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Complete mineralization of acetic acid using catalytic ozonation with a high energy efficiency enhanced by MnO$_2$/$\gamma$-Al$_2$O$_3$

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Abstract

The complete mineralization of acetic acid in a biodegradation process is difficult due to the $\alpha$-position methyl on the carboxyl group of acetic acid. This study explores the complete oxidation of acetic acid by catalytic ozonation. Metal oxides of MnO$_2$, Co$_3$O$_4$, Fe$_3$O$_4$, and CeO$_2$ loaded on $\gamma$-Al$_2$O$_3$ powder were used as the catalysts. The experimental results showed that MnO$_2$/$\gamma$-Al$_2$O$_3$ catalyst had the best mineralization performance for acetic acid. Typically, the mineralization of acetic acid is as high as 88.4% after 300 min ozonation of 100 mL of 1.0 g L$^{-1}$ acetic acid catalysed by 3.0 g 1.0wt.% MnO$_2$/$\gamma$-Al$_2$O$_3$ catalyst powder with an energy efficiency of 15 g kWh$^{-1}$. However, without a catalyst, the mineralization of acetic acid is only 33.2% with an energy efficiency of 5.1 g kWh$^{-1}$. The effects of MnO$_2$ loading, catalyst dosage, acetic acid concentration, O$_3$ concentration, ozonation temperature, and initial pH value of the acetic acid solution were systematically investigated. Radical quenchers and in-situ DRIFTS analyses indicated that •OH radical and reactive oxygen species on catalyst surface played an important role in the ozonation of acetic acid to CO$_2$ and H$_2$O. The mechanism of acetic acid oxidation on MnO$_2$/$\gamma$-Al$_2$O$_3$ is proposed.

Keywords: Acetic acid•Ozonation•MnO$_2$ catalyst•Energy efficiency•Oxidation mechanism

Introduction

The production of acetic acid is common in chemical industries such as petrochemicals and wood pulp mills, and these industries usually produce wastewater containing acetic acid (Wisniewski and Pierzchalska 2005; Shan et al. 2017). In addition, acetic acid has always been a by-product in some conventional wastewater treatment processes of macromolecular organic matter, since it is difficult to further oxidize the $\alpha$-position methyl group on the carboxyl group of acetic acid to CO$_2$ and H$_2$O (Centi et al. 2000). It was found that by-products, such as acetic acid, were formed when O$_3$ was used for 2-propanol oxidation (Reisz et al. 2019). Zhong et al. (2018) reported several short-chain acids, such as acetic acid and formic acid, as major by-products that formed during the ozonation degradation of humic acids. Acetic acid-contaminated water not only causes great harm if ingested by livestock and to crop irrigation but also adversely affects the respiratory system and sensory organs of human beings (Sedjame et al. 2018; Zhao et al. 2018). Therefore, the effective degradation of acetic acid is of great significance for the complete mineralization of organic compounds in wastewater.
Several physical approaches, such as adsorption and membrane separation methods, have been investigated for the removal of acetic acid. Borhan et al. (2016) used activated carbon with zinc chloride to remove acetic acid using the adsorption method. Lee (2013) developed an emulsion membrane system for the selective removal of acetic acid from simulated hemicellulose hydrolysates. Acetic acid decreases the pH of the waste water. The neutralization with alkali would lead to an enormous load of total dissolved solid in the treated effluent for biodegradation. An early literature reported that 1.0 kg of NaOH or 0.62 kg of CaCO$_3$ needed to neutralize 500 g of acetic acid in the wastewater for further biodegradation (Jin 1989). Biodegradation, on the other hand, while not impossible, will be a very slow process (Sinha and Annachhatre 2007).

