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Treatment of bactericide wastewater by combined process chemical coagulation, electrochemical oxidation and membrane bioreactor

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Abstract

Bactericide wastewater (BIW) contains isothiazolin-ones, high salinity, toxicity and non-biodegradable organic concentrations. In order to enhance biodegradable capacity, chemical coagulation and electrochemical oxidation were applied to pretreatment processes. $FeSO_4·7H_2O$, pH 12 and 20 mmol/l were determined as optimal chemical coagulation condition; and 15 mA/cm^2 of current density, 10 ml/min of flow rate and pH 7 were chosen for the most efficient electrochemical oxidation condition at combined treatment. The wastewater which consisted mainly of isothiazolin-ones and sulfide was efficiently treated by chemical coagulation and electrochemical oxidation. The optimal pretreatment processes showed 60.9% of chemical oxygen demand (COD), 99.5% of S^{2-} and 96.0% of isothiazolin-ones removal efficiency. A biological treatment system using membrane bioreactor (MBR) adding powder-activated carbon (PAC) was also investigated. COD of the wastewater which was disposed using a MBR was lower than 100 mg/l.

Keywords: Bactericide wastewater; Combined process; Isothiazolin-ones; Chemical coagulation; Electrochemical oxidation; Membrane bioreactor

1. Introduction

Isothiazolin-ones is a bactericide widely used in industry [1]. The bactericide wastewater contains a number of different kinds of pollutants such as greases, organic acids, organic sulfide, inorganic sulfide, salts and isothiazolin-ones. The concentration of isothiazolin-ones in the wastewater typically reaches as high as 120 mg/l and the concentration of sulfide reaches as high as 450 mg/l. And the concentration of COD is 25,000 mg/l. Conventional treatments of wastewater include biological degradation [2], advanced oxidation [3], incineration [4] and resin adsorption [5]. The biological treatment of wastewater is cheaper than the others. Unfortunately, isothiazolin-ones and sulfide in wastewater are very difficult to break down biologically, due partly to the toxicities of isothiazolin-ones and sulfide to microbes. The cost of advanced oxidation is relatively high, because of additional chemical requirements. The reaction condition is typically so severe that it is not feasible for practical application. The incineration is an expensive procedure, and the hazardous wastes incinerating in incinerators change new toxic wastes giving off and into the air. The resin adsorption is applied to callback value substances. In an attempt to find treatments that do not have the aforementioned drawbacks, attention has been focused on chemical coagulation for sulfide and on electrochemical methods for isothiazolin-ones.

Recently, there has been increasing interest in the use of chemical coagulations and electrochemical methods for the treatment of recalcitrant toxic wastes. The cost of chemical coagulation is low, cheapness and widely used in treating wastewater.

The electrochemical methods are environmentally friendly and do not produce new toxic wastes. The organic matters and toxic pollutants are usually destroyed by anodic oxidation as a result of the production of oxidants such as hydroxyl radicals, ozone, etc. Electrolytic processes generally have lower temperature requirements than those of other equivalent non-electrochemical treatments, such as wet air oxidation, and there is no need for additional chemicals for advanced and Fenton oxidation. This electrochemical process requires neither chemical pre-testing nor chemical adjustment of the wastewater and little space, and produces fewer by-products or sludge. Recently, electrochemical methods have been successfully applied in the purification of several industrial wastewaters, such as fine chem-

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ical manufacturing effluent [6], landfill leachate [7], textile dyes and dyehouse effluents [8] and olive oil mill wastewaters [9]. However, few reports have been published on the treatment of bactericide wastewater by the electrochemical method. Generally, platinum-coated titanium electrodes (Pt/Ti) are suitable for the oxidation of organic substances, although their cost poses a major restriction for their widespread use [10]. On the other hand, cheaper substituents such as titanium electrodes coated with active oxides (e.g., RuO_2, PbO_2, SnO_2, etc.) have been successfully used in order to oxidize the organic pollutants in aqueous media [11–13]. And lead dioxide coated titanium electrodes (PbO_2/Ti) were widely used for the electrochemical oxidation of the organics.

