Optimized degradation removal of 2-nitrotoluene by combination of cathodic reduction and electro-oxidation process

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ABSTRACT

Electro-reduction is a promising method to pretreat anti-oxidative and bio-refractory wastewater. 2-Nitrotoluene (2-NT) was chosen as the probe compound to investigate the electro-reduction process. The electro-reduction of 2-NT is a diffusion-controlled process according to cyclic voltammograms of 2-NT at the Ti electrode. The reductive activation of [H] contributed to 2-NT removal and 2-toluidine formation in the electro-reduction process. The influence of several operating parameters, such as current density, electrolyte concentration, initial pH value, and initial concentration of 2-NT was investigated using a multifactor orthogonal experiment. Current density and initial 2-NT concentration were significant factors that influenced 2-NT removal efficiency. Although pH was not a significant factor for 2-NT removal efficiency, it significantly influenced the 2-toluidine formation efficiency. The kinetics of 2-NT removal followed a pseudo-first-order reaction. It was clear that the reduction of 2-NT could be enhanced by adding the current density. However, $10\,mA\,cm^{-2}$ was selected as the working current density in subsequent experiments to reduce energy consumption. 2-Nitrosotoluene, 2-toluidine, azotoluene, and azoxytoluene were the transformation products detected in the system by gas chromatography/mass spectrometry (GC/MS) and the pathway of the reduction of 2-NT on Ti cathode was proposed. In the pretreatment of Nitroaromatic compounds (NACs) containing wastewater, the electro-reduction-oxidation process was superior to the electro-oxidation process according to the improvement of water quality. Thus, the electro-reduction-oxidation process can reach high efficiency for treatment of toxic NACs containing wastewater under mild conditions.

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1. Introduction

Nitroaromatic compounds (NACs), characterized with at least one nitro group attached to an aromatic ring, are important starting materials and intermediates for the manufacture of many valuable chemicals, such as dyes, drugs, explosives, pesticides and plastics [1,2]. In the last decades, numerous studies have addressed the high acute toxicity, carcinogenicity and mutagenicity of NACs [3–5], and several NACs, such as nitrotoluenes, dinitrotoluenes and nitrophenols, have been listed as the priority pollutants by the United States Environmental Protection Agency. Hence developing efficient treatment technologies for NACs containing wastewater has been an important and urgent issue in many industrial sections [6].

Due to the strong electron-withdrawing effect of nitro group, NACs are usually refractory and recalcitrant to aerobic biodegradation and oxidation [7]. Although NACs can be oxidized by powerful •OH radicals [8], advanced oxidation processes are chemical-intensive and expensive, and not suitable to high NACs containing wastewater. Additionally, the direct oxidation of NACs has been reported to form much more toxic intermediates, e.g., 1,3-dinitrobenzene [9]. On the hand, the electron-withdrawing effect of nitro group makes molecules succumb to electrophilic attack. Hence the most common degradation routes of NACs in biological systems start initially with anaerobic reduction [10,11], transferring nitro groups into electron-donating amino groups. Compared with NACs, aromatic amines are still toxic but more susceptible to the following aerobic oxidation [12,13].

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NACs containing wastewater effluents from industries are usually characterized with relatively high concentration as well as soluble inorganic salts, which might limit the practical application of anaerobic degradation of NACs. As results, pretreatment methods to reduce toxicity and enhance biodegradability have drawn great attentions in recent years. Initially applied for remediation of ground water contamination [14], zero-valent iron (ZVI) reductive technologies have been applied for industrial wastewater [15–17]. Previously, we developed an integrated ZVI-Fenton system, demonstrating an efficient and cost-effective treatment alternative for NACs containing wastewater treatment [9]. However, corrosion of ZVI produces various kinds of oxide, hydroxide, ferrous, and/or ferric ions. Although the resulting iron oxide or ions can enhance the contaminant degradation via a Fenton reaction [18], the formation of an oxide layer generally prevents the adsorption of contaminants on a fresh iron surface and inhibits the reduction reaction. Furthermore, large amounts of iron sludge were produced [19]. With more stringent legislation, such iron sludge is regulated as hazardous waste and requires safe disposal [20], which increases wastewater treatment costs.

Due to its rapid reaction rate, mild reaction conditions and low apparatus cost [21], electrochemical reduction has drawn great interests as a pretreatment alternative for anti-oxidative and bio-refractory wastewater, e.g., decolor of azo dyes [22], reductive dehalogenation [21,23,24], reduction of NACs [25–27]. In previous study, the removal of NACs had an excellent effect by electrochemical system, and it can be easily reduced to aniline species on cathode surface [10,21,28,29].