Advanced oxidation processes have been widely used to remove organic matter from aqueous environments (Giardina et al. 2019). In addition, reactive species, such as ·OH and ·O, can effectively break down organic matter into small molecules, such as CO$_2$ and H$_2$O (Miklos et al. 2018). However, these methods have disadvantages, such as the large scale of the removal unit, where secondary contamination would occur because the contaminant was not fully degraded (Mu et al. 2019). Cihanoğlu et al. (2017) combined ultrasound with a catalyst to oxidize acetic acid, and the chemical oxygen demand (COD) degradation was only 25.5%. Sannino et al. (2011) studied the heterogeneous photo-Fenton oxidation of acetic acid on LaFeO$_3$, LaMnO$_3$, and LaFeO$_3$ chalcogenides with total organic compound removals of 60%, 54%, and 100% after 5-h oxidation, respectively. Experimental results showed that the presence of SO$_4^{2-}$/ZrO$_2$–Fe$_2$O$_3$ can greatly improve the oxidative efficiency of H$_2$O$_2$/O$_3$ for acetic acid ozonation in the pH range from 0 to 5.0 (Wang et al. 2016). Although the ozonation process can be conducted at ambient temperature and atmospheric pressure and is a cleaner wastewater treatment process that does not produce sludge, the reaction rate should be further improved (Malik et al. 2020). Furthermore, the high energy consumption of O$_3$ generation makes the ozonation process costly (Nur et al. 2016).

Catalytic ozonation has been proven to be an effective method to effectively degrade organic matter and to produce more reactive oxygen species, and this can greatly reduce the ozonation process cost. Transitional metal oxides have exhibited superior O$_3$ decomposition ability. It was deduced that the increased degradation ability was due to the formation of more reactive hydroxyl radicals (·OH) with higher redox potentials with the help of specific catalysts, which can then be used to further degrade the target pollutants (Chen et al. 2016; Sui et al. 2010). It has been found that nano-CeO$_2$ greatly improved the oxidation efficiency of the H$_2$O$_2$/O$_3$ system and promoted the degradation of acetic acid small molecules (Ding et al. 2018). Peng et al. showed that the O$_3$ oxidation efficiency of succinic acid reached 100% in combination with a Ni/Al$_2$O$_3$ catalyst (Peng et al. 2018). Nevertheless, little attention has been paid so far to the effective degradation of acetic acid by catalytic ozonation, and therefore there is a great need to improve the degradation of acetic acid.

In this work, the best catalyst for the mineralization of acetic acid is firstly screened from the metal oxides of MnO$_2$, Co$_3$O$_4$, Fe$_3$O$_4$, and CeO$_2$ loaded on γ-Al$_2$O$_3$. The influencing factors (such as metal oxide loading, catalyst dosage, acetic acid concentration, O$_3$ concentration, pH, and ozonation temperature) are also investigated. Tert-butanol (TBA) and p-benzoquinone (PBQ) are used to explore reactive species for acetic acid oxidation. The gas-liquid-solid system is demonstrated by applying in-
situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and the mechanism of acetic acid ozonation on MnO$_2$/γ-Al$_2$O$_3$ catalyst is revealed.

**Materials and methods**

**Catalyst preparation**

Nitrates of manganese, cobalt, iron, and cerium were used as the precursors of MnO$_2$, Co$_3$O$_4$, Fe$_3$O$_4$, and CeO$_2$, respectively. The nitrates in a water solution were loaded on γ-Al$_2$O$_3$ powder (as support, 2000 mesh, 99%) using the sequential impregnation method. The impregnated powder was dried at 100°C for 5 h and calcined in air at 500 °C for 3 h to obtain the MnO$_2$/γ-Al$_2$O$_3$, Co$_3$O$_4$/γ-Al$_2$O$_3$, Fe$_3$O$_4$/γ-Al$_2$O$_3$, and CeO$_2$/γ-Al$_2$O$_3$ catalysts. The loading amounts of the metal oxide were adjusted by changing the amounts of nitrate precursors.

**Catalyst characterization**

The crystalline phases of the catalysts were determined using X-ray diffraction (XRD, Rigaku Ultima IV powder diffractometer, Japan) with a Cu Ka radiation. The morphological properties of the catalysts were measured using scanning electron microscopy (SEM, Supra 55, Zeiss, Germany) with energy-dispersive X-ray spectroscopy (EDS). The surface elements on MnO$_2$/γ-Al$_2$O$_3$ were analysed using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi+, Thermo, USA).

