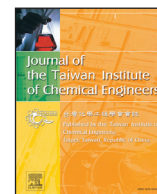




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Removal of thiophene in air stream by absorption combined with electrochemical oxidation

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ABSTRACT

As typical heteroaromatic compounds, thiophene is an air pollutant that pose serious environmental and health related impacts due to its volatility and toxicity. This work reports a hybrid process of absorption combined with electrochemical oxidation to degrade thiophene. The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄) was employed as the absorbent to capture thiophene from air stream. Linear sweep voltammetry (LSV) demonstrated that thiophene could be oxidized on β -PbO₂ anode modified with fluoride at 1.28 V versus Ag/Ag⁺ electrode (RE) with a scan rate of 100 mV/s while [BMIM]BF₄ was used as the electrolyte. Results of bulk electrolysis showed that thiophene could be thoroughly degraded within 60 min in [BMIM]BF₄ under 50 mA/cm² due to the successive attack of hydroxyl radicals (\cdot OH) produced by electrolysis on the surface of β -PbO₂ anode. Acetic acid was determined as the main intermediate and could be further mineralized to fumaric acid, maleic acid and oxalic acid, while sulfur atom in thiophene was finally converted to sulfate ions (SO₄²⁻). Based on the HPLC analysis and a precipitation of BaSO₄, degradation pathway of thiophene was proposed and the thiophene sulfur could be degraded completely into sulfate. The kinetics of the electrochemical oxidation process for thiophene can be described by the pseudo-first order model. This absorption-electrochemical oxidation method with continuous operation would be a promising way for the clean and safe removal of heteroaromatic compounds from waste gases.

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1. Introduction

Thiophene is one of the main sulfur-containing compounds widely used in the synthesis of pesticides, pharmaceuticals, biological products, dyes, etc [1,2]. Like many volatile organic compounds (VOCs), thiophene is easily released into the atmosphere and causing serious environmental pollution. Several researches have confirmed the toxic, carcinogenic and mutagenic effects in the metabolism of thiophene [3–5]. Many developed countries have planned to achieve little-to-no sulfur fuels (S-content < 10 ppm) to reduce the sulfur oxide emission [6]. Therefore, a control technique that can effectively eliminate its detrimental effects has to be developed. Conventional methods such as activated carbon adsorption and organic solvent absorption are non-destructive techniques resulting in complicated procedures and expensive secondary treatment. Thermal incineration and catalytic combustion are not cost-effective and have the risks of second pollution, fire

hazards and explosion accidents. Since its potential toxicity to microorganisms, thiophene is recalcitrant to biodegradation, and is regarded as the most refractory compound [7,8]. It is the most difficult compound to be oxidized by conventional oxidative desulfurization processes due to the aromaticity and the low electron density of the sulfur atom [9]. In China, 80% components in gasoline are the FCC (fluid catalytic cracking) naphtha and the important sulfur molecules in FCC naphtha is thiophene [10–12]. Therefore, the removal of thiophene is an important technique in petroleum refining that is achieved by catalytic processes at elevated temperatures and pressures [13]. It is reported that thiophene and thiophene derivatives are commonly decontaminated by hydrogen peroxide under mild conditions. Several catalysts such as MoO₃/ γ -Al₂O₃ [14], Ti-zeolite [15] and silica gel loaded with copper and cobalt [16] can enhance the oxidation of thiophene as Fenton-like reactions, which lead to the formation of hydroxyl radicals (\cdot OH), a more powerful and clean oxidizing agent than H₂O₂ [17].

Electrochemical reactions can directly generate \cdot OH without addition of chemicals like H₂O₂. Experimental evidence has been

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proved for the generation of hydroxyl radicals on the surface of β -PbO₂ electrode modified with fluorine resin by electron spin resonance (ESR) spectroscopy [18]. This improved β -PbO₂ electrode exhibits better electrochemical performance, activity and stability for organic pollutants degradation, such as aniline and chlorobenzene, phenol, chlorophenol and *p*-nitrobenzene [18–20]. It has been proved that hydroxyl radicals played a critical role in destruction of the above-mentioned toxic or biorefractory organic compounds, becoming more apt to biological treatment [19]. Therefore, it can be envisioned that electrochemical oxidation might also be effective to reduce the toxicity of heteroaromatic compounds like thiophene through the molecule destruction. If thiophene can be captured from the air stream by a liquid absorbent which has electrical conductivity, it can be degraded in electrochemical reactions. The difficulty is that thiophene has poor solubility in water. On the other hand, traditional organic absorbents of thiophene have the low electrical conductivity. Thus, finding a certain substance that can play the roles of absorbent and electrolyte which serves as electron or ions carrier to reduce the resistance of solution simultaneously becomes crucial.

In the recent academic and patent literature, ionic liquids (ILs) are normally taken as being liquids entirely made of ions that are fluid below a threshold temperature of approximately 100 °C [21]. ILs are non-volatile, non-flammable, thermally stable, miscible with a lot of organic or inorganic substances [21,22]. Therefore ILs can replace the traditional flammable and volatile solvents due to its environmental benign and good properties [23]. Besides, ILs can be directly used as electrolyte for electrochemical oxidation due to its high ionic conductivity [24]. Herein, ILs may be a potential substance to solve the problem mentioned above.

