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Treatment of high explosive production wastewater containing RDX by combined electrocatalytic reaction and anoxic–oxic biodegradation

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ABSTRACT

Treatment of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) wastewater by combined process of electrocatalytic reaction and anoxic–oxic (A/O) activated sludge process was investigated. The degradation intermediates of RDX during the synergistic system of electrochemical reduction and electrochemical oxidation were analyzed by tandem mass spectrometry (MS/MS), and a pathway for electrocatalytic degradation of RDX was proposed. In order to remove RDX from the wastewater, an electrochemical system using TiO_2-NTs/SnO_2-Sb anode was applied to the pretreatment process. The effect of the operating parameters on the electrochemical process performance was studied. The electrocatalytic process removed 39.2% of COD and 97.5% of RDX, and increased biodegradability index from 0.18 to 0.51, which resulted in a great improvement in the biodegradability. The start-up and operation period for the anoxic–oxic activated sludge process were also investigated. As a conclusion, the toxic and refractory organic pollutants were effectively removed in the electrochemical pretreatment and this combined process was successfully employed.

1. Introduction

Hexahydro-1,3,5-trinitro-1,3,5-triazine (royal demolition explosive or RDX) is used worldwide as commercial and military explosive. RDX is a heterocyclic nitramine compound that is known to be toxic to most classes of organisms including mammals and humans [1]. RDX is one of the major constituents in munitions manufacturing wastewater [2] and is of particular environmental concern. Due to its toxicity and possible carcinogenicity [3], RDX must be removed from wastewater before discharge.

Activated carbon is often used for the treatment of RDX-containing wastewaters, but the exhausted carbon cannot be safely regenerated or disposed. Biological treatment is usually used for the treatment of "readily degradable" (biocompatible) organic pollutants present in the wastewater. The cost of biological treatment is relatively lower. However, conventional biological treatment (e.g., activated sludge) is not effective in removing RDX in wastewater, because the electron-withdrawing nitro groups in RDX inhibit electrophilic attacks by enzymes [4]. Pure and mixed anaerobic microbial cultures have been employed to biotransform RDX [5–7]. RDX has also been found to decompose photochemically [8], and electrochemically [9]. Nevertheless, most of these studies have been carried out on pure RDX.

In the past two decades, electrochemical method for the treatment of wastewater containing toxic or refractory organic pollutants has attracted a great deal of attention due to its ease of operation, high efficiency, and environmental compatibility [10–14]. The electrode material is the key factor in the development of electrochemical techniques. Ti/SnO_2 electrode, world-wide known as dimensionally stable anodes, is one of the most attractive electrodes for the treatment of refractory organic pollutants because of its high oxygen overpotential [15]. However, the short lifetime of this electrode has raised major concerns about its commercial application [16]. Recently, TiO_2-NTs/SnO_2-Sb electrode has been fabricated by anodization, electrodeposition and annealing. Compared with the traditional Ti/SnO_2 electrode, TiO_2-NTs/SnO_2-Sb electrode has higher stability and better electrochemical performance [17].

Electrochemical method has been successfully applied in the treatment of actual wastewaters, such as textile wastewater [18], landfill leachate [19], olive mill wastewater [20], distillery spent wash [21] and carwash wastewater [22]. Practically, complete mineralization of organic pollutants to carbon dioxide by electrochemical treatment might not be economical due to high-energy consumption [23]. In addition, the biodegradability of the organic pollutants is enhanced when subjected to electrochemical method [12,24]. Thus, electrochemical method also provides us a valuable pretreatment technique for subsequent cheap biological treatment

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Table 1
Physicochemical characteristics of the RDX wastewater.

Parameter	Value
pH	2.0
COD ($mg\,L^{-1}$)	3420
BOD_5 ($mg\,L^{-1}$)	615
BOD_5/COD	0.18
Concentration of RDX ($mg\,L^{-1}$)	32.5
Suspended solids ($mg\,L^{-1}$)	260
UV absorbance 254 nm	5.6
Total nitrogen-Kjeldahl ($mg\,L^{-1}$)	172

[23,25]. The coupling of electrochemical and biological stages for the treatment of wastewater containing recalcitrant compounds is extremely promising [26].

In this paper, the combination of electrocatalytic reaction and anoxic–oxic biodegradation was employed to treat a high explosive production wastewater containing RDX. Electrochemical process was used to remove RDX from the wastewater, and a pathway for electrocatalytic degradation of RDX was proposed. The anoxic–oxic (A/O) activated sludge process was used as a post-treatment method.

2. Materials and methods

2.1. Characterization of RDX wastewater

The RDX wastewater was obtained from the 805 factory of China North Industries Group Corporation, located in Gansu, China. Physicochemical characteristics of the high explosive production wastewater are presented in Table 1.