**Ozonation of acetic acid**

The ozonation of acetic acid was investigated using the experimental system in Fig. 1a. The system was primarily composed of a dielectric barrier discharge (DBD) reactor and an ozonation reactor. Pure oxygen (99.999%, 100 mL min$^{-1}$) was supplied to the DBD reactor using a mass flow controller (D07, Sevenstars, Beijing, China). A pulse power supply (M10K-08, Suzhou Allftek, China) was used to drive the DBD reactor to generate O$_3$. The temperature of the ozonation reactor was controlled using a water bath and an electric heater. The ozonation reactor contained 100 mL of an acetic acid solution with or without catalyst. The acetic acid solution was stirred with a magnetic stirrer to promote the suspension of the catalyst powder and the contact of acetic acid with the catalyst powder and O$_3$ gas bubbles from a bubbler head (BSJ1348-1/8, Langfang Shengguang Filter, China).

The acetic acid degradation was studied by investigating the loadings of metal oxide on the γ-Al$_2$O$_3$ powder, the catalyst dosage, the acetic acid concentration, the O$_3$ concentration, pH, and the oxidation temperature on the acetic acid degradation.

The pH value of the acetic acid solution was modified using sodium hydroxide and measured using a pH meter (AZ 86505, Hengxin, China). The O$_3$ oxidation mechanism of acetic acid was investigated by adding OH quencher tert-butanol (TBA, 362 mM) and the superoxide radical (·O$_2^-$) quencher p-benzoquinone (PBQ, 1.1 mM) to the acetic acid solution.

**Analytical methods**
The concentrations of acetic acid and oxidation products (CO and CO\textsubscript{2}) in the gases from the outlet of the ozonation reactor were on-line analysed using a gas chromatograph (GC) (GC2014, Shimadzu, Japan) equipped with two flame ion detectors (FIDs) and two columns: a 2-m Porapark N column (Dalian Institute of Chemical, China) with a methanizer prior to the FID to analyse CO and CO\textsubscript{2}; and a capillary column (SH-Stabilwax-DA, Shimadzu, Japan) to analyse the acetic acid concentration in the water liquid solution. The liquid samples without the catalyst powder were injected directly into the injection port of the GC. For the liquid samples with the catalyst powder, the catalyst powder was separated by centrifugation, and the supernatant liquid was used for the GC analyses. The O\textsubscript{3} concentrations in the gases from the water saturator and the ozonation reactor were measured using an O\textsubscript{3} meter, and two ice baths were used to remove the water in the gas before entering the O\textsubscript{3} meter (BMOZ-200T, Weifang Shenxing, China). By-products from acetic acid oxidation were analysed using high-performance liquid chromatography (HPLC, Agilent 1260, USA) equipped with an Eclipse Plus C18 column and an ultraviolet (UV) detector. The mobile buffers of A (KH\textsubscript{2}PO\textsubscript{4}, 0.015 mol L\textsuperscript{-1}) and B (Acetonitrile with 0.5 mL min\textsuperscript{-1}) were used.

The catalytic ozonation of acetic acid on the MnO\textsubscript{2}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts of 0.5wt.%, 1.0wt.% and 10wt.% MnO\textsubscript{2} loadings was studied using an in-situ DRIFTS system (Fig. 1b). The system primarily consisted of an acetic acid/water bubbler, an O\textsubscript{3} generator, an in-situ cell (HVC-DRP-5, Harrick, USA), and the DRIFTS system (Nicolet iS50, Thermo Scientific, USA). Gases containing acetic acid and water were obtained by bubbling an acetic acid solution (100 mL, acetic acid concentration 1.0 g L\textsuperscript{-1}), and this was supplied to the in-situ cell to simulate the reactions within acetic acid, water, and O\textsubscript{3} on MnO\textsubscript{2}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst. O\textsubscript{3} with a concentration 37.5 g Nm\textsuperscript{-3} was obtained from the O\textsubscript{3} generator. The temperature of the in-situ cell was 25 °C. The DRIFTS spectra were processed using OMNIC software and converted using the Kubelka-Munk function.
Fig. 1 Diagram of the experimental setup for acetic acid ozonation (a) and the in-situ DRIFTS system (b)

Definitions

The degradation ($X$, %) was calculated using Eq. 1.

$$ X = \frac{C_0 - C_t}{C_0} \times 100\% $$

Where $C_0$ is the initial concentration of acetic acid in g L$^{-1}$, and $C_t$ is the concentration of acetic acid in g L$^{-1}$ at reaction time $t$ (min).

