

Magnéli-phase Ti_4O_7 Conductive Membrane for Effective Electrochemical Degradation of 4-chlorophenol in the Presence of Sulfate

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Abstract. Electrochemical advanced oxidation has been receiving a growing attention in wastewater treatment because of its advantages of environmental friendliness, less secondary pollution and ease-to-handle operation. Magnéli-phase titanium oxides (Ti_nO_{2n-1} , $n=4\sim 10$) represent the most promising electrode materials, due to its high conductivity, strong corrosion resistance and high oxygen evolution potential. In this study, we fabricated a Magnéli-phase Ti_4O_7 conductive membrane for electrochemical oxidation of 4-chlorophenol pollutant. The results demonstrated that the Ti_4O_7 electrode has lower charge transfer resistance and solution diffusion resistance compared with carbon cloth. Based on the optimization of key operating parameters, the optimum electrolyte concentration, current density and membrane flux conditions are determined to be 0.03 mol/L, 5 mA/cm² and 0.023 m³/(m² s), respectively. The overall removal of 4-chlorophenol could reach the level higher than 95% under these conditions.

1. Introduction

Recently, the electrochemical advanced oxidation process (EAOP) has attracted growing attention for treating a variety of refractory wastewater by its virtue of environmental friendliness, less secondary pollution, high efficiency and ease-to-handle operation [1]. At present, the feasibility of EAOP has been verified by a large number of studies that report the treatment of wastewater containing various pollutants such as refractory carboxylic acids [2, 3], and perfluorocarboxylic acids [4]. However, there remain several aspects of EAOP that need further efforts if the engineered applications are to be better implemented and developed. The most important factor that affects the performance of EAOP is the choice of electrode materials on the basis of the electrical conductivity, electrochemical activity, chemical stability, economic reliability and environmental friendliness. For example, the SnO_2 -doped electrode is a high-performance electrode, but its engineered application may be limited by its instability [5]. Likewise, the PbO_2 -doped electrode has also been used with very limited success due to the potential of leaching of toxic lead ions into solution at anodic polarization condition [6, 7]. Although boron-doping diamond (BDD) may be expected to address these problems, its extremely high cost and complicated fabrication are also concern in practical applications for wastewater treatment [8, 9].

Recently, it has been found that TiO_2 after establishing oxygen deficiencies within the crystalline lattice can produce a kind of unique structure leading to a combination of excellent electrical conductivity approaching to that of metals and great corrosion resistance close to that of ceramic materials [10]. This material has been called Magnéli-phase titanium oxides with a generic formula of $\text{Ti}_n\text{O}_{2n-1}$ ($n=4\sim 10$). Ti_4O_7 offers higher oxygen evolution potential (+2.6 V vs standard hydrogen electrode) than BDD [11]. Additionally, the Magnéli-phase titanium oxides are also cost effective because it is made of TiO_2 , one of the most available metal oxides on the earth. These outstanding properties make the Magnéli-phase titanium oxides particularly suitable serving as anode material for EAOP [12].

Since the electrochemical reaction occurs on the surface of electrode, the convection of electrolyte and diffusion of reactants cause the flow of reaction region and the uneven distribution of concentration [13]. Based on the consideration of combining electrochemical oxidation and membrane filtration, the electrolyte can be forced to flow inside the porous structure of conductive membrane electrode. It will be highly desirable to increase the contact probability between electrochemical active sites and organic pollutants, such that the mass transfer can be enhanced for electrochemical reactions [14-17].

Herein, we have fabricated Magnéli-phase Ti_4O_7 conductive membrane as anode for electrochemical oxidation of 4-chlorophenol, a kind of recalcitrant contaminant that often occurs in many industries. Following the characterization of morphology, crystal, and surface area, the electrochemical properties of Ti_4O_7 electrode were investigated. Thereafter, the electrochemical oxidation performances of Magnéli-phase Ti_4O_7 conductive membrane was examined and assessed for removing 4-chlorophenol in synthetic wastewater. Last, the operating conditions were also optimized and discussed.

2. Materials and methods

2.1. Characterization of the Magnéli-phase Ti_4O_7 conductive membrane

The surface structures of the Magnéli-phase Ti_4O_7 electrode was observed by using field-emission scanning electron microscopy (SEM, Helios Nano-lab600i, FEI, U.S.). The powder X-ray diffraction (XRD) analysis was conducted on an X-ray diffractometer (Bruke D8 Adv., Germany). The electrode surface area was calculated based on the adsorption and desorption branches measured by BET surface area measurement (3H-2000BET-A, China).

