



Enhancement of heavy metals removal efficiency from liquid wastes by using potential-triggered proton self-exchange effects



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ABSTRACT

A concept of electrochemically switched ion exchange (ESIX) film with potential-triggered proton self-exchange effect (PTPS) for removal of Cu^{2+} ions was proposed. Based on this concept, a novel ESIX film made of poly (2,6-pyridinedicarboxylic acid) (PPDA) was successfully fabricated, and applied to remove Cu^{2+} ions from aqueous solution. It is found that Cu^{2+} ions were rapidly removed with a high selectivity and this film was reproducible by simple changing the applied potential. Herein, the mechanism of the potential-triggered proton self-exchange (PTPS) effect on the ion-exchange process using this kind of film was proposed. Electrochemical quartz crystal microbalance, IR spectroscopy and X-ray photoelectron spectra methods were used to characterize and attest the proposed mechanism. This PPDA film showed high potential for the Cu^{2+} detection and the treatment of wastewater containing heavy metal ions in various industrial processes.

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1. Introduction

Heavy metal pollution has become serious problem throughout the world because heavy metals are easily accumulated into the food chain and harmful to our health [1]. The selective removal of industrial heavy metals from wastewater is consequently the subject of considerable ecological and economic interest. The conventional methods include electrochemical and chemical precipitations [2], ion exchange [3], membrane separation [4], coagulation-flocculation [5], adsorption [6], and so on. Among them, ion exchange and adsorption are considered to be the most effective and efficient process for dealing with large volumes of wastewater [7]. Unfortunately, the regeneration of these exchangers and adsorbents will produce a large amount of secondary waste from the eluting and washing processes. In addition, some organic exchangers could lose approximately 3% of their capacity per cycle [8]. Furthermore, the limitation of the absorption/desorption rate restrains the development of timely heavy metal ion removal in many facilities. Therefore, finding a way for rapid, green and selective removal of heavy metal ions is needed.

Electrochemically switched ion exchange (ESIX), which combines ion exchange and electrochemistry, is a selective and reversible approach for the separation of objective ions with little or no secondary waste [8]. Therefore, development of potential-responsive ESIX films with diverse functional characteristics is attracting increasing interest from various fields. However, most of the relevant studies focused on solo inorganic transition hexacyanometalates or composites for removal of alkaline or alkaline earth metals [9–13]. Recently, conducting polymers have attracted a great deal of attention due to their unique electrical and electrochemical properties. Polyaniline (PANI) and polypyrrole (PPy) are the most commonly investigated conducting polymers because of their high electrical conductivity, ease of preparation, and environmental stability [14–16]. To date, the most attention has focused on the ESIX behaviors of different conducting polymer-based composites for anion, such as perchlorate (ClO_4^-) or fluoride removal [14–16]. However, ESIX of heavy metal ions using conducting polymers, to the best of our knowledge, has not been reported so far. Due to the existence of carboxyl-containing functional groups with chelating heavy metal ion effect and free proton, it is expected that conducting polymers are of more advantageous to the ESIX of heavy metal ions by internal proton self-exchange.

Since poly (2,6-pyridinedicarboxylic acid) (PPDA) film has the rich electroactive center and three-dimensionally available field potential, PPDA film-modified electrode has been found to have stable performance with good infusible and insoluble capability. It has

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been used in biosensors with different immobilized biomolecules in its film [17–20]. Through electrochemical polymerization reaction, analogous to that of polyaniline, the film made of the PPDA analogue has also been produced [17–20]. In the present study, a concept of electrochemically switched ion exchange (ESIX) film with potential-triggered proton self-exchange effects (PTPS) for removal of Cu^{2+} ions was proposed. PPDA films were prepared on the electrodes and used for the ESIX of Cu^{2+} in the wastewater. As-prepared PPDA film was characterized by X-ray photoelectron spectra (XPS) and Fourier transform infrared spectrometer (FT-IR). The uptake/elution of Cu^{2+} ions on the PPDA electrode and the mechanism of ESIX with PTSPS and the structure variations of PPDA film at different redox states were investigated by EQCM, FT-IR and XPS.

2. Experimental

The main reagents used for the synthesis of the material were obtained from National Medicine Group Chemical Reagent Co., LTD. All reagents were analytical grade and all solutions were prepared using deionized water.

Electrochemical experiments were performed using a VMP3 Potentiostat with the QCM922 Quartz Crystal Microbalance (Princeton, USA) controlled with EC-Lab software. A three-electrode system was used with an AT-cut Platinum quartz crystal wafer working electrode (9 MHz, electrode area: 0.2 cm^2 , electrode thickness: $\sim 300 \text{ nm}$) and a platinum sheet counter electrode. All reported potentials here were referenced to a saturated calomel electrode (SCE). PPDA films were prepared by unipolar pulse electro-polymerization (UPEP) in an aqueous solution containing 0.01 M 2,6-pyridinedicarboxylic acid and 0.5 M KCl. The procedure for hybrid film preparation has been detailed in our previous works [21,22]. In particular, the potential V_{on} applied during the on-times was 1.8 V . On-time of 0.4 s and off-time of 0.3 s was used. Deposited time was 600 s . Cyclic voltammetry and chronocoulometry were performed in 0.1 M $\text{Cu}(\text{NO}_3)_2$ solution.