Mineralization ($Y_{i+1}$) and energy efficiency ($\eta_i$) (g kWh$^{-1}$) were defined as follows:

$$ Y_{i+1} = \frac{m_{i+1}}{m_0} \times 100\% $$

$$ \eta_i = \frac{m_{i+1}}{P_{i+1}} \times 100\% $$

Eq. 4 was used to calculate the amount of CO$_2$ and CO generated from acetic acid oxidation.

$$ m_g = \sum_{t=0}^{t_{i+1}} \left( \frac{60.5F}{22.4} \left( [CO] + [CO_2] \right)_{i+1} - \left( [CO] + [CO_2] \right)_{i} \right) (t_{i+1} - t_i) $$

Where $m_0$ is the initial amount of acetic acid in g, $m_g$ is the amount of acetic acid in g and calculated
from the average concentration of \([\text{CO}_2]\) and \([\text{CO}]\) at \(t_{i+1}\) and \(t_i\) time (min) with the difference in oxidation time \((t_{i+1}-t_i)\). \(P\) is the discharge power in W, 60 is the conversion factor between hour and minute, and 1000 is the conversion factor between W and kW. \(F\) is the flow rate of the bubbling gas, 0.100 \(\text{L min}^{-1}\); 22.4 is the molar volume (L) of a gas at standard state and 60.5 is the molecular weight of acetic acid.

The discharge power \((P)\) was calculated from waveforms of the pulse voltage supplied from the pulse power supply, using the voltage probe (P6015A, Tektronix, USA) and current probe (CP8030H, Cybertek, China) and oscilloscope (MDO 3022, Tektronix, USA).

Results and discussion

Catalytic activity investigation

The \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\), \(\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3\), \(\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3\), and \(\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3\) catalysts were used to screen for the best metal oxide for acetic acid degradation. The degradation of acetic acid as a function of ozonation time is shown in Fig. 2a. The acetic acid was not obviously degraded by \(\text{O}_2\) bubbling only, suggesting that \(\text{O}_2\) had difficulty oxidizing acetic acid. The degradation of acetic acid was 39.9% with \(\text{O}_3\) bubbling without a catalyst at a 300 min ozonation time. The degradation of acetic acid with \(\text{O}_3\) bubbling and \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) increased rapidly to 49.2% at 20 min and gradually to 88.4% at 300 min. It was obvious that the degradation of acetic acid was enhanced by the application of the \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) catalyst in comparison with the result of \(\text{O}_3\) bubbling without a catalyst. The rapid increase in degradation during the first 20 min of ozonation time was primarily due to the adsorption of acetic acid on the \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) surface. Similar adsorption effects were found on the surfaces of \(\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3\), \(\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3\), and \(\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3\). The adsorption effect and acetic acid degradation had the same order of \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) > \(\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3\) > \(\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3\) > \(\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3\). This order did not change when the metal oxide loading increased from 1.0wt.% (Fig. 2a) to 10wt.% (Fig. 2b).

The mineralization of acetic acid is important to explore the ability of the catalyst that promotes acetic acid oxidation to CO and \(\text{CO}_2\). The mineralization of acetic acid is linear to ozonation time, and the slopes of the mineralization of acetic acid using \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) (both 1.0wt.% and 10wt.%) were the largest (Figs. 2c and 2d). This demonstrated that the \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) was the best catalyst for the mineralization of acetic acid. The energy efficiency using \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) was approximately 14.9 g kWh\(^{-1}\) and also the highest in comparison with the other three catalysts (Figs. 2e and 2f).
Fig. 2 Degradation, mineralization, and energy efficiency of acetic acid degradation in O₃ bubbling with or without metal oxides or in O₂ bubbling alone. Mn, Co, Fe, and Ce are denoted as MnO₂, Co₃O₄, Fe₂O₃, and CeO₂, respectively. Experimental condition: 100 mL solution, 1.0 g L⁻¹ acetic acid concentration, 3.42 initial pH, 3.0 g catalyst dosage, 30.0–40.0 g Nm⁻³ O₃ concentration (for O₂ bubbling, 0 g Nm⁻³), and 25 °C ozonation temperature.