The electrochemistry impedance spectroscopy (EIS) analysis of the magnéli-phase Ti_4O_7 electrode were tested by making a comparison with carbon cloth upon PARSTAT electrochemical workstation (CHI 750D, Chenhua Co. Ltd., China). The EIS data obtained from the test were fitted by using Zsimpwin software to determine the ohmic resistance, charge transfer resistance and diffusion resistance of the tested electrode materials.

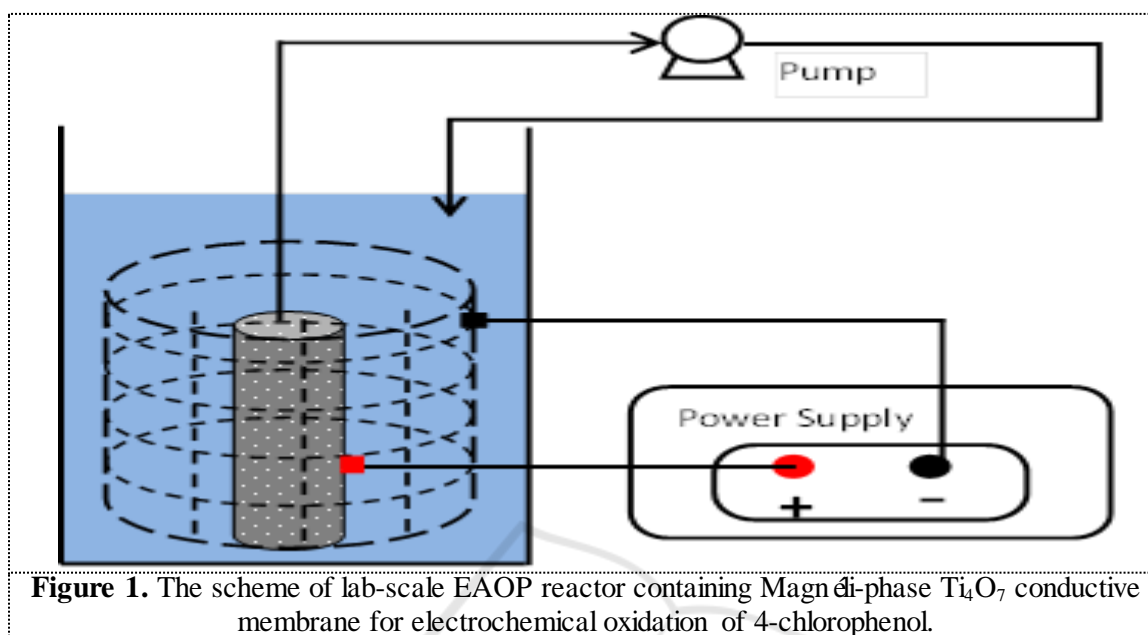
2.2. Experimental setups

The EAOP containing Magnéli-phase Ti_4O_7 conductive membrane anode is schematically illustrated in Figure 1. Unless stated otherwise, the experiments were conducted with 4-chlorophenol and Na_2SO_4 electrolyte solution. The initial concentration of 4-chlorophenol was 20 mg/L and the volume was 580 mL. The effects of Na_2SO_4 concentration, current density, and membrane flux on the degradation of 4-chlorophenol were studied and optimized at the reaction time of 2 h.

2.3. Analyses methods

The samples were taken of 1.00 mL at regular time intervals. The 4-chlorophenol was determined by using High Performance Liquid Chromatography (HPLC, Waters 2695, U.S.A) with a C18 column (250×4.6, 5 μm) and a photodiode array detector (wavelength=254 nm). The flow phase was V

(methanol): V (hyperpure water) = 80:20, and the flow rate was 1.0 mL Min⁻¹. The sampling amount was 20 μL and the column temperature was 25 °C.



3. Results and discussion

3.1. Electrode characterization

The XRD profiles (Figure 2A) were indexed to the characteristic peaks of Ti₄O₇ according to reference spectrum (JCPDS No. 18-1402) and prior literatures [18]. At the same time, a small amount of diffraction peaks of Ti₅O₉ was also shown in the profiles, which indicated that it is difficult to generate a single Ti₄O₇ phase during the preparation of the titanium oxide material. Figure 2B provided the surface morphology structures of the magnéli-phase Ti₄O₇ electrode, and results indicated surficial pores on the order of 1-2 μm. The phenomenon of sintering and melting caused particles to adhere to each other, thus forming a rich porous structure, which expected beneficial for facilitating interfacial mass transfer during electrochemical reaction with the electrode BET surface area of 0.1884 m² g⁻¹.