This investigation extended the final work using a MBR. Membrane technology has attracted much attention from scientists and engineers in recent years as a new separation process in water and wastewater treatment. These separation processes have been applied to treat municipal and industrial wastewaters. Combining membranes with biological treatment is an attractive technique and has resulted in a new concept: MBR. The recent development of a new generation of more productive and less expensive ultrafiltration and microfiltration membranes makes this possible. In the MBR, the entire biomass is confined within the system, providing both exact control of the residence time for the microorganisms in the reactor (solids retention time) and the disinfection of the effluent.

MBR process offers numerous advantages over conventional biological processes, elimination of settling basins, independence of process performance from filamentous bulking or other phenomena affecting settleability [14,15]. The separation of biomass from effluent by membranes also allows the concentration of mixed liquor-suspended solids (MLSS) in the bioreactor to be increased significantly, thus giving good effluent and reducing its size for a given sludge. Effects of dilution of wastewater and adding adsorbent of PAC were studied using MBR treatment.

The treatment and safe disposal of hazardous organic waste material in an environmentally acceptable manner and at a reasonable cost is a topic of great universal importance. There is little doubt that biological processes will continue to be employed as a baseline treatment process for most organic wastewaters, since they seem to fulfil the above two requirements. However, biological processes do not always give satisfactory results, especially applied to the treatment of industrial wastewaters, because many organic substances produced by the chemical and related industries are inhibitory, toxic or resistant to biological treatment. Therefore, advanced technologies based on chemical oxidation may be the only viable options for decontaminating a biologically recalcitrant wastewater. Oxidation technologies may be used either for the complete mineralization of all pollutants to carbon dioxide, water and mineral salts or for the partial removal of certain target pollutants and their conversion to intermediates. In general, a chemical oxidation method aiming at complete mineralization might become extremely cost-intensive since the highly oxidized end-products that are formed during chemical oxidation tend to be refractory to total oxidation by chemical means. Total chemical oxidation of these intermediates to carbon dioxide and water may be difficult and require severe oxidative conditions. Biological treatment of intermediates becomes more attractive than chemical oxidation of intermediates [16]. Then many combined processes chemical oxidation and biological treatment were suggested in these days. One of reported combined methods showed that green table olive wastewater was treated by the combined process (Fenton's reagent oxidation and aerobic biological treatment) [17]. And Lin and Peng [18] employed combined coagulation, electrochemical oxidation and activated sludge for textile wastewater treatment. And Alaton et al. [19] employed combined chemical and biological oxidation for penicillin formulation effluent treatment. Because of complicacy and toxic of BIW composition, it would be of more practical significance to BIW to operate the combined process.

However, no report has ever been published regarding treatment by combined process adopting chemical coagulation, electrochemical oxidation and MBR in BIW. This research suggests a combined process which is composed of chemical coagulation and electrochemical oxidation pretreatment, and MBR final-treatment. The purpose of this study was to investigate the performance of the combined BIW treatment.

2. Materials and methods

Wastewater used in this research was obtained from a fine chemical factory located in Xuzhou China. The characteristics of BIW were showed in Table 1.

The combined process for BIW treatment consists of chemical coagulation, electrochemical oxidation and MBR. A flow diagram of the combined BIW treatment system used in this study was shown in Fig. 1.

Chemical coagulation and electrochemical oxidation were placed before MBR treatment step. Before the continued test, jar-test at the laboratory scale was carried out in order to choose the adequate coagulant and the reaction condition (pH, dosage). Poly-$AlCl_3$, $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ were tested as chemical coagulant candidates. One normal H_2SO_4, NaOH solution were added to adjust pH of the solution to the desired value. Chemical coagulant was added and mixed for 2 min under rapid mixing condition (250 rpm) and the solution was mixed at slow flocculation (40 rpm) for 5 min after rapid mixing. And then, COD, S^{2-} and pH of supernatant were measured after settling for 30 min.

Three hundred milliliters of mixing tank and 7 l (Ø15 cm × 50 cm) of sedimentation tank were equipped

Table 1
Characteristics of BIW

Parameter	Range	Average
pH	3–5	4
Temperature (°C)	40–25	43
COD (mg/l)	20,000–25,000	23,000
BOD_5 (mg/l)	200–250	225
S^{2-} (mg/l)	400–450	430
Isothiazolin-ones (mg/l)	90–120	100