

Research Plan of Final Year Project**Topic:** High-performance electroactive membrane for enhanced wastewater treatment**Name:** XXX**Number:** XXXXXXXX**Supervisor:** Prof. XX XXX**Mentor:** XXX**Abstract:**

Antibiotics are a substantial threat to both the ecological environment and biological health because of their extensive usage and indiscriminate disposal. Electroactive membranes are now widely used to remove antibiotics and they have attracted much attention due to their ability to solve membrane fouling problems and better remove pollutants compared to ordinary membrane filtration. To investigate a high-performance electroactive membrane for enhanced wastewater treatment, we decided to fabricate a blended conductive CNT-PTFE membrane. Firstly, we make the CNT-PTFE membrane by vacuum filtration. Secondly, we characterize and test its performance by a range of methods. Thirdly, we use the prepared membrane to build an electrochemical filtration apparatus. In the research, we measure the quality of influent and effluent to evaluate the effectiveness of CNT-PTFE membrane in removing conventional pollutants and antibiotics compared to ordinary PTFE membrane. We also change the applied voltage to measure its influence on the removal of antibiotics.

1. Introduction

Antibiotics are chemical substances, produced by micro-organisms, which have the capacity to inhibit the growth of and even to destroy bacteria and other micro-organisms. Therefore, antibiotics are widely used in medical, biological research, agriculture, the food industry, etc. Due to their extensive usage and indiscriminate disposal in the environment, antibiotics are currently recognized as emerging pollutants, which can be found prevalent in wastewater and groundwater^{1,2}. Wastewater treatment plants (WWTPs) have long been recognized as the primary sources of antibiotics being discharged into aquatic environments^{3,4}. The continuous input of antibiotics in wastewater treatment systems would exert an ongoing selection pressure on microorganisms, resulting in the amplification of antibiotic-resistant bacteria (ARB) and antibiotic-resistance genes (ARGs). This situation presents a substantial threat to both the ecological environment and biological health⁵⁻⁷. Consequently, antibiotic wastewater needs to be treated with caution before it is discharged into the environment.

At present, the main methods of removing antibiotics in wastewater was conventional treatment processes and advanced treatment units. The former is based on physicochemical processes, like coagulation, sedimentation and so on. The other is advanced treatment units, such as adsorption, advanced oxidation, biological treatment, membrane filtration, etc.⁸. Membrane filtration is one of the most effective methods for removing small molecules and low concentrations of antibiotics⁹. Antibiotics are mainly rejected on the membrane surface by size exclusion¹⁰. According to the previous study reported by Alnajrani and Alsager¹¹, the use of polymers of intrinsic microporosity materials can potentially eliminate at least 80% of initial antibiotic concentrations under ideal conditions. However, it is important to note that membrane technology, although effective in the removal of antibiotics, is hindered by challenges such as the processing of high-concentration liquids and membrane fouling. Membrane fouling is a key issue that currently deteriorates membrane performance. The occurrence of membrane fouling results in a decrease in flux or an increase in trans-membrane pressure and leads to frequent membrane cleaning and membrane replacement¹². Therefore, to better remove antibiotics, a more economical and efficient method is needed.

In this study, CNTs are incorporated with PTFE to fabricate novel blended CNT-PTFE membranes using the vacuum filtration method. The prepared membranes are characterized by scanning electron microscopy (SEM) and electrochemically evaluated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Then the blended CNT-PTFE membranes are used to build an electrochemical filtration apparatus and a normal PTFE membrane filtration is running as a control experiment. Among all the antibiotics currently present in the environment, sulfonamides (SAs) are the most widely used class in the farming industry and the main antibiotic content detected in wastewater. Performance of the CNT-PTFE and a control PTFE (without applied voltages) are evaluated for removing 2 main types of SAs (sulfamethoxazole, SMX; sulfadiazine, SDZ) in pure antibiotic solution and synthetic wastewater to evaluate the potential of this electroactive membrane technology in practical applications and provide theoretical guidance for it. We also investigate the removal effect of CNT-PTFE membrane on some comprehensive pollution indicators, including chemical oxygen demand (COD), ammonia nitrogen ($\text{NH}_4^+\text{-N}$), and total nitrogen (TN) to evaluate the wastewater treatment effect. Besides, by changing the voltage of the applied electric field, we investigate and analyze the removal effects of different applied voltages on antibiotics. Overall, our studies prove a paradigm for wastewater antibiotics control using an electroactive CNT-PTFE membrane.