Since MnO₂/γ-Al₂O₃ was the best catalyst for acetic acid degradation, the primary factors influencing the catalytic performance, such as MnO₂ loading, catalyst dosage, acetic acid concentration, O₃ concentration, pH, and ozonation temperature, were further investigated.

The effect of MnO₂ loading on the degradation of acetic acid was investigated in detail, and the results are shown in Fig. 3. The acetic acid concentration decreased from 1.0 g L⁻¹ to a level of 0.6 g L⁻¹ at 20 min and gradually to approximately 0.1 g L⁻¹ at 300 min. The highest degradation of acetic acid was 88.4% at 300 min of ozonation time (Fig. 3b). Figs. 3c and 3d indicate that the CO₂ was the primary
product from acetic acid ozonation since the CO₂ concentration was approximately 6.5–43 times as many as CO. The mineralization increased linearly to a maximum level of 88.9% (Fig. 3e). The energy efficiency using the 1.0wt.% MnO₂/γ-Al₂O₃ catalyst was the highest at 15.3 g kWh⁻¹ (Fig. 3f). Fig. 3g illustrates the relationships of the average energy efficiencies between 20 and 300 min as a function of MnO₂ loading. It is obvious that the 1.0wt.% MnO₂/γ-Al₂O₃ catalyst had the maximum average energy efficiency of 14.9 g kWh⁻¹ and was the best catalyst for acetic acid degradation. Fig. 3h shows O₃ concentrations in the gases from the inlet ([O₃]in) and outlet O₃ ([O₃]out) of the ozonation reactor and the O₃ concentration drop ([O₃]drop) = [O₃]in − [O₃]out with ozonation time when O₃ bubbling with the 1.0wt.% MnO₂/γ-Al₂O₃ catalyst. The [O₃]drop was 14.0 g Nm⁻³ (at 20 min) and tended to stabilize at a level of 4.0–6.0 g Nm⁻³ after 150 min, which was significantly higher than the [O₃]drop without a catalyst (about 1.0 g Nm⁻³, Fig. S1). Thus, it is clear that the MnO₂/γ-Al₂O₃ catalyst promoted O₃ consumption for acetic acid oxidation.

The above average energy efficiencies and O₃ concentrations implied that the 7.1 kWh (= 500/14.9 × 8/38) electric energies are required for treating a tone waste water of 500 g acetic acid with 90% mineralization for 300 min ozonation; where 8/38 represents the remained O₃ is reused for acetic acid oxidation using O₃ recycling utilization. The cost of 7.1 kWh electric energies is only 3.55 Chinese Yuan (0.55 US$), this cost is not expensive to be accepted, as the current ozonation can save the cost for neutralization and biodegradation, and can realize the complete mineralization without sludge formation.
Fig. 3 (a) Acetic acid concentrations as a function of ozonation time; (b) degradation of acetic acid as a function of ozonation time; (c) CO concentrations as a function of ozonation time; (d) CO$_2$ concentrations as a function of ozonation time; (e) mineralization of acetic acid as a function of ozonation time; (f) energy efficiencies of acetic acid as a function of ozonation time; (g) energy efficiencies of acetic acid as a function of MnO$_2$ loadings; (h) O$_3$ concentrations while the 1.0wt.% MnO$_2$/γ-Al$_2$O$_3$ catalyst was
used. Experimental condition: 1.0 g L\(^{-1}\) acetic acid concentration, 3.42 initial pH, 3.0 g catalyst dosage of \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) with different \(\text{MnO}_2\) loadings, 30.0–40.0 g Nm\(^{-3}\) \(\text{O}_3\) concentration, and 25 °C ozonation temperature

