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Advanced treatment of triazole fungicides discharged water in pilot scale by integrated system: Enhanced electrochemical oxidation, upflow biological aerated filter and electrodialysis

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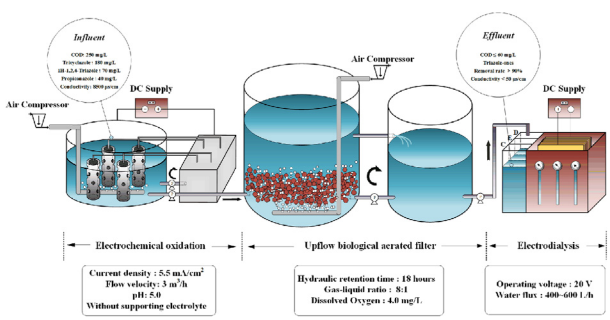
HIGHLIGHTS

- Efficient removal of N-heterocyclic contaminants and salts by a novel integrated process.
- A novel pilot-scale tubular electrochemical reactor which overcame diffusion control bottleneck.
- Each process was optimized and integrated with relatively low energy consumption.
- High level quality of final effluent for industrial water reuse.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a novel integrated system in pilot plant scale of electrochemical oxidation, upflow biological aerated filter and electrodialysis was investigated for high level standard reuse of triazole fungicides discharged water. In order to enhance biodegradable property of discharged water to be easier to recycled, a novel enhanced electrochemical oxidation reactor was designed and applied as pretreatment process. Effects of operating parameters on the performance of each process were studied with the discussion of economic evaluation. The results indicated that the optimal condition was current density of 5 mA/cm^2, flow velocity of 3 m^3/h, pH value of 5.0 and without supporting electrolyte. The target species including N-heterocyclic contaminants (tricyclazole, 1H-1,2,4-triazole and propiconazole) were removed over 90% from the discharged water by this process. Within upflow biological aerated filter, the remained COD would decrease further to the level less than 60 mg/L from 250 mg/L. Then the salt was removed efficiently during electrodialysis. Final effluent revealed a very low level of COD of 58.32 mg/L, TOC of 20.56 mg/L, $EC_{50,48h}$ of 73.1 ± 2.1%, consistent with an excellent removal of the target species of 94.19% tricyclazole, 90.11% 1H-1,2,4-triazole and 100% propiconazole, >99% salt and a low operating cost of $0.85. The excellent performance as well as the low energy consumption confirmed that this integrated system is highly applicable for the advanced treatment of triazole fungicides discharged water.

1. Introduction

Triazole fungicides (TFs) are a diverse group of commercial fungicides commonly used in the planting of vegetables and fruits, cereal crop protection programs, wood preservation and lawn care

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[1,2]. Although the traditional technology, to a certain extent, can treat discharged water generated by the production of triazole fungicides, it still has shortcomings of containing a number of different kinds of contaminants such as nitrogen heterocyclic rings (NHCs), organic acids and salts. Tricyclazole (TC), 1H-1,2,4-triazole (Tz) and propiconazole (PPC), known as three typical nitrogen heterocyclic rings compounds have been identified in this kind of discharged water. The exposure of these pollutants to surface and groundwater may damage the whole environment, especially the aquatic ecosystem [3,4]. Besides, they are toxic to plants, microorganisms, animals and humans [5,6]. A case that water discharged by a pesticide production company contains these organic pollutants does exist in Changzhou, China. Moreover, the concentration of TC, Tz, PPC and COD of this discharged water reaches as high as 175 mg/L, 67 mg/L, 40 mg/L, 240 mg/L, respectively. If we can take advanced treatment and achieve resource recycling of discharged water, we will not only reduce the cost of processing water, but also avoid the damage to lives and the environment [7].

Conventional treatments of wastewater include biological degradation [8], advanced oxidations [9], distillation [10] and incineration [11]. However, nitrogen heterocyclic rings in discharged water are very difficult to biologically decompose due to the toxicity of triazole-ones. If we can firstly break the ring of the nitrogen heterocyclic compounds and turn into low molecular weight organic matter with low toxicity, biological degradation will be the optimal choice. Based on practical experience, distillation and incineration would not be appropriate for local WWTP because their huge investment and new inevitable hazardous wastes. To overcome the drawbacks mentioned above, attempt to find a new and efficient treatment method has been made in recent years.