2. Research Objectives:

- (1) Fabricate a novel blended carbon nanotubes (CNT) based membrane using CNTs and polytetrafluoroethylene (PTFE) through vacuum filtration.
- (2) Compare some conventional indicators (COD, $\text{NH}_4^+\text{-N}$, TN) to evaluate the wastewater treatment effect.
- (3) Measure the concentrations of 2 main types of SAs (sulfamethoxazole, SMX; sulfadiazine, SDZ) in the effluent of pure antibiotic solution to evaluate the removal effect on antibiotics of the CNT-PTFE membrane. Then by measuring the concentration of SMX/SDZ in the effluent of the synthetic wastewater, evaluate the potential of this electroactive membrane technology in practical applications and provide theoretical guidance for it.
- (4) Change the voltage of the applied electric field to further investigate and analyze the removal effects of different applied voltages on antibiotics.

3. Research Gaps/Research Questions

- (1)
- (2)

4. Methodology (*Optional, detailed operation steps is not required*)

4.1 Materials

CNT, PTFE, N, N-dimethylformamide (DMF), SDZ/SMX, NaAc, Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, KH_2PO_4 , $\text{MgSO}_4 \cdot 0.7\text{H}_2\text{O}$, CaCl_2 , NaHCO_3 , trace element solution, HCl, NaOH.

4.2 Electroactive membranes fabrication

The PTFE microfiltration membrane is selected as the substrate for the preparation of CNT-PTFE membrane. The microfiltration membrane is cut into circular pieces with a diameter of 40 mm using a film cutting knife, and then wash with deionized water to remove impurities from the surface of the membrane. A certain amount of carbon nanotubes is weighed and dispersed in 0.01 mol/L DMF solution in water, and ultrasonic treatment is performed using an ultrasonic cell disruptor. The PTFE filtration membrane (0.22 μm pore size) is placed in a homemade filtration device, and c. After filtration, the membrane is washed with deionized water to remove any residual SDS. The membrane is then dried overnight while sandwiched between absorbent paper, and the CNT-PTFE membrane is peeled off from the paper.

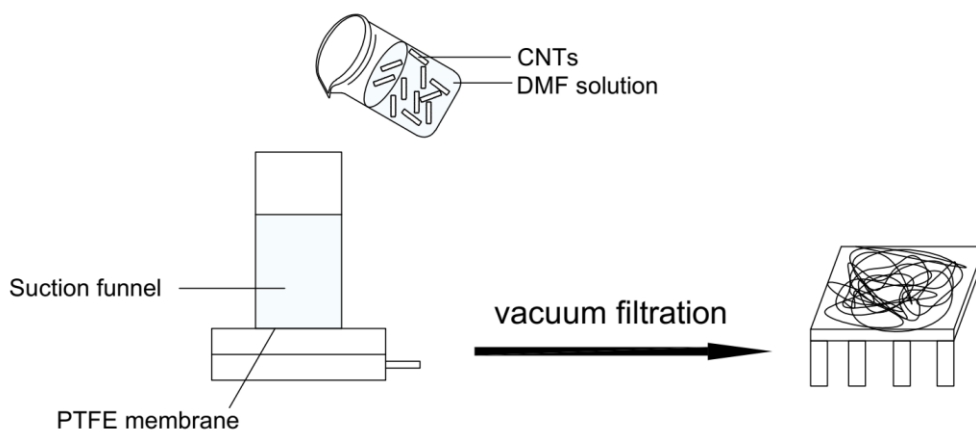


Fig. 1 Schematic diagram of CNT-PTFE membrane preparation

5. Research Content (*Drafted In separate chapters/parts*)

Part 1: Photocatalyst preparation, characterization, and photo-electrochemisry analysis

1. Synthesis of TiO_2

1 g tetrabutyl titanate (TBOT) will be added into a solution of 30 mL ethanol (EtOH) under constant stirring, then the solution will be transferred into a Teflon-lined autoclave and heated at 180 °C for 10 h. The obtained powders will be collected, rinsed with absolute ethanol for several times, dried at 60 °C overnight.

