

Catalytic ozonation for Norfloxacin using $\text{MnO}_x/\text{SBA-15}$ as catalyst

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II. MATERIALS AND METHODS

Abstract—Comparative experiment was conducted to investigate the catalytic activity of $\text{MnO}_x/\text{SBA-15}$ in Norfloxacin (NFX) ozonation. The characterization results showed that the prepared catalysis possessed a large surface area and a well ordered hexagonal mesoporous structure. Though the degradation of NFX was barely increased, the introduction of $\text{MnO}_x/\text{SBA-15}$ in ozonation process successfully enhanced its mineralization. A high mineralization efficiency (53.74%) was achieved by $\text{MnO}_x/\text{SBA-15}/\text{O}_3$ (pH=5.0, 298K, 2% manganese loading) process at 60 min, 1.26 times higher than ozone alone. The increase of mineralization rate was due to the generation of more hydroxyl radicals in $\text{MnO}_x/\text{SBA-15}/\text{O}_3$ process.

Keywords—Catalytic ozonation, $\text{MnO}_x/\text{SBA-15}$, Norfloxacin, Hydroxyl radicals

I. INTRODUCTION

IN recent years, reports about the pollutions caused by pharmaceuticals and personal care products (PPCPs) have drawn the public attention [1],[2],[3],[4]. These compounds, either in their original form or in partially degraded state, may cause disruption of endocrine systems or affect the hormonal control of development in aquatic organisms and wildlife even in trace concentrations [5],[6]. However, conventional water treatments have low efficiency in removing PPCPs from urban wastewater. Researches have revealed that effluents from wastewater treatment plants contain a variety of PPCPs [7],[8]. Therefore, an efficient treatment technology is urgently needed to deal with these kinds of compound. Among the available treatments, heterogeneous ozonation, due to its higher mineralization rates and an enhanced efficiency for removal of refractory organic compound, has drawn much attention of researchers [9].

In this work, $\text{MnO}_x/\text{SBA-15}$ was prepared and used as catalyst in ozonation of Norfloxacin. Norfloxacin was chosen as model compound in the process since it was widely used as antiseptic at present and might pose threaten to human security. Series of experiments with the change of the metal content, and reaction temperature were conducted. Also the mechanism of the catalytic ozonation process were investigated.

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A. Catalytic ozonation procedure

The reaction was carried out in a 1.3 L cylindrical reactor ($h=500$ mm, $\Phi_{in}=60$ mm) made of borosilicate glass. Temperature was controlled by circulating water from a thermostatic bath (SDC-6, Ningbo, China). Ozone (100 mg h^{-1} output) was produced in situ from pure oxygen (1.2 L min^{-1}) by an ozone generator (DHX-SS-IG, Harbin jiujiu Electrochemistry Technology Co., Ltd., China). The generated ozone came into the solution through a porous glass plate at the bottom of the reactor. $\text{Na}_2\text{S}_2\text{O}_3$ was used to absorb the excess ozone coming out from the reactor. The withdrawn samples were filtered by a 0.45 μm prefilter. pH of the reaction solution was adjusted using 0.1 M NaOH and HCl.

B. Catalysts preparation

SBA-15 was synthesized by a hydrothermal synthesis method. First, 4.5 g P123 was dissolved in 140 ml hydrochloric acid solution (HCl, 4 M) with stirring at 313 K for 5 h, followed by the addition TEOS with continuous stirring for 24 h at 313 K. Next, the mixture was transferred into a Teflon-lined autoclave and aged for 48 h at 373 K. The after-aged product was then filtered, washed, and dried at 353 K. Finally, the sample was calcined at 823 K in air for 6 h to get the SBA-15.

$\text{MnO}_x/\text{SBA-15}$ samples were prepared according to an incipient wetness impregnation method using manganese acetate tetrahydrate [$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$] as manganese precursor. Pure SBA-15 was first dried at 353 K for 8 h. $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in deionized water and then was diluted to a certain volume of a concentration depending on desired metal loading. Next, proper amount of SBA-15 was dispersed into the diluted solution under ultrasonic vibration for 90 min. After that, the mixture was dried at 353 K and then calcined in air at 823 K for 3 h to get $\text{MnO}_x/\text{SBA-15}$.

