced ability to recover Cu(II) from the solution after it is used for several cycles.

SEM and XRD of SSM-ppy electrodes

The SEM micrographs display the morphology of ppy-coated SSM in Figure 5(a,b). It can be observed clearly from Figure 5(b) that the ppy film is very regular in texture, with a small nucleus less than 1 μm in diameter. Figure 5(c) presents the morphology of the ppy film after immersion in a Cu(II) solution; it is difficult to tell the differences from the film before immersion [Fig. 5(b)], except for the dark color. However, the copper deposits on the surface of the ppy film have been proved by XRD, as shown in Figure 6. After being rinsed in strong sulfuric acid for the removal of the copper deposits, a large number of eroded pits occur on the surface of the ppy film, as shown in Figure 5(d).

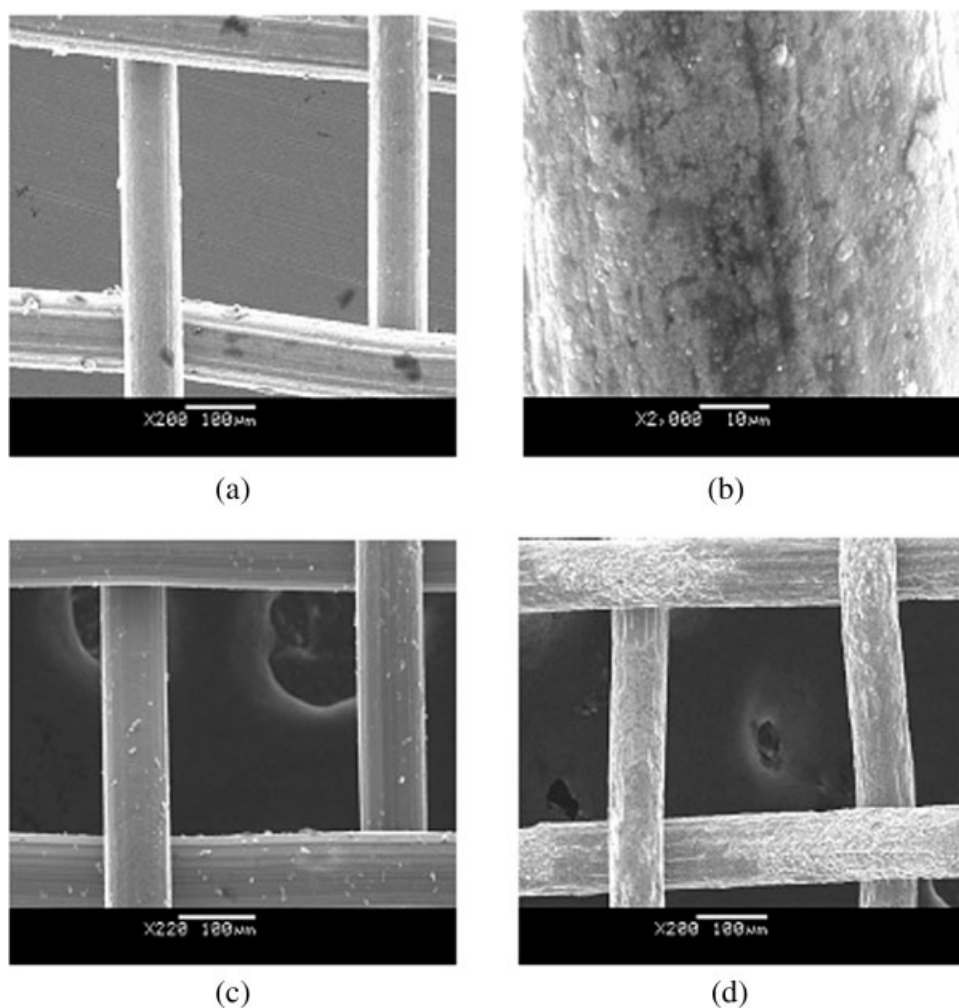


Figure 5 Scanning micrographs of different samples: (a) ppy-coated SSM (200 \times), (b) ppy-coated SSM (2000 \times), (c) SSM-ppy film after immersion in a Cu(II) solution, and (d) SSM-ppy after rinsing in sulfuric acid.

