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Advanced ozone treatment of heavy oil refining wastewater by activated carbon supported iron oxide

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ABSTRACT

The catalytic ozonation of heavy oil refining wastewater (HORW) was investigated over activated carbon supported iron oxides (FAC) catalysts using activated carbon (AC) as the reference. The catalyst was characterized by chemical analysis, XRD, N_2 adsorption–desorption and SEM. A significant increase in COD removal efficiency was observed in FAC + ozone compared with AC + ozone due to more hydroxyl radicals, identified by tert-butyl alcohol (TBA). The composition analysis of organic pollutant in HORW by FT-ICR MS discovered organic pollutants chain scission and oxidation process during the treatment. A great improvement of biodegradability for treated HORW had been obtained. The investigation uncovered the catalytic potential of FAC catalysts for ozonation of HORW.

1. Introduction

The proportion of the heavy oil as one of main alternative resource has been gradually increased in the traditional petroleum refinery industry considering non-renewable crude oil source shortage. Accordingly, a great quantity of heavy oil refining wastewater (HORW) is generated [1,2], which has distinctive quality characteristics [3–5] of complicated components, high-concentration organic pollution, acute toxicity and poor biodegradability. On the other hand, more stringent environmental legislation has been implemented according to effluents standards. Thus, it inevitably will aggravate the burden of subsequent wastewater treatment system and challenge the treated technology. A great deal of effort has been devoted to treating the oil refining wastewater [6–15]. Generally, more investigation has been centered on the pretreatment, which is primarily based on the mechanical and physicochemical methods. Only a few studies have tended to develop high efficient treatment technologies at the advanced stage for heavy oil refining wastewater [14,15], though far-reaching investigation on advanced wastewater treatment has been mainly aimed at single pollutant or easy-treated wastewater.

Actually, an attractive advanced treatment technology is absorption-catalytic oxidation degradation. For the technology, many efforts have focused on creating materials for pollutants removal in the way of more efficiency and more economy [16–25]. Nevertheless, most of catalysts synthesized have been cost-intensive, which limits their application in full-scale systems. A major trend that addresses this issue is the development of increasingly stringent requirements for the efficiency and cost of the catalysts. A potentially feasible approach to meet these requirements is to develop catalysts based on cheap materials. It is found that iron oxides and iron supported materials have played a great role in pollutants degradation [26–37]. However, the activated carbon supported iron oxide (FAC) combined with ozone system with low cost has not been touched aiming at advanced treatment of heavy oil refining wastewater.

Here, the activated carbon supported iron oxide coupled with ozone was developed to treat Liaohe heavy oil refining wastewater (HORW) at the advanced stage in order to meet the updated environmental requirements. Meanwhile, the influence of catalyst amount, pH, ozone amounts, temperature, and treatment time on treatment efficiency was investigated. Besides, the degradation mechanism was discussed according to $^{\bullet}OH$ inhibitor TBA function in the system. In addition, organic pollutant composition of HORW before and after treatment was characterized by FT-ICR MS method and the biodegradability performance of the treated oil wastewater was further analyzed according to BOD_5/COD, biochemical respiratory-line method and analog bioreactor experiments.

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2. Materials and methods

2.1. Materials and reagents

The HORW samples were referred in particular to cyclic activated sludge system (CASS) effluents of wastewater treated plant in Liaohe Petrochemical Branch Company (LPBC) of Petrochina. The initial heavy oil refinery wastewater in LPBC was mainly composed of 13% (volume percent) sulfur-containing wastewater from point sources, 15% refractory oily wastewater with high concentrations from point sources and 72% easily degradable oily wastewater with low concentration from point sources. The above sewage source and water quantities in LPBC will influence the characteristics of HORW in this article, which were listed in Table 1. It was noted that HORW was weak alkaline with poor biodegradability and further advanced treatment was required according to the new discharge water quality.

Activated carbon was obtained from Chengde North Activated Carbon Factory (Chengde, China). Its basic properties was as follows: bulk density, 0.49 g/cm^3; iodine value by ASTM4607-1994 method, 950 mg/g; weight loss upon drying, 8%; mechanical strength by ball-milling methods, 95%; Methylene blue adsorption value by GB/T 7702.6-1997, 137 mg/g. TBA, sodium hydroxide, hydrochloric acid and ferric nitrate were purchased from Beijing Chemical Regent Company (Beijing, China).

2.2. Preparation of FAC

The activated carbon (AC) was impregnated sequentially by 10% (mass percent) sodium hydroxide solution for 24 h and 1:1 (volume ratio) hydrochloric acid solution for 24 h, respectively. The resulting product was filtrated and washed with deionized water, dried at 393 K for 2 h, calcinated at 533 K for 4 h.