3.2. Electrochemical properties

The ohmic resistance of monolithic Ti₄O₇ electrode was measured to be 58.07 Ω, which was an indication of high conductivity similarly like the carbon cloth (Figure 2C). However, further analysis of the EIS data revealed that the charge transfer internal resistance and diffusion internal resistance of the two electrodes are quite different. The charge transfer internal resistances of the Ti₄O₇ electrode and the carbon cloth anode were 10 Ω and 588.3 Ω respectively, the former was far lower than the latter. The diffusion internal resistance of the Ti₄O₇ electrode was 11.89 Ω, while that of the carbon cloth was 3411 Ω, which was two orders of magnitude higher than that of the Ti₄O₇ electrode. It means that under the same reaction conditions, the Ti₄O₇ electrode is more conducive to the diffusion and reaction of the solute in the solution during the reaction process, which provides a good condition for the electrochemical reaction to take place quickly and efficiently.

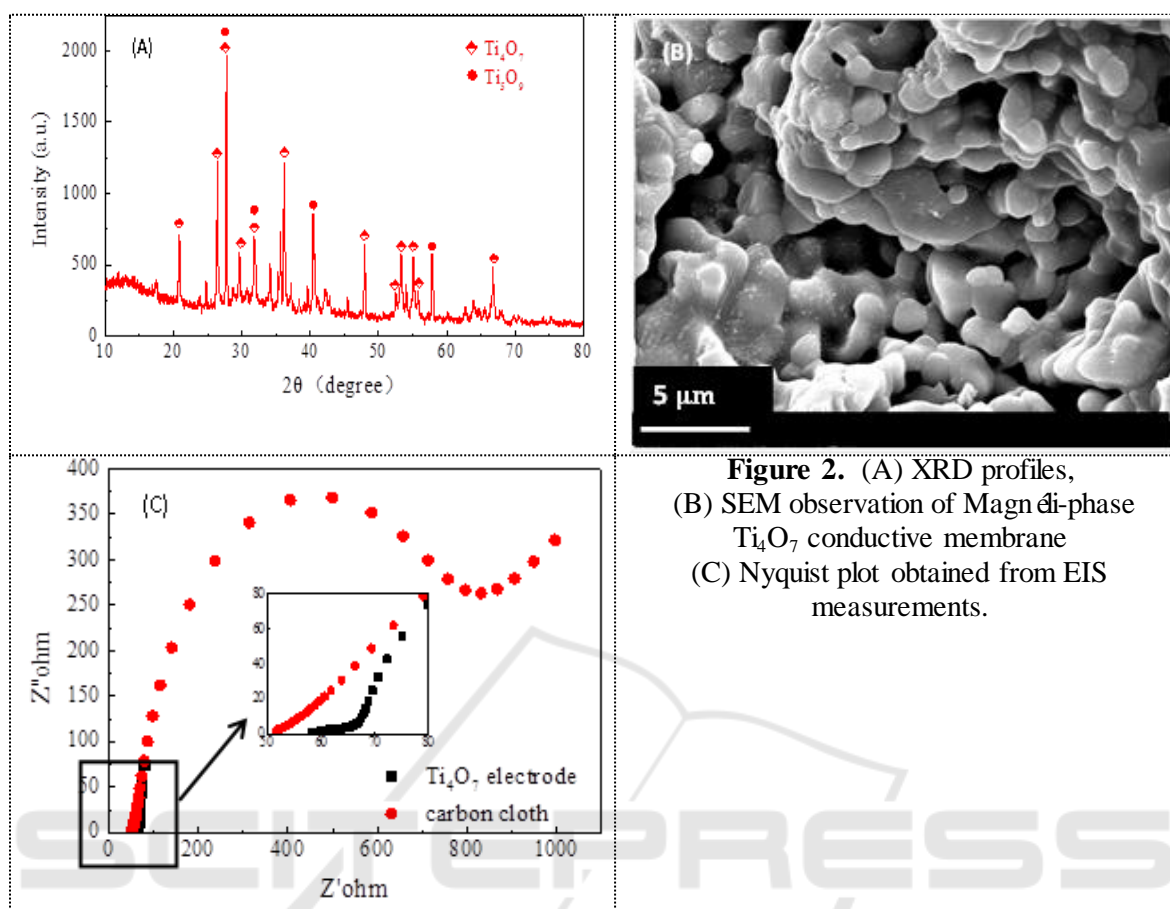


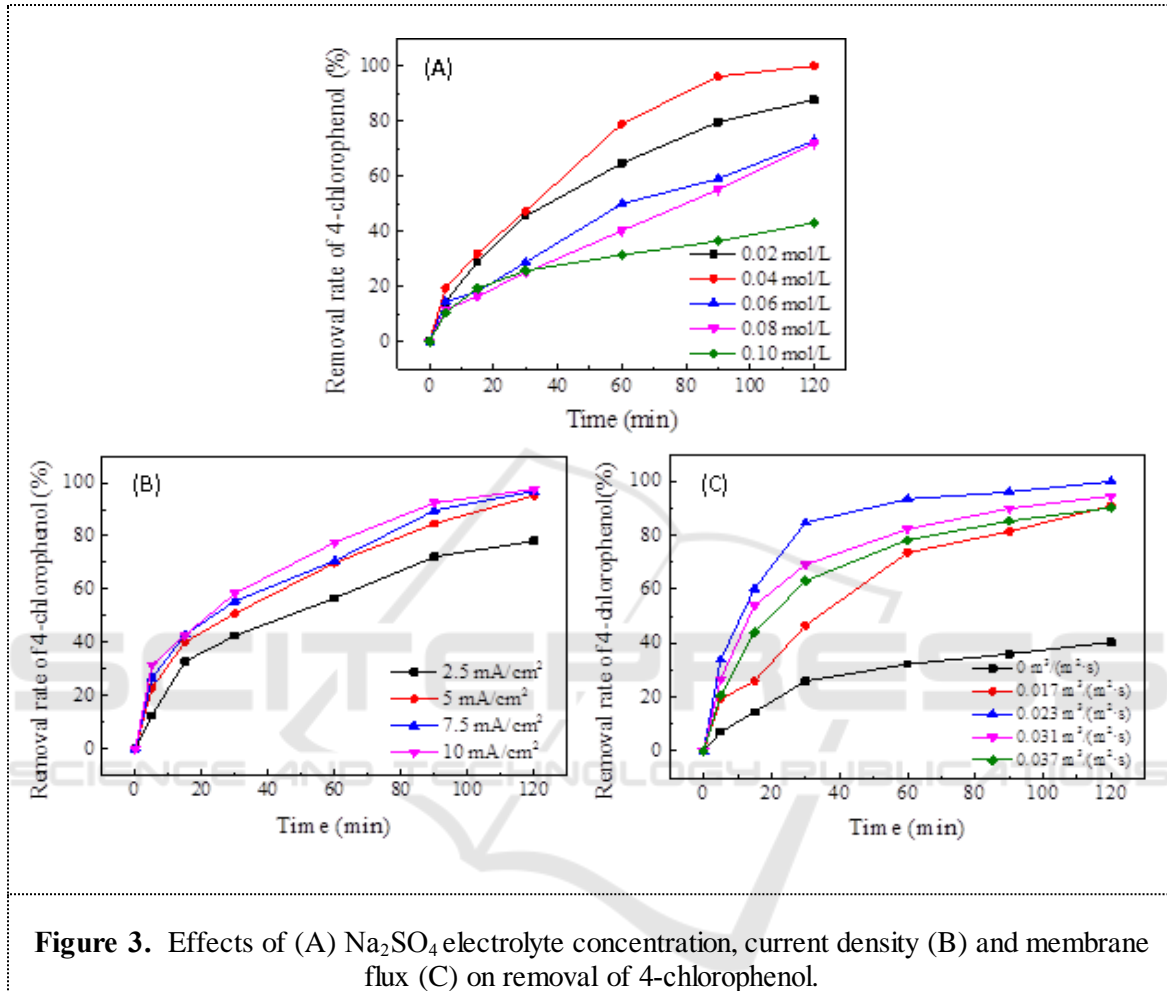
Figure 2. (A) XRD profiles, (B) SEM observation of Magnéli-phase Ti_4O_7 conductive membrane (C) Nyquist plot obtained from EIS measurements.