C. Analytical procedures

The concentration of Norfloxacin was analyzed by a high performance liquid chromatography (HPLC, LC10A, Shimadzu, Japan) with a UV detector (SPD-10AV) at 268 nm. A Diamon-sil 5U C18 column (250 mm \times 4.6 mm, Dikma technologies) was used. The mobile phase was a mixture of Oxalic acid (10 nmol \cdot L⁻¹), methanol and Ultrapure water at $67:22:11$ (v/v), and its flow rate was 1.0 ml \cdot min⁻¹. Total

organic carbon (TOC) was measured by a Shimadzu TOC 5000 analyzer. Sample for total organic carbon analysis was firstly filtered.

III. RESULTS AND DISCUSSIONS

A. Characterization of the catalysts

Textural properties of the samples were test by XRD and N₂ adsorption-desorption. As shown in Fig.1, both samples had characteristic diffraction peaks at 2θ = 0.8°, 1.5°, 1.7°, which suggested that the materials synthesized in this study possessed a highly ordered hexagonal mesostructure [10]. N₂ adsorption-desorption isotherms and pore size distribution of the catalysis were given in Fig.2. Both the isotherms are type IV, which is typical for the highly ordering mesoporous material. And the narrowed size distribution was depicted by Fig.3, showing that the narrow mesoporous structure of SBA-15 retained after MnO_x were loaded to it .

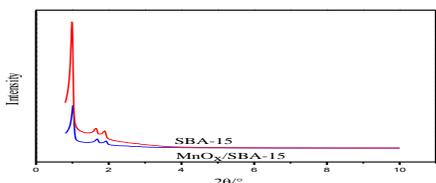


Fig.1 The XRD pattern of SBA-15 and MnO_x/SBA-15

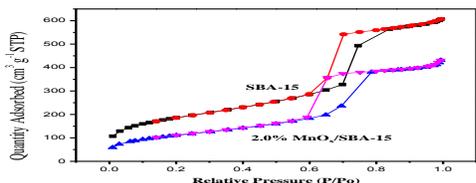


Fig.2 the N₂ adsorption-desorption isotherms of the SBA-15 and MnO_x/SBA-15

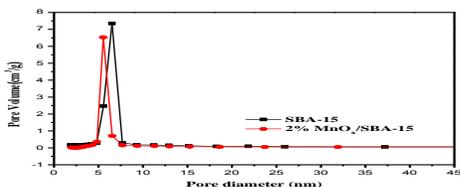


Fig.3 the pore size distribution of the SBA-15 and MnO_x/SBA-15

B. Ozonation of NFX in the presence of manganese-loaded SBA-15

Comparative experiment was conducted to investigate the catalytic activity of MnO_x/SBA-15 and the result was shown in Fig.4. Compared with single ozonation process, the presence of SBA-15 without metal loading had little influence on both the mineralization rate and removal efficiency of NFX, which meant that pure silicon SBA-15 had little activity in this process. However, the mineralization rate of NFX was obviously increased after manganese were loaded to SBA-15 and the enhancement of catalytic activity might be attributed to the presence of manganese on the surface of the catalyst. Previous studies of our group had found that the manganese on

the surface of SBA-15 were mainly in trivalent and tetravalent form [11]. As showed in Eqs.(1)~(3) [12], the electron transfer of different valence states of manganese would accelerate the transformation of ozone into ·OH radical.

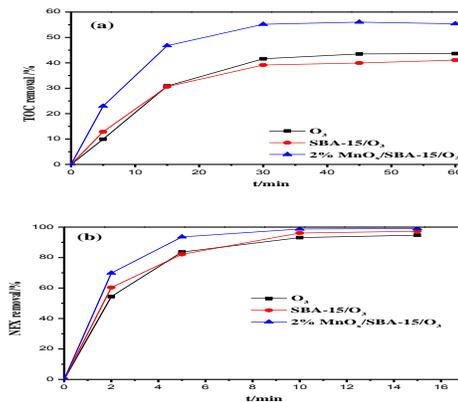
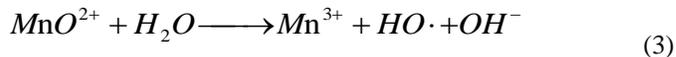
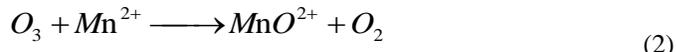
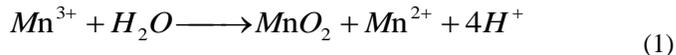


Fig.4 Influence of MnO_x/SBA-15 on removal of TOC (a) and NFX (b).