2.2. Electrolysis

Experiments were conducted using the apparatus given in Fig. 1. To form an electrochemical reactor (15 cm × 10 cm × 9 cm, 1.35 L), the working anode was sandwiched between two cathodes of stainless steel plates 3 cm away from the anode. The dimension of the anode and cathodes was 14 cm × 9 cm. This electrochemical reactor was a synergistic combination of electrochemical reduction and electrochemical oxidation. The detailed procedure for the preparation of the TiO_2-NTs/SnO_2-Sb anode has been described in our previous research [17]. Briefly, this Sb-doped SnO_2 electrode have been prepared by anodization, electrodeposition and annealing. The performance of electrochemical process was studied. Aqueous NaOH was added to adjust pH of the solution to the desired value.

2.3. Bioreactor

The anoxic–oxic (A/O) activated sludge process was conducted in anoxic tank (2 L) and oxic tank (6 L), as shown in Fig. 1. The activated sludge was obtained from a wastewater treatment plant of chemical industry (Taizhou Bailly Chemical Co. Ltd., China). The anoxic and oxic activated sludge were respectively cultivated for 10 days, using glucose as the external carbon source, and then were incubated in the A/O bioreactor. The influent was continuously fed to the reactor using peristaltic pumps with a desired flow rate. The water temperature in the anoxic tank was kept at 30 °C by a temperature controller. The pH was controlled at 6.5–7.5 by means of the addition NaOH. The mixed liquor suspended solids (MLSS) concentration in the anoxic tank and oxic tank was 4500 ± 200 and 3500 ± 200 $mg\,L^{-1}$, respectively. The concentration of dissolved oxygen (DO) in the anoxic and oxic tank was maintained at 0.5 and 5 $mg\,L^{-1}$, respectively.

2.4. Analytical methods

To determine the amounts of RDX, samples were passed through a 0.22 μm filter and submitted to analysis. RDX was identified and quantified by HPLC (Waters 2996, Waters Incorporation, USA) conducted at room temperature using a Waters RP18 column (5 μm, 3.9 mm × 150 mm) and a diode array detector at a flow rate of 1.00 $mL\,min^{-1}$. The mobile phase consisted of 50% water and 50% methanol (v/v). The analysis was performed at 254 nm, with column temperature at 35 °C. The mechanism of RDX degradation was further analyzed by tandem mass spectrometry (MS/MS). The mass spectrometer (TSQ Quantum Ultra AM, Thermo Finnigan, USA) was equipped with an electrospray ionization (ESI) source and operated in positive ESI mode.

The pH values were measured by a pH meter (PHS-3B, Shanghai Precision & Scientific Instrument Co. Ltd., China). The DO concentration was measured using a DO analyzer (JPSJ-605, Shanghai Precision & Scientific Instrument Co. Ltd., China). The absorbance measurement was taken with the UV-visible spectrophotometer at 254 nm (TU-1901, Beijing Purkinje General Instrument Co. Ltd., China). Chemical oxygen demand (COD), five-day biological oxygen demand (BOD_5), total nitrogen-Kjeldahl (TNK), suspended solids (SS) and MLSS were analyzed according to standard methods [27].

3. Results and discussion

3.1. Electrocatalytic process

3.1.1. Pathway of RDX degradation

Since conventional biological treatment is not effective in removing RDX, study on the intermediates and pathway

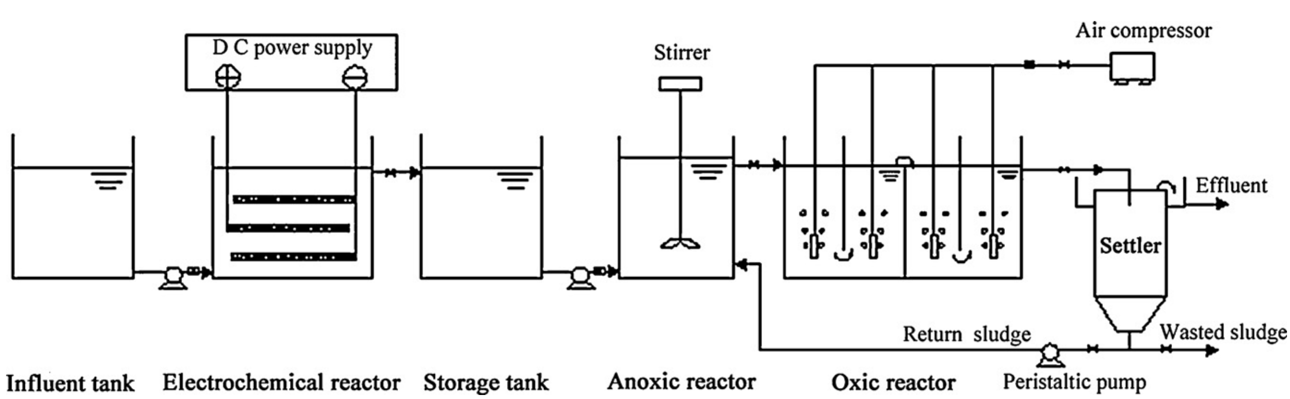

Fig. 1. Flow diagram of the combined process for RDX wastewater treatment.