3.3. Electrochemical oxidation of 4-chlorophenol

3.3.1. Effect of Na_2SO_4 concentration on removal of 4-chlorophenol. At a current density of 5 mA/cm^2 , the synthetic 4-chlorophenol wastewater was electrolyzed with the Na_2SO_4 concentration in the electrolyte solution increased from 0.02 mol/L to 0.10 mol/L , the removal rate is shown in Figure 3A. It can be seen that the removal rate of 4-chlorophenol increases from 87.78% to 100% as the concentration of electrolyte increases from 0.02 mol/L to 0.04 mol/L . When the electrolyte concentration was continued to increase further, the removal rate of 4-chlorophenol started to reduce, and at a electrolyte concentration of 0.10 mol/L , the 4-chlorophenol removal rate dropped to 43.21%. Considering multiple factors comprehensively, 0.03 mol/L was used as the optimal sodium electrolyte concentration condition in this paper.

3.3.2. Effect of current density on the removal of 4-chlorophenol. At a concentration of sodium sulfate in the electrolyte solution of 0.03 mol/L , the synthetic 4-chlorophenol wastewater was electrolyzed with the current density increased from 2.5 mA/cm^2 to 10 mA/cm^2 , the removal rate is shown in Figure 3B. Within the experiment time range of 120 min, the removal rates of 4-chlorophenol were 78.14%, 95.17%, 96.78% and 97.54%, respectively. From the data, it can be seen that the removal rate of 4-chlorophenol increases with the current density, but the increasing rate gradually decreases. When the current density increases from 2.5 mA/cm^2 to 10 mA/cm^2 in turn, the removal rate increased by 21.79%, 1.69%, 0.79%. It means the percentage increase of 4-chlorophenol removal rate is far less than that of current density and electrolysis under large current

density obviously causes great waste of electric energy. Therefore, in the electrolysis reaction, the current density should be appropriately increased within a certain range, which cannot be too large to cause the waste of energy. This study selected 5 mA/cm² as the optimal current density of the experiment.



3.3.3. Effect of membrane flux on the removal of 4-chlorophenol. When the concentration of the electrolyte solution was 0.03 mol/L and the current density was 5 mA/cm², the membrane flux was adjusted by changing the rotation speed of the peristaltic pump. 0, 0.017 m³/(m² s), 0.023 m³/(m² s), 0.031 m³/(m² s), 0.037 m³/(m² s) were selected as flux gradients to apply to the Magnéli-phase Ti₄O₇ electrochemical membrane, the removal rate is shown in Figure 3C. At 0 m³/(m² s), there was no suction of the peristaltic pump and only the Magnéli-phase Ti₄O₇ electrode played the role of electrolysis. After 60 min, the removal rate of 4-chlorophenol reached 32.32%, and then the removal process was almost performed stagnated. Compared with zero flux, i.e. 0 m³/(m² s), the removal rate of 4-chlorophenol increased significantly after increasing the suction of peristaltic pump, and could reach more than 90% under all membrane fluxes. However, it was worth noting that the removal rate of 4-chlorophenol did not increase with the increase of membrane flux, but first increased and then decreased. At the end of the experiment, the removal rate was 90.98%, 100%, 94.59% and 90.21%, respectively. Taken together, 0.023 m³/(m² s) was selected as the optimal membrane flux condition in this study.

4. Conclusions

In this study, the Magnéti-phase Ti_4O_7 conductive membrane was fabricated for electrochemical oxidation of 4-chlorophenol in the presence of sulfate electrolyte. The Ti_4O_7 electrode achieved efficient abatement of recalcitrant organic pollutants without any extra addition of chemicals.

The XRD profiles were indexed to the characteristic peaks of Ti_4O_7 and a small amount of diffraction peaks of Ti_5O_9 for the membrane electrode. The Ti_4O_7 electrode had surficial pores on the order of 1-2 μm and BET surface area of $0.1884 m^2 g^{-1}$, which would be beneficial for facilitating interfacial mass transfer.

The Ti_4O_7 electrode has lower charge transfer resistance and solution diffusion resistance compared with the carbon cloth, suggesting high activity for oxygen evolution to produce hydroxyl radicals and organic degradation at anodic polarization conditions.

Based on the optimization of key operating parameters, the optimum Na_2SO_4 electrolyte concentration, current density and membrane flux conditions were determined to be 0.03 mol/L, 5 mA/cm² and 0.023 m³/(m² s), respectively. More than 95% 4-chlorophenol could be removed under these conditions.

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