This paper aims to study a new hybrid process combining absorption with electrochemical oxidation. The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄), which has a good solubility of thiophene, was used as absorbent to remove thiophene from influent gas. Then the absorption liquid with thiophene was moved into a novel electrochemical reactor devised with modified β -PbO₂ electrode. Thiophene could be degraded to non-toxic substances by \cdot OH. Linear sweep voltammetry (LSV) was used to investigate the oxidation behavior of thiophene on β -PbO₂ electrode. Bulk oxidation of thiophene was carried out to explore the final form of sulfur atom transformed and further clarify the reaction mechanism between thiophene and hydroxyl radical. Sulfur conversion during the electrochemical oxidation was also investigated to demonstrate the destruction of thiophene. The influences of operation parameters such as the inlet gas flow rate, power applied to the electrochemical reactor were experimentally examined.

2. Experimental

2.1. Absorption

The absorption system consisted of a liquid thiophene container, an absorption reactor, a N₂ cylinder and a buffering tank. A drying tower was used before the gas vent to prevent the [BMIM]BF₄ from absorbing water in the air. N₂ passed through the liquid thiophene container and carried thiophene into the absorption reactor by bubbling. The experimentation was carried out at ambient temperature of the air stream (25 °C \pm 3 °C) and atmospheric pressure (\sim 0.1 MPa) for homogenizing the absorbent of the [BMIM]BF₄. Lower temperature will benefit the efficient of absorption, thus the absorption was undergone at ambient temperature. The thiophene-loaded stream flowed into a buffering tank to homogenize the gas concentration in advance. Flow rate of this stream was controlled by a mass flow meter.

Before the absorption experiment, the whole system was saturated with N₂, including the absorbent. Ten grams of water, [BMIM]BF₄ and di(2-ethylhexyl) adipate (DEHA) were employed as absorbents to test their capacity to absorb thiophene respectively. The amount of thiophene absorbed by the absorbent was weighed every 30 min.

2.2. Linear sweep voltammetry investigation

Linear sweep voltammetry (LSV) was carried out in a 5200 mg/L thiophene solution. A three electrode system was used which was controlled by the Electrochemical Workstation (CHI660C, Chenhua Shanghai). A modified β -PbO₂ electrode was used as the working electrode while the counter electrode was platinum wire and the reference electrode was non-aqueous Ag/Ag⁺ electrode (RE). The fluoride modified β -PbO₂ electrode was prepared according our previous work [18]. This experiment was carried out to confirm the thiophene oxidation in electrochemical reaction. The potential was set from 0 to 1.8 V under different scan rates. All potentials were recorded against the reference electrode.

2.3. Electrochemical oxidation of thiophene

Electrochemical oxidation experiments were carried out in a glass cube reactor (20 mm \times 20 mm \times 50 mm). A β -PbO₂ electrode doped with fluoride was employed as the anode (12 mm \times 45 mm \times 6 mm). The cathode was AISI 304 stainless steel net (15 mm \times 45 mm \times 2 mm, mesh 4#) with a wire diameter of 0.8 mm. The two electrodes were fixed parallel inside the reactor. The distance between them was 12 mm. The mixture of [BMIM]BF₄ with thiophene flowed into the reactor submerging both the anode and the cathode. During the experiment, the applied voltage supplied by a DC power source (WYL3010, China) was adjusted regularly to provide a constant current density. Before the experiments, 1 mL of deionized water was added into the reactor as the hydrogen source to generate hydroxyl radicals, and 15 μ L of deionized water was added into the reactor in every 10 min. All experiments were implemented at atmospheric pressure and ambient temperature (25 \pm 3 °C). During the experiment, samples were periodically taken and analyzed. In order to quantify the yield of sulfate ions during the electrochemical reactions, enough barium chloride (BaCl₂) solution was prepared to precipitate all sulfate ions generated after a given reaction time.

2.4. Absorption-electrochemical oxidation

The applied experiments were carried out to investigate the feasibility of the hybrid process which combines absorption and electrochemical oxidation, with [BMIM]BF₄ working as the absorbent and the electrolyte simultaneously. Fig. 1 showed the experiment setup. The thiophene contaminated air was generated by injecting liquid thiophene into dry air stream. The concentration of thiophene was controlled by the gas flow rate and the injecting rate. After homogenizing in the buffering tank, thiophene carried by the air stream flowed through the self-made absorption column (length = 100 mm, inner diameter = 10 mm) padding with stainless steel mesh. The [BMIM]BF₄ served as absorbent was spraying down from the top of the column. After contacting with the air stream, the absorbent of the [BMIM]BF₄ flowed into the reservoir that was also served as the electrochemical oxidation reactor, in which the captured thiophene was oxidized by electricity at a current density of 50 mA/cm². A peristaltic pump was employed to drive the [BMIM]BF₄ circulating in the system. Incoming and outgoing gases were analyzed by a gas chromatograph with flame-ionization detector (GC Model FL9790, China). Thiophene degradation efficiency was calculated by the reduction of peak area.

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