C. Influence of manganese content of MnO_x/SBA-15

It was shown in Fig.5 that the mineralization rate of NFX reduced with the Mn percentage of the catalyst after an initial increase and no significant difference was observed for the removal rate of NFX. When the Mn loading percentage reached 2%, 53.74% of total organic carbon were removed, and the mineralization rate was 1.26 times of sole ozonation process. However, when the loading amount continued to increase, the mineralization efficiency showed a downward trend. These phenomena might be attributed to the difference of the surface area and pH_{PZC} of the catalysts with different manganese loading amount. When introduced into water, H₂O molecules would be adsorbed to the surface of catalyst to form surface hydroxyl groups which were thought to be catalytic centers of metal oxides [13]. Since the pH_{PZC} of MnO_x/SBA-15 were ranged from 5.33-6.06, all exceeded the initial solution pH (pH=5.0). So more surface hydroxyl groups generated as the increase of MnO_x amount. However, the hydroxyl radicals were scavenged by MnO_x when metal loading was high [14].

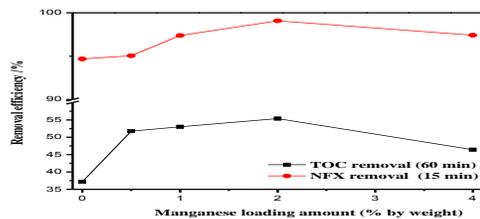


Fig.5 Influence of manganese content of MnO_x/SBA-15 on removals of TOC and NFX.

D. Influence of reaction temperature

Catalytic ozonation process, involved with synthetic effect of aqueous-gaseous-solid phase, is largely influenced by temperature. As shown in Fig.6, an increase of temperature from 278 K to 298 K caused an increase in both TOC and NFX removal efficiency. However when the temperature continued to climb up to 308 K, both the removal of TOC and NFX decreased. Although an increase of temperature would cause an increase of the rate of the chemical reaction but also led to a decrease of ozone solubility, which hindered the efficiency at higher temperatures [15].

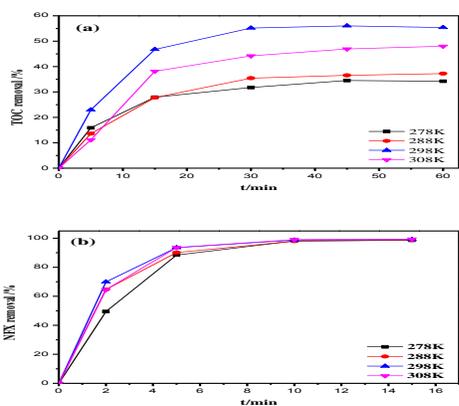


Fig.6 Influence of temperature of on removals of TOC (a) and NFX (b).

E. Influence of TBA

To verify the mechanism of catalytic process, TBA was selected as radical scavenger. As illustrated in Fig.7, NFX removal decreased by 6.6% when 5 mg L⁻¹ TBA was added. And the efficiency further decreased as the dosage of TBA. The interrelation between NFX removal rate and dosage of TBA implied that ·OH generated in the catalytic process played a role in NFX removal.

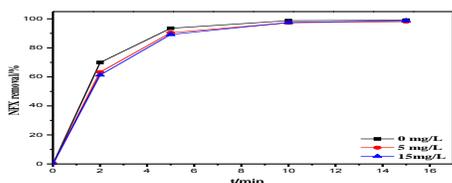


Fig.7 Influence of TBA concentration on NFX removal in catalytic ozonation

IV. CONCLUSION

MnO_x/SBA-15 was prepared by a hydrothermal synthesis method and an impregnation method. Characterizations showed that the catalysts processed a large surface area and highly ordered hexagonal mesoporous structure. The catalytic ozonation process towards NFX showed that MnO_x/SBA-15 could accelerate the removal rate and the mineralization rate of NFX. And hydroxyl radicals was found to play a role in the catalytic process.

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