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Treatment of pharmaceutical wastewater using interior micro-electrolysis/Fenton oxidation-coagulation and biological degradation

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HIGHLIGHTS

- IME—FO lab-scale tests and IME—FOC—biological treatment full-scale experiments were conducted.
- Optimal parameters were obtained and the BOD_5/COD of wastewater improved 2.8 times after pretreatment.
- IME effluent with appropriate pH and high Fe^{2+} concentration was suitable for the FO process.
- The combined system had a high pollutant removal efficiency and good operating stability.

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ABSTRACT

The synthesis of steroid hormones produces wastewater that is difficult to manage and characterize due to its complex components and high levels of toxicity and bio-refractory compounds. In this work, interior micro-electrolysis (IME) and Fenton oxidation—coagulation (FOC) were investigated as wastewater pretreatment processes in combination with biological treatments using a hydrolysis acidification unit (HA) and two-stage biological contact oxidation (BCO) in laboratory and field experiments. In laboratory experiments with an average initial COD load of about 15,000 mg/L, pH of 4, Fe—C/water (V/V) ratio of 1:1, air/water ratio of 10, and reaction time of 180 min, IME achieved a COD removal efficiency of 31.8% and a 1.7-fold increase in the BOD_5/COD (B/C) ratio of wastewater. The Fe^{2+} concentration of 458.5 mg/L in the IME effluent meets the requirements of the Fenton oxidation (FO) process. FOC further reduced the COD with an efficiency of 30.1%, and the B/C ratio of the wastewater reached 0.59. Excitation-emission matrix (EEM) analysis showed that complex higher molecular weight organic compounds in the wastewater were degraded after the pretreatment process. In addition, a field experiment with a continuous flow of 96 m^3/d was conducted for over 90 d. The combined process system operated steadily, though the Fe—C fillings should be soaked in a sulfuric acid solution (5‰) for 12 h to recover activity every two weeks. The COD and BOD_5 concentrations in the final effluent were less than 90 mg/L and 15 mg/L, respectively.

1. Introduction

Steroid hormones are widely used in the field of medicine (e.g., for improving metabolism and immune systems). Pharmaceutical wastewater from steroid hormone synthesis is characterized by complex components, high organic concentrations, and variable concentrations of salts, toxins, and bio-refractory compounds such as pyridine, hydroxylamine hydrochloride, cyclohexanone, toluene, tetrahydrofuran, methylene chloride, and metals (Hu, 2008). Such substances are difficult to manage in pharmaceutical plants.

As documented in many previous studies (Kelly et al., 2004; Ren, 2004), toxicants and macromolecules in wastewater may inhibit microbial activity to some extent and even cause process failure. Therefore, it is necessary to develop proper pretreatment methods to improve the biodegradability of sewage before it enters biological treatment units. Physicochemical pretreatment units combined with biological treatments have been widely applied to treat refractory wastewater, because of their efficient hazard removal and cost-effectiveness. The commonly used physicochemical/biological

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combined techniques include interior micro-electrolysis (IME)/biological processes (Fan et al., 2009; Zhu et al., 2014), Fenton oxidation (FO)/biological processes (Badawy et al., 2009; Ben et al., 2009; Diya Uddeen et al., 2015; Xu et al., 2014; Pi et al., 2015), photo-Fenton/biological processes (Liu et al., 2012; Anfruns et al., 2013; Silva et al., 2013), ozone/biological processes (Lester et al., 2013; Cui et al., 2014; Punzi et al., 2015), and other multi stage physicochemical/biological systems (Manenti et al., 2014; Klauson et al., 2015; Nogueira et al., 2015).

In preliminary research involving the treatment of chemical industry and pharmaceutical wastewater, IME (Fan et al., 2009; Ying et al., 2012) and FO (Lopez et al., 2004; Bautista et al., 2008; Badawy et al., 2009; Segura et al., 2013; Riaño et al., 2014) technology have been proposed as an attractive alternative for the pretreatment of bio-refractory organic wastewater due to their high efficiency, simple operation, and low cost. Hydrolytic acidification (HA) (Ye et al., 2008; Rajagopal and Béline, 2011) has strong impact resistance, which can be used for pretreatment and biological treatment at the same time.

It is believed that during the IME process, which uses iron as a sacrificial anode and carbon as a cathodic catalyst (Xia et al., 2007; Fan et al., 2009), macromolecular organic contaminants can be broken down into small organic matter molecules, which tend to biodegrade during IME due to the strong reducibility of Fe, Fe^{2+}, and [H]. A portion of compounds can also be adsorbed to the surface of Fe–C fillings by adsorption and electrophoresis, after which they can then be separated from wastewater. Moreover, Lan (Lan et al., 2012) and Ying (Ying et al., 2012) demonstrated that oxygen can compete as an electron acceptor under aerated conditions, thus generating H_2O_2 in the process of IME. The reactions are listed below.

