



A sunlight assisted dual purpose photoelectrochemical cell for low voltage removal of heavy metals and organic pollutants in wastewater



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HIGHLIGHTS

- Principle and demonstration of a novel dual purpose photo-electrochemical cell.
- Simultaneous removal of heavy metals and organic pollutants from wastewater.
- Metal removal on cathode with nearly 100% current efficiency.
- Sunlight assisted anodic decomposition of organic pollutant.
- 60% Reduction of the working voltage of the photo-electrochemical cell.

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ABSTRACT

Photoelectrochemical cells that consisted of a Pt (small cells) or Ti (large cells) cathode and a sunlight responsive WO_3 photoanode were built for simultaneous removal of heavy metal ions and organic pollutants. Synthetic wastewater samples containing 0.5 M of NaCl, 10 ppm of methylene blue (MB, organic pollutant), 500 ppm of Cu^{2+} or 500 ppm Ni^{2+} were tested as the first examples for demonstration of the principle, device and process. The results showed that upon irradiation of simulated sunlight on the photoanode, metal ions (Cu^{2+} and Ni^{2+}) can be recovered as metals or hydroxide at the cathode. MB was simultaneously decomposed at the photoanode without using any additional chemicals as sacrificial agents. The cell voltage required for this dual purpose process was as much as 71% or 60% lower than that required for conventional electrodeposition of Cu or Ni respectively with an inert anode. Charge efficiency was close to 100% for the cathodic processes, and over 70% for the photoanodic degradation of MB through a combined mechanism of partial oxidation and mineralisation according to UV–Vis spectroscopic evidence and reaction pathway analysis.

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1. Introduction

Wastewaters are often highly complex in composition, and may require several different technologies to clean up the pollutants such as heavy metals and organic species. At present, a large amount of wastewater containing a wide range of heavy metals is discharged from various industries such as metal plating, metal surface treatment, wood processing and petroleum refining [1]. Once discharged to the environment, and due to their high solubility in water and non-biodegradable characteristics, heavy metal ions can be easily absorbed by, and accumulated in living organisms. Although trace amounts of some heavy metals are essential for metabolic function, they become toxic or carcinogenic when accumulated beyond the maximum permitted concentrations

[2,3]. Therefore, it is necessary to control the concentration of toxic heavy metals in the aquatic environments.

Electrodeposition, one of the electrochemical techniques for the removal of heavy metals, is regarded as a clean technology in that it does not produce any permanent residues or byproducts that require further separation and treatment. Moreover, heavy metals dissolved in wastewater can be recovered as pure solid metals even at low concentrations [4]. However, heavy dependence on electricity is considered as a noticeable disadvantage of this process.

In contrast to conventional electrochemical techniques, a photocatalytic process does not consume expensive electricity, but utilises abundant solar energy by the use of photocatalysts. The *n*-type semiconductor with a large band gap such as titanium dioxide (TiO_2) (~3.2 eV) and tungsten trioxide (WO_3) (~2.8 eV) has been widely utilised as a photocatalyst in various processes for the decomposition of organic pollutants since it produces highly oxidative holes under light irradiation [5–9]. It was also reported that

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TiO₂ can be hybridised with carbon nanotubes to enable modulation of the photo-catalytic activity through imposition of an electric field. Such efforts have resulted in highly efficient photo-electrochemical decomposition of organic species in water [10–14].

However, due to the position of its conduction band minimum (CBM), the large band gap *n*-type photocatalyst normally shows a limited capability to assist reduction reactions. A reduction reaction by photo-generated electrons can only occur when the reduction potential of a species is located at more positive position than the semiconductor's CBM. Unfortunately, the reduction potential of most heavy metal ions is similar to or even more negative than the CBM of the semiconductor. Therefore, it is hardly achievable to reduce metal ions into metals by only the electrons from anodic photocatalysis unless additional energy is provided.

Nevertheless, there have been efforts to develop photocatalytic heavy metal remediation processes in which TiO₂ nanoparticles were simply dispersed into heavy metal containing wastewater under stirring and UV irradiation. Several studies have confirmed the photocatalytic reduction of the simple or complex ions of copper (Cu) [15–17], chromium (Cr) [18–21], zinc (Zn) [22], nickel (Ni) [23,24], and lead (Pb) [25].

Some limitations of the photocatalytic process for removal of heavy metals could be inferred from the aforementioned research. Firstly, the reduction of metallic species is solely dependent on the electronic structure of photocatalysts, which restricts the applications of photocatalytic processes. For example, TiO₂ is not able to completely remove chromium species from the wastewater as a metal. It can only convert high oxidation-state Cr(IV) ions into less harmful Cr(III) ions that might still be potential pollutants. Secondly, the heavy metal removal process is uncontrollable. Metal ions could be converted into less harmful ions or fully reduced to metals or just adsorbed onto photocatalysts. It becomes even more complicated when multiple heavy metal ions are present in wastewater. In addition, the recovery of a used photocatalyst becomes difficult once it is covered by the reduced metals.