After selecting the optimal loading of Mn, a further study was conducted on the dosage of the catalyst. The influence of the dosage of the 1.0wt.% \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) catalyst on acetic acid degradation is shown in Figs. 4a and 4b. The highest energy efficiency was also found when using 3.0 g of the 1.0wt.% \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) catalyst (Fig. 4a). It was evident that the higher energy efficiency was obtained since a generally higher \(\text{O}_3\) consumption occurred when using 3.0 g of the 1.0wt.% \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) catalyst (Fig. 4b). The distinct \(\text{O}_3\) concentration drop within the first 100 min was deduced to be the adsorption effect of the \(\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3\) catalyst.
Fig. 4 (a) Energy efficiency and (b) O$_3$ concentration drop as a function of ozonation time at various catalyst dosages; experimental condition: 1.0 g L$^{-1}$ acetic acid concentration, 3.42 initial pH, 1.0 wt.% MnO$_2$/$\gamma$-Al$_2$O$_3$ catalyst, 30.0–40.0 g Nm$^{-3}$ O$_3$ concentration, and 25°C ozonation temperature. The influences of the initial acetic acid concentration on energy efficiency (c) and a comparison of mineralization and the amount of acetic acid mineralized (d); experimental condition: 1.0 g L$^{-1}$ acetic acid concentration, 3.42 initial pH, 3.0 g 1.0 wt.% MnO$_2$/$\gamma$-Al$_2$O$_3$ catalyst dosage, 30.0–40.0 g Nm$^{-3}$ O$_3$ concentration.
concentration, and 25 °C ozonation temperature. Energy efficiency (e) and O₃ concentration and O₃ concentration drop (f) versus ozonation time at various pulse frequencies; experimental condition: 1.0 g L⁻¹ acetic acid concentration, 3.42 pH, 3.0 g 1.0wt.% MnO₂/γ-Al₂O₃ catalyst dosage, and 25 °C ozonation temperature. Energy efficiency as a function of ozonation time (g) and relation of energy efficiency and ozonation temperature (f); experimental condition: 1.0 g L⁻¹ acetic acid concentration, 3.42 initial pH, 3.0 g 1.0wt.% MnO₂/γ-Al₂O₃ catalyst dosage, and 30.0–40.0 g Nm⁻³ O₃ concentration

In addition to the dosage of the catalyst, the concentration of acetic acid also had a certain effect on its degradation. Fig. 4c illustrates the influence of initial acetic acid concentration on energy efficiency at various ozonation time. The highest and lowest energy efficiencies were obtained when the initial acetic acid concentrations were 1.0 g L⁻¹ and 0.5 g L⁻¹, respectively. Since the ozonation of acetic acid related with the adsorption of acetic acid and O₃ on catalyst surface, the presence of the highest initial concentration of acetic acid is possibly due to the optimum adsorption of acetic acid and O₃ on catalyst surface under the experimental condition. Fig. 4d shows the mineralization of acetic acid at 300 min ozonation time as a function of initial acetic acid concentration. The mineralization reached 89%, 84%, 67%, and 50%, when the initial acetic acid concentration was 0.5, 1.0, 1.5, and 2.0 g L⁻¹, respectively. The mineralization decreased with increasing the initial acetic acid concentration, however, the amount of acetic acid mineralized increased. This finding implied that in order to get a large amount of mineralized acetic acid, a high initial acetic acid concentration is required; however, in order to get the highest energy efficiency, the ozonation should be carried out with optimized initial acetic acid concentration.

O₃ played a vital role in the degradation of acetic acid. The O₃ concentration was concisely adjusted by changing the frequency of the voltage pulses to the DBD reactor, and the O₃ concentrations were 20.7, 35.6, 47.0, and 55.0 g Nm⁻³ when the frequencies were 50, 100, 150, and 200 Hz, respectively (Fig. 4f). The maximum energy efficiency (25.5 g kWh⁻¹) at 20 min was obtained when the frequency was 50 Hz. However, the energy efficiency decreased with increasing frequency (Fig. 4e). It was found that the O₃ concentration drop was within 4.0–6.0 g/Nm³ after 140 min of ozonation time (Fig. 4f), although the O₃ concentration increased with the frequency. This indicated that the amount of O₃ used for acetic acid was limited, and most of the O₃ did not take part in acetic acid ozonation and flowed away from the ozonation reactor.