2. Synthesis of W- TiO_2 (W = 15 at.%)

1 g TBOT and 20 mL EtOH will be mixed with stirring until clear to obtain solution A. Meanwhile, 0.0432 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and 1 mL H_2O will be mixed after dissolution to ensure the final W/Ti ratio appropriate (In pre-experiment, make W/Ti ratio equals to 5%, 10%, 15%, 20% and 25%, then get the optimal ratio). The obtained solution will be heated at 180 °C for 10 h.

3. Synthesis of $\text{V}_{\text{Ti}}\text{-TiO}_2$

0.5 g W- TiO_2 and 10 mL 1M NaOH will be mixed under constantly stirring at room temperature for 24 h. After that step, the solution will be centrifugated repeatedly and washed until the solution is neutral. Next, the solution will be dried at 60 °C to obtain A1. Meanwhile, 0.5 g W- TiO_2 and 10

mL 1M NaOH were mixed at with stirring at 100 °C for 1 h. After that step, the solution was centrifugated repeatedly and washed until the solution was neutral. Next, the solution was dried at 60 °C to obtain A2. According to the situation, adjust the dosage used.

4. characterization and photo-electrochemisry analysis

The structure and composition of modified TiO₂ will be studied by XRD, TEM, XPS, UV-vis DRS and EPR. The basic mechanism and charge transfer behavior of modified TiO₂ photocatalytic reaction will also be studied by means of photochemical analysis.

Part 2: Photocatalytic experiment

The photocatalytic activities of the prepared photocatalyst were investigated by using 300 W Xenon lamp (PLS-SXE300E, Perfect Light, China) and filter (320 nm <λ< 400 nm) to degrade tetracycline hydrochloride (TCH), sulfadiazine, and norfloxacin (Next, take TCH as an example) under ultraviolet light irradiation. In order to avoid the effects of temperature, the photocatalytic reaction is carried out under a constant temperature water bath of 25 °C and the photocatalytic reactor is located at a constant distance of 10 cm away from the Xenon lamp. In a typical measurement, 10 mg photocatalyst is added to 100 mL pollutants solution (10 μM) and magnetically stirred in the dark for 60 minutes to establish an adsorption-desorption equilibrium. At predetermined time intervals, the residual pollutant concentration will be detected after filtration through 0.22 μm polyether sulfone membrane syringe filters. The pollutant concentration in extracts will be analyzed using high performance liquid chromatography system.

1. Effects of water quality parameters

The study included the effects of water quality parameters such as reactive substances, initial solution pH, coexisting anions, natural organic materials on the photocatalytic activity.

2. Environmental implications

To investigate catalyst's potential application in natural water matrices, tap water, lake water, and river water will be used as the background. Stability is also an important index to evaluate photocatalysts' practical research. Hence, the reusability of photocatalysts will be conducted by

repeating the photodegradation tests for five times.

Part 3: Catalytic mechanisms

1. Effects of reactive species

The effects of reactive species such as holes, hydroxyl radicals and superoxide radicals will be investigated by trapping experiments using ammonium oxalate, isopropyl alcohol and benzoquinone as trapping agents, respectively.

2. Degradation pathway of pollutants

6. Annual Timetable

Date	Experimental content
1 Oct to 20 Oct 2023	Literature reading and consulting with mentor and supervisor to confirm the project theme
23 Oct to 31 Oct 2023	Electroactive membranes fabrication
1 Nov to 8 Nov 2023	Characterization and performance tests
9 Nov to 17 Nov 2023	Set-up of electrochemical filtration apparatus
20 Nov to 20 Dec 2023	Pollutants removal performance & Data collection (measuring conventional pollutants and antibiotics)
21 Dec to 29 Dec 2023	Data processing
Jan 2024	FYP assessment
26 Jan to 18 Feb 2024	Winter holiday
19 Feb to 15 Mar 2024	Pollutants removal performance & Data collection (change voltage)
16 Mar to 25 Mar 2024	Data analysis
26 Mar to 8 Apr 2024	Essay writing
22 April to 15 May 2024	FYP final assessment

7. References

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