This weight loss is another reason explaining why the reduction efficiencies decline with the number of contact cycles after the regeneration and reuse of ppy.

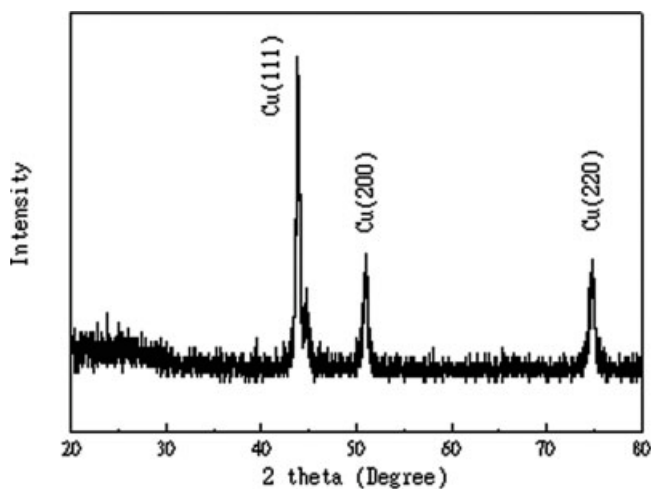


Figure 6 XRD spectra of a ppy film after immersion in a Cu(II) solution.

Diluted sulfuric acid has little impact on the morphology of the ppy film. However, a strong acid can erode the surface of the polymer significantly and cause an obvious conductivity decay. The effect of acid on the ppy film has been studied in our laboratory and will be discussed in detail in an other article.

The reduced SSM-ppy after the reaction with Cu(II) has been investigated with XRD, and the results are shown in Figure 6. The diffraction peaks appear at 2θ values of 43.86, 50.98, and 74.80, which correspond to Cu (111), Cu(200), and Cu(220), respectively, indicating the presence of metallic copper on the film surface.

CONCLUSIONS

Films of ppy grown on SSM substrates were obtained, and the reduced composites of the SSM-ppy electrodes were used as reducing agents for the reduction of aqueous Cu(II) solutions. The kinetics show that the reaction process between SSM-ppy⁰

and Cu(II) is very fast, with 90% efficiency at 20 min. XRD spectra have proved that metallic copper deposits form on the surface of the film. The dissolution of the deposited copper in the solution leads to a decrease in the reduction efficiencies with an increase in the contact time. The reduction percentages increase at a comparatively low temperature but decline sharply when the temperature is higher than 80°C because of the dissolution of the deposited copper in an acidified solution. The ppy film can be regenerated and reused for the reduction of Cu(II). One to six contact cycles yield 92–42% removal efficiencies at a contact time of 20 min and 86–28% removal efficiencies at a contact time of 10 min; this

indicates that the stability of the ppy film needs to be improved further for better cyclability.

References

1. Piatnicki, C. M. S.; Azambuja, D. S.; Hasse, E. E. S.; et al. *Sep Sci Technol* 2002, 37, 2459.
2. Alatorre, M. A.; Gutiérrez, S.; Páramo, U. *J Appl Electrochem* 1998, 28, 551.
3. Rodríguez, F. J.; Gutiérrez, S.; Ibanoz, J. G.; Braro, J. L.; Batina, N. *Environ Sci Technol* 2000, 34, 2018.
4. Wampler, W. A.; Basak, S.; Rajeshmar, K. *Carbon* 1996, 34, 747.
5. Conroy, K. G.; Breslin, C. B. *J Appl Electrochem* 2004, 34, 191.
6. Liu, Y.-C.; Hwang, B.-J. *J Electroanal Chem* 2001, 501, 100.