FT-IR of the sample in KBr pellet was recorded on Fourier transform infrared spectrometer (Shimadzu FTIR-8400) workstation. XPS studies were performed using a VG Scientific ESCALab250i-XL unit with a monochromatized Al $K\alpha$ line at 1486.6 eV . Fixed analyzer pass energy of 20 eV was used for C1s core level scans. The ESIX process of the PPDA film electrode samples were performed by cycling the potential from 0.2 to 1.0 V at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ for 10 times, and then reduced/oxidized by chronocoulometry at $0.2/1.0 \text{ V}$ for 120 s in the 0.1 M $\text{Cu}(\text{NO}_3)_2$ aqueous solution, respectively. The electrode samples were rinsed with water and dried in the vacuum drying oven before characterizing its structure before XPS analysis.

3. Results and discussion

The concept of the proposed electrochemically switched ion exchange (ESIX) film with potential-triggered proton self-exchange effect (PTPS) for removal of Cu^{2+} ions and the procedure for ESIX of Cu^{2+} ions are schematically illustrated in Fig. 1. Herein, the ESIX film is electroactive PPDA. It is known that the pyridine rings are protonated/deprotonated when the PPDA chains are reduced/oxidized [23,24]. This cation exchange behavior is analogous to that of PPy modified with large counterions, e.g. polyvinylsulfonate (PVS^-), polystyrenesulfonate (PSS^-), with the immobility in the polymer matrix. Therefore, the charge compensation during the reduction involves incorporation of cations in the film to balance the negative charge of permanently incorporated large COO^- anions. Furthermore, the PTSPS between the pyridine and carboxyl group means that the PPDA-based film has potential responsive and reversible

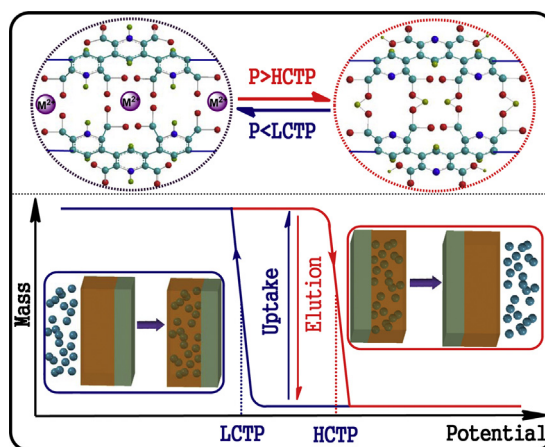


Fig. 1. Schematic illustration of the proposed electrochemically switched ion exchange (ESIX) film with potential-triggered proton self-exchange effects (PTPS) for removal of Cu^{2+} ions and the ESIX Cu^{2+} ion procedure. P: Potential of PPDA film electrode; LCTP: the lowest critical transfer potential; HCTP: the highest critical transfer potential.

proton self-exchange characteristics. In other words, intermolecular hydrogen bonds in the PPDA film transfer from carboxyl group to the pyridine when the electrode potential is lower than the lowest critical transfer potential (LCTP), and the intermolecular hydrogen bonds transfer from pyridine to the carboxyl group emerges when the electrode potential is higher than the highest critical transfer potential (HCTP). Furthermore, this film can uptake and elute Cu^{2+} ions by coupling effect following PTSPS. The intake of Cu^{2+} ions from the solution is executed by coupling to the carboxyl group, and the Cu^{2+} ions are excluded from the film to solution via proton exchange. Therefore, the proposed potential response film imbed Cu^{2+} ions by coupling to the carboxyl group at electrode potential below the LCTP as a result of intermolecular hydrogen bonds transfer from carboxyl group to the pyridine, and Cu^{2+} ions are excluded by proton exchange at electrode potential above the HCTP as a result of intermolecular hydrogen bonds transfer from the pyridine to carboxyl group. Consequently, the electroactive PPDA film achieves removal of Cu^{2+} ions and the removal process should be effective and reproducible.

3.1. Electrodeposition of PPDA film

The kinetic of electrochemical polymerization of conducting polymers is typically governed by the diffusion-limited transport of the supplies around the electrode surface. Hence, if a facile way to control this transport is devised, the structure and property of electroactive film can be precisely tuned. In this study, this was accomplished by a UPEP method [21,22]. The optimum operation parameters for the electrochemical polymerization of PPDA employing the UPEP method was found to be an on-potential of 1.8 V , on-time of 0.4 s and off-time of 0.3 s over 850 cycles (corresponding to 10 min deposition time). Fig. 2A shows the first 10 s potential/current-time transient curves during the pulse polymerization process for the fabrication of PPDA film. As pulse polymerization began and the film started to form, the open circuit potential measured during the off-time decreased rapidly from 1.8 V to approximately 1.2 V (blue line) and then increased gradually over time as the film thickened. This is also reflected by the fact that the maximum current was reached when the on-time was increased to 4.05 mA (black line). The oxidation state of the synthesized PPDA film could be maintained at t_{off} since the open circuit potential on the working electrode was over 1.2 V throughout the polymerization process. During a relatively long off-time,

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