There has not yet been any reported research effort to combine electro-deposition of metals and photocatalytic decomposition of organic compounds into the same cell for simultaneous removal of both types of pollutants. In this research, as an initial effort to combine two processes: photocatalysis and electrodeposition, a photoelectrochemical cell (PEC) was constructed with the well known low cost WO₃ as the photoanode and a platinum (Pt) disk (small cells) or a titanium (Ti) plate (large cells) as the cathode. The effort aims to demonstrate the principle of this novel PEC and related processes to utilise sunlight for the simultaneous removal of heavy metals and organic pollutants from wastewaters. Preliminary findings have revealed that the photoanode reactions can contribute to a significant decrease of the cell voltage for electrodeposition of heavy metals in the PEC. The performance and rationale are discussed in detail.

2. Experimental

2.1. Preparation of electrodes

The WO₃ photoanode was prepared by mixing 500 mg of WO₃ (Sigma–Aldrich, crystalline powder (monoclinic), ≤20 μm, ≥99% purity on the trace metals basis) with 0.5 mL of anhydrous ethylene glycol (Sigma–Aldrich, 99.8%) and 50 μL of Triton™ X-100 (Sigma–Aldrich) to make a uniform dispersion. 200 and 450 μL of the dispersion were cast onto one side of a 1 cm × 1 cm or 1.5 cm × 1.5 cm Ti plate and dried overnight at 60 °C. Finally, the electrode was heated for 30 min at 200 °C to remove any remaining ethylene glycol. As shown in the [Supporting Information](#),

XRD analysis confirmed no change of the crystallinity of the WO₃ powder following this drying process. The cathode consisted of a 0.2 cm diameter Pt disk electrode (CH Instruments, Inc.), polished using a 1 μm alumina (Al₂O₃) paste and then rinsed with Millipore grade water and acetone. In the work presented in Section 4.8 only, the Pt disk cathode was replaced by a larger 0.5 cm × 0.5 cm Ti plate cathode (rinsed with Millipore grade water and acetone) to demonstrate methylene blue (MB) decomposition at an increased scale.

2.2. Synthetic wastewater

The synthetic wastewater tested in this research contained both heavy metal ions and organic pollutants. Depending on heavy metal contents, two types of synthetic wastewater (A and B) were prepared as detailed in Table 1. As an initial research effort, only chloride salts were selected for the preparation of the synthetic wastewaters, partly because MB would release Cl⁻ ions when dissociated in water, and also in order to eliminate the effect of other anions (SO₄²⁻, NO₃⁻, etc.) on the electrochemical study. Sodium chloride (NaCl, Fisher, laboratory reagent grade), anhydrous copper(II) chloride (CuCl₂, Acros organics, 99%) and nickel(II) chloride hexahydrate (NiCl₂·6H₂O, Fisher, AR grade) were used as received for the preparation of the synthetic wastewater. Dissolved oxygen was removed from the synthetic wastewaters before experiments by bubbling the analytical grade argon gas through the solution.

2.3. Electrochemical analysis

Electrochemical experiments to demonstrate the dual purpose cell were carried out in both the two and three-electrode cell configurations with the components and structure illustrated schematically in Fig. 1. An advantage of the three electrode cell is that with the use of a reference as the third electrode, the potential of, and hence the reaction on the working electrode can be controlled. The data obtained from the three electrode cell can therefore function as references for analysis of the data from the conventional two electrode cell in which the individual electrode potentials can be monitored but not controlled. The electrochemical properties of the WO₃ photoanode were first studied in the three electrode cell (working electrode (WE): WO₃ photoanode; counter electrode (CE): graphite rod (6 mm in diameter); reference electrode (RE): Ag/AgCl in 3 M KCl). The deposition potential of each metal in the two synthetic wastewaters was then identified in another three electrode cell (WE: Pt disk electrode; CE: graphite rod; RE: Ag/AgCl in 3 M KCl). Afterwards, a conventional two electrode cell (WE: Pt disk electrode; CE: WO₃) was constructed in order to investigate the electrochemical behaviour of metal deposition and the decomposition of MB by chronoamperometry (CA) and cyclic voltammetry (CV) in a manner closer to industrial practices. The potential of each electrode was simultaneously monitored by a multi-channel potentiostat (IviumStat) while applying a cell voltage to the two electrode cell.

Experiments were conducted under both light and dark conditions to study the effect of photocatalysis on heavy metal deposition and MB oxidation. A xenon lamp-based Oriel 96000 150 W

Table 1
Compositions of synthetic wastewaters.

Wastewater	Heavy metals	Organic pollutant (MB)	Supporting electrolyte
A	500 ppm Cu ²⁺	10 ppm MB	0.5 M NaCl
B	500 ppm Ni ²⁺	10 ppm MB	0.5 M NaCl

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