For the past few years, electrochemical oxidation treatment, which was mainly for the removal of toxic and persistent organic pollutants, has attracted wide attention, such as pesticide wastewater [12–14], textile dyes effluents [15,16], landfill leachate wastewater [17], explosive wastewater [18] and pharmaceutical wastewater [19,20]. The outstanding characteristic of this kind of treatment lies in the ability to reach the total mineralization without any new toxic wastes produced. In 2014, our research group have conducted the electrochemical degradation of TC in aqueous solution on a Ti/SnO_2-Sb/PbO_2 anode [21]. Though results showed that Ti-substrate PbO_2 anodes coated with a $SnO_2 + Sb_2O_3$ interlayer could increase electro-catalytic performance of electrodes and service life, anode modified by electrodeposition seemed not suitable for industrial production considering that this process needed reduplicative electrodeposition and different calcination programs. Moreover, traditional plate electrode is limited by mass transfer. Based on these considerations, in early 2015, our group invented a small-scale electrochemical oxidation reactor using tubular macro-porous titanium membranes electrode which had overcame the diffusion control bottlenecks and obtained an excellent performance at relatively low current density [22]. To continue previous work, this paper established a pilot-scale tubular reactor for the industrialized application.

Biological treatment is relatively an economical method because of its cost-effective removal of organic compounds [23]. Upflow biological aerated filter (UBAF) is the most representative technology which is an alternative to the traditional activated sludge process commonly used in biological wastewater treatment. It has been developed extensively due to several advantages, such as less occupied area [24,25] and excellent performance at much higher hydraulic loading than that of conventional biological process and high removal efficiencies for SS, COD, biodegradable organic substances and ammonia nitrogen [26].

At present, the treatment aimed at wastewater with high salinity is fairly single which has been one of intractable issues for so long. Making cyclic utilization after advanced treatment will not only alleviate serious pressure for water use but also greatly reduce environmental pollution. Li et al. [27] used artificial fast ooze biological filter for deeply treating organic pesticide wastewater. Wang et al. [28] presented a combined process with membrane bioreactor, advanced oxidation and ultrafiltration to treat heterocyclic pesticides wastewater. However, these studies only directed at organic pesticide in discharged water but lack of researches on the removal of salinity. Applied to advanced treatment of discharged water in the pesticide production, electrodialysis can achieve desalination and separation of small molecule organic salt so as to reduce the effluent concentration of COD.

Therefore, in this paper, we put forward a combined process including enhanced electrochemical oxidation, upflow biological aerated filter (UBAF) and electrodialysis methods. The optimal parameters of this process, which used to purify and reuse the discharged water preferably, was also discussed.

2. Materials and methods

2.1. Characterization of TFs discharged water

Wastewater in this project was acquired from final sedimentation tank in Jiangsu Fengdeng environmental technology service co., LTD located in Changzhou China which was a real-raw TFs discharged water. The physical and chemical properties of the TFs discharged water were shown in Table 1.

2.2. Pilot plant

The combined process for the TFs discharged water consists of electrochemical oxidation, upflow biological aerated filter (UBAF) and electrodialysis. All the process equipment was built in target corporation. A flow diagram of this combined treatment process was presented in Fig. 1.

The whole treatment comprises three stages: electrochemical oxidation, UBAF and electrodialysis.

2.2.1. Enhanced electrochemical oxidation

Before the pilot plant test, to determine the optimal current density and electrochemical oxidation elapsed time, we carried out pilot test. The apparatus of electrochemical oxidation consists of 40 pairs of electrodes, a DC power supply (SOYI-15300, 0–15 V, 0–300 A) and two vertical centrifugal pumps (ISG30-125, 5.0 m^3/h, 0.75 Kw). It was important to make sure that each anode and cathode cannot short out and every joint is sealed in case of leaking water. The anode was made of macro-porous titanium membranes electrode (Φ60 mm × 1.15 m, external surface area 130.0 cm^2, aperture 50 μm) coated with RuO_2, while tubular and fenestrated stainless steel (Φ90 mm × 1.2 m) was used as cathodes; the distance between each pair of electrodes was 1 cm. Six cubic meters TFs discharged water was pumped into the reaction tank

Table 1
Characteristic of TFs discharged water.

Parameter	Range	Average
Temperature (°C)	18–25	23
pH	7–7.5	7.2
SS (mg/L)	800–1000	900
Conductivity (μs/cm)	8000–9000	8500
COD (mg/L)	200–300	250
BOD_5 (mg/L)	5.6–8.4	7.0
BOD_5/COD	0.025–0.032	0.028
Tricyclazole (mg/L)	150–200	180
1H-1,2,4-Triazole (mg/L)	50–75	70
Propiconazole (mg/L)	25–55	40