Cathode (under acidic and aerobic conditions):

$$O_2\ (g) + 4H^+\ (aq) + 4e^- \rightarrow 2H_2O,\ E^0(O_2/\ H^+) = +1.23\ V \quad (1)$$

$$O_2\ (g) + 2H^+\ (aq) + 2e^- \rightarrow H_2O_2,\ E^0(O_2/\ H_2O_2) = +0.68\ V \quad (2)$$

With the Fenton process, hydroxyl radicals (•OH, $E^0 = 2.87$), which have a strong ability to oxidize organic compounds, can be obtained in the presence of H_2O_2 and Fe^{2+} under acidic conditions. After FO, the pH of the solution should be adjusted to around 9.0. Under these conditions, the Fe^{n+} (Fe^{2+}, Fe^{3+}) compounds generate nascent $Fe(OH)_n$ compounds, which have a good flocculation effect and may contribute to further contaminant removal (including organics and inorganics (e.g. mineral salts)) by a rolling–sweeping action and hydrogen bond and van der Waals forces.

Previous studies have reported that IME pretreatment can achieve high COD removal efficiency and improve the BOD_5/COD (B/C) values of refractory wastewater with high organic matter concentration (Xia et al., 2007; Yang, 2009). Moreover, numerous studies have indicated that FO is an effective method for removing many hazardous organic pollutants in wastewater and significantly transforming refractory organic compounds into biodegradable matter (Badawy et al., 2009; Elmolla and Chaudhuri, 2012; Pi et al., 2015). However, it is difficult to realize an economical and effective treatment for synthetic pharmaceutical wastewater using single FO or IME processes.

Because Fe^{2+}-rich IME-treated effluent is generally suitable for a subsequent FO treatment without Fe^{2+} addition or pH adjustment, the combined process of IME-Fenton oxidation-coagulation (FOC) has been used on specific industrial wastewaters, such as landfill leachate and electroplating wastewater, with better treatment efficiency and lower reagent dosage (Lan et al., 2012; Ying et al., 2012). However, few studies have investigated the removal efficiency of organic matter or the factors influencing Fe^{2+} generation due to the combination of IME-FOC and biological treatments for synthetic pharmaceutical wastewater (steroid hormone production) with high COD concentrations. As such, the goals of this paper were to: 1) evaluate the COD removal effects and IME-FOC process performance in batch tests with different operating parameters (initial pH, Fe–C/water (V/V) and air/water (V/V) ratios, reaction time, Fe^{2+} generation, H_2O_2 dosage, etc.); 2) analyze changes in wastewater characteristics before and after pretreatment; and 3) demonstrate the removal efficiency of pollutants and the operating stability of continuous flow experiments using IME-FOC and HA and biological contact oxidation (BCO) treatments.

2. Materials and methods

2.1. Raw wastewater

The raw wastewater (RW) was collected from a synthetic steroid hormone pharmaceutical plant (Hunan, China), whose main products are intermediates of eplerenone and medroxyprogesterone acetate. The RW was a mixture of three waste streams including the mother liquor of the synthesis workshop, centrifugal wastewater, and wash wastewater from the reaction tanks. The characteristics of the RW are presented in Table 1, and the best characterized compound is pyridines.

2.2. Experimental methods and equipment

Batch tests and continuous full-scale experiments were conducted using IME-FOC pretreatment, HA, and two-stage BCO biological treatments. Fig. 1 shows the general schematic of the experiments.

2.2.1. Batch tests of pretreatment

The pretreatment experiments were performed with the jar test method to investigate the effects of operating conditions on the degradation of COD, the B/C ratio, pH, and Fe^{2+} variations during IME-FOC. The IME tests were performed in beakers with a 400-mL working volume. Small aerators were set at the bottom of the beaker, and the airflow was controlled with a flow meter.

During the FO process, the pH of the IME effluent was adjusted to the required value using 1 M sulfuric acid (H_2SO_4) or 1 M sodium hydroxide (NaOH). The required amount of H_2O_2 was added once at the beginning of the FO process and mixed with a magnetic stirrer. After the FO reaction, coagulation experiments with a 30-min settling time were conducted. This procedure was preceded with 2 M NaOH addition and proper mixing to adjust the pH to about 9.0 to achieve a satisfactory coagulation efficacy. The pretreatment tests were carried out at room temperature (18°C–26 °C).

2.2.2. Full-scale combined process experiments with continuous flow

A combined IME-FOC-HA-BCO process was applied to study the removal efficiency and stability under the optimum conditions obtained from the above batch tests. The RW was pumped into an equalization tank to obtain a relatively stable influent for subsequent structures. During the FOC process, supernatant from chemical sludge dewatering was added to the equalization tank. The chemical sludge was treated as hazardous waste. After coagulation, the effluent's pH was adjusted to 7–7.5 using an acid solution in a buffer tank. The flow rate was 96 m^3/d and nutrients were supplied according to the Biological Wastewater Treatment (Second Edition, Revised Expanded) (Grady et al., 1999). The continuous monitoring program was carried out for more than 90 d (excluding inoculation time).

Before the continuous tests, biofilm formation was activated in