FAC samples were prepared by impregnation methods. The pretreated AC was impregnated with ferric nitrate solution with different iron mass, air-drying for 4 h, drying at 353 K for 6 h and calcination at 873 K for 3 h. According to the iron mass percent of 5 wt%, 20 wt% and 35 wt%, the nomination of FAC was FAC-1, FAC-2 and FAC-3, respectively.

2.3. Catalytic ozonation procedure

The catalytic ozonation experiments were carried out in semi-continuous ozonation system, which composed of oxygen machine (5 L/min), ozone generator ($\leq$10 g/h), flowmeter (20–40 L/h), ozone reactor and exhaust gas absorption bottle. The ozone reactor was made of glass with height 55 cm and inner diameter 6 cm. The catalysts was added in the reactor and fixed in the range by porous supporting plates and clamping plate in order to avoiding catalysts effluence before 1 L targeted HORW was added in the reactor. The excess ozone in the outlet gas was trapped by $Na_2S_2O_2$ solution. Water samples were taken at regular intervals to analyze COD, BOD_5 and TOC.

Table 1
Characteristics of HORW.

Parameter	Range	Average
pH	5.6–9.7	7.8
COD_{cr} (mg/L)	54.6–256	80.8
BOD_5 (mg/L)	6.5–20.4	13.8
TOC (mg/L)	22.3–42.8	33.5
NH_4-N(mg/L)	2.42–11.17	6.51
B/C	0.096–0.253	0.171

2.4. Analytical methods

2.4.1. Catalysts

The X-ray diffraction of the samples was analyzed by Shimadzu XRD-6000 powder diffraction instrument (Shimadzu, Japan) with 40.0 kV working voltage and 40.0 mA electric current of the cube target X-ray tube. Surface area and pore size distribution of the samples were measured by N_2 adsorption–desorption method on the QUADRASORB SI Micromeritics instrument (Quantachrome, USA). A Mettler Toledo TGA/DSC 1 was used for the measurement of chemical composition of samples. The pH of Zero Point Charge (pH_{pzc}) was measured by zeta electric potential method, where the net charge of catalyst surface was zero. The surface crystal structure and composition analysis was analyzed by SEM&EDS in the QUANTA 200F (FEI, Netherlands).

2.4.2. Water quality

COD was measured by 5B-6 COD speed meter (LianHua, China) and BOD_5 was determined by OxiTo system (WTW Co., Germany). TOC was performed on Aurora 1030 TOC meter (OI analytical Co., USA) and pH was analyzed by PHS-3C pH meter (LeiCi, China). The ozone concentration in the gas was determined by iodometric titration method.

The simulative activated sludge test was as follows: (1) the active sludge suspension (obtained from Liaohe Petrochemical Branch Company (LPBC) of PetroChina Inc.) with the active sludge concentration 3–4 g/L and SV 15–35% was firstly pretreated by aeration overnight in order to remove organic substrate; the resulting mixture was further treated by sedimentation for 2 h, after which the supernatant liquids was removed and the left was used for subsequent experiments; (2) HORW sample was diluted to avoid high sludge loading and then added into the prepared activated sludge along with aeration; COD was measured for the water samples at certain time intervals.

Biochemical respiratory curves of HORW samples were made as follows: (1) 1 L mixture of sludge and water from CASS pool was treated by settlement to remove the supernatant layer; (2) HORW sample was added keeping 1 L mixture; (3) the resulting mixture was introduced in the reactor and simultaneously 10 mg/L allyl thiourea (ATU), a typical digestion inhibitor, was added in the reaction system; (4) magnetic stirring, aeration and dissolved oxygen (DO) monitoring every 3 min was carried out and then oxygen consumption (ΔDO) with time can be obtained. In addition, internal respiration line was made as reference using the deionized water in place of HORW without ATU addition.

Electrospray ionization (ESI) Fourier transform ion cyclotron resonance (FT-ICR) Mass spectrometry (MS) was used to quantitatively analyze HORW operated in the negative-ion mode on an Apex-ultra FT-ICR MS (Bruker Daltonics, USA) with a 9.4 T actively shielded magnet. Ions were generated from a micro-electrospray source along with a 50 μm i.d. fused silica-capillary. The operation condition is as follows: flow rate of HORW samples 180 μL/h, mass to charge ratio (m/z) scanning 115–1000 and signal to noise (S/N) > 4. Each mass spectrum was overlapped by 64 scans spectrums in order to reduce S/N and increase resolution. Moreover, 1 mL wastewater sample was added with 20 μL 30% (v/v) NH_4OH to accelerate the deprotonation of acidic compounds in ion ESI [38]. The data were acquired on the software of XMass version 6.0 (Bruker Daltonics, USA) and analyzed by Kendrick method.

3. Results and discussion

3.1. Characterization of the catalysts

Fig. 1 depicted XRD pattern of different samples. There was no pronounced difference in the XRD pattern between AC and FAC.