The objectives of this study were to assess electrochemical reduction followed by electrochemical oxidation as pretreatment processes for bio-refractory NACs containing wastewater. To this end, 2-Nitrotoluene (2-NT) was chosen as probe compound to investigate the electrochemical process. In order to optimize operation parameters, the effects of current density, electrolyte concentration, initial pH value, and initial concentration of 2-NT were systematically studied by multifactor orthogonal experiment. The electrochemical performance of Ti for 2-NT reduction was assessed in terms of 2-NT removal efficiency, 2-toluidine formation percentage, and coulombic efficiency (CE, %). The reductive pathway of 2-NT to 2-toluidine was also explored with GC-MS. Finally, electro-processes were applied in the pretreatment of nitrification wastewater.

2. Experimental

2.1. Chemicals

2-Nitrotoluene was analytical grade and purchased from J&K Scientific Ltd. All the other chemicals in this study were analytical grade and used without further purification.

A cylindrical double-chamber cell was applied for the electrochemical experiments, of which the dimensions were 10 cm (Diameter) × 12 cm (Height). The chambers were divided by a cationic exchange membrane (HengRui 0585). The cathode electrode was made of Titanium (Ti) while the anode electrode was alloy of $RuO_2/IrO_2/Ti$. The effective area of electrodes was both 75 cm^2 and the interelectrode gap was 3 cm. A digital multimeter was used to supply the current and potential measurements.

2.2. Electrochemical experiments

A SP 150 electrochemical workstation was used for the electrochemical studies. The electrochemical workstation worked with the conventional three-electrode system: a Ti electrode as the working electrode, a platinum electrode as the auxiliary electrode and an SCE electrode as the reference electrode. Cyclic voltammetry (CV) was performed using 0.1 M Na_2SO_4 solution with and without 2-NT. The solution was purged with nitrogen gas for 10 min to drive away the dissolved oxygen. The scanning rates were set ranging from 10 to 70 mV s^{-1}.

For the kinetics experiments, galvanostatic electrolyses were carried out on Ti and $RuO_2/IrO_2/Ti$ electrodes, with current density ranging from 5 to 30 mA cm^{-2}. Runs were performed at 293 K. Solutions of 90 mg L^{-1} of pure 2-NT were used. Electrolysis was conducted with 0.1 M of Na_2SO_4 as electrolyte with pH around 2.0. All electrolyses were conducted in the aforementioned thermo-stated double-chamber cell containing a 500 mL solution stirred with a magnetic bar. Reaction times for the kinetics experiments were all 120 min (Scheme 1).

To compare the electro-reduction-oxidation with the direct electro-oxidation process, solutions of 90 mg L^{-1} 2-NT were used. Electrolysis was done with 0.1 M of Na_2SO_4 as electrolyte with pH around 2.0. Electrolyses were carried out at Ti and $RuO_2/IrO_2/Ti$ electrodes, with current density set at 20 mA cm^{-2}. Runs were performed at 293 K. In electro-reduction-oxidation process, oxidation for 180 min was performed after 120-min reduction. However, in electro-oxidation process, oxidation proceeded for 300 min.

2.3. Optimization of electrolysis conditions

The electrolysis conditions were optimized using a multifactor orthogonal experiment. Previous studies on electrolysis demonstrated that the factors largely influencing the electrochemical efficiency were current density, electrolyte concentration, pH value, and initial concentration of organics [8,30,31]. Four parameters were investigated at four levels using an L$_{16}$ (4^4) orthogonal array in Table S1. The number of experiments was reduced to 16 by orthogonal design, which is much less than 256 (4^4) by conventional full factorial experiments.

Three statistical coefficients ($\overline{RE}$, $\overline{FP}$, and F-ratio) were used to evaluate the orthogonal data. $\overline{RE}$ is the average removal efficiency of 2-NT for each impact factor at each level, which was used to assess the optimal level of each factor so as to determine the optimum combination of experimental conditions. Similarly, $\overline{FP}$ is the average formation percentage of 2-toluidine. The F-ratio was applied to evaluate whether the impact factors were statistically significant or not, which was calculated using the method previously described by Gonder et al. [32]. Then it was compared with the critical F value [33]. The reaction times for the multifactor orthogonal experiments were all 20 min.
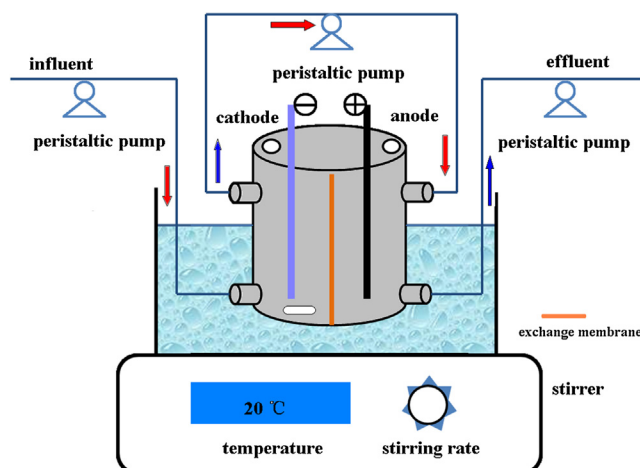
Scheme 1. Scheme illustrating for the electro-reduction-oxidation process.