The acetic acid degradation was characterized at different ozonation temperatures with or without a catalyst. The degradation, mineralization, and energy efficiency generally increased with an increase in the ozonation temperature (Figs. 4g and 4h), indicating that the ozonation reaction was temperature sensitive. The energy efficiency increased from 8.81 g kWh⁻¹ at 0 °C to 17.9 g kWh⁻¹ at 40°C and slightly to 18.4 g kWh⁻¹ at 70 °C (Fig. 4g). The energy efficiency without a catalyst increased from 4.40 g kWh⁻¹ at 0 °C to the maximum level of 8.46 g kWh⁻¹ at 55 °C and decreased to 6.74 g kWh⁻¹ at 70 °C (Fig. S2d). The highest degradation, mineralization, and energy efficiencies were achieved, and they were 95.2%, 96.6%, and 18.4 g kWh⁻¹, respectively, at 70 °C. The O₃ concentration drop was enhanced in the presence of the 1.0wt.% MnO₂/γ-Al₂O₃ catalyst within the ozonation temperature range (Fig. S3).

The initial pH value of the acetic acid solution was adjusted with 0.1 M NaOH. Fig. S4 shows the energy efficiencies at different pH values as a function of ozonation time. When the pH was 3.42 (the
original pH of acetic acid solution), the energy efficiency was at the maximum level of 14.9 g kWh⁻¹, higher than that when the pH value was 7.06 or 11.26. It has been reported that •OH radical has a higher oxidation ability than other types of reactive oxygen species (such as O₂⁻), especially under acidic conditions, the similar pH effect was reported by Sahni et al. (2005) during the degradation of polychlorinated biphenyls using liquid-phase discharge plasma. Therefore, it was deduced that the •OH radicals played a major role in acetic acid ozonation, and more details are discussed in next section.

Characteristics of the MnO₂/γ-Al₂O₃ catalysts

The crystalline structures of γ-Al₂O₃ and MnO₂/γ-Al₂O₃ with 0.5wt.%, 1.0wt.%, and 10wt.% MnO₂ loadings were characterized, and the XRD patterns are shown in Fig. 5a. The peaks ascribed to γ-Al₂O₃ were clearly observed, indicating that the crystalline structure was well reserved after the addition of MnO₂. The peaks at 28.68°, 37.32°, 42.82°, 56.65°, and 72.38° were indexed to the (110), (101), (111), (211), and (112) planes of the MnO₂ phase (PDF#24-0735), respectively. The peaks at 28.88°, 31.02°, 32.32°, 36.08°, and 59.84° were indexed to the (112), (200), (211), and (224) planes of Mn₃O₄ (PDF#24-0734), respectively. When the MnO₂ loadings were 0.5wt.% and 1.0wt.%, no characteristic peaks were found, indicating MnO₂ was amorphous or highly dispersed on the surface of γ-Al₂O₃. In addition, it was noted that as the MnO₂ addition increased to 10wt.% (Fig. 5iv), the peaks belonging to the MnO₂ phase were present, while the Mn₃O₄ phase could not be found. This suggested that MnO₂, rather than Mn₃O₄, was the primary phase on the γ-Al₂O₃ support. The SEM images showed that the Mn and O elements were uniformly dispersed (Fig. 5b), which was consistent with the result of XRD.

The surface chemical states of the 1.0wt.% MnO₂/γ-Al₂O₃ catalysts before and after acetic acid ozonation were characterized using XPS. As shown in Fig. 5c, the Mn 2p½ spectra were deconvoluted into three peaks at 640.6, 641.7, and 643.0 eV, which were ascribed to the Mn²⁺, Mn³⁺, and Mn⁴⁺ species, respectively (Gao et al. 2020). The peak areas of the Mn⁴⁺ species accounted for 43.8% and 48.1% before and after acetic acid ozonation. A high Mn⁴⁺ ratio for the manganese-based catalysts is typically strongly linked to a superior catalytic activity (Liu et al. 2021; Saputra et al. 2014), and this also corresponded to the excellent catalytic ozonation performance of the MnO₂/γ-Al₂O₃ catalyst. In addition, it was noted that the ratio of Mn²⁺ decreased from 27.5% to 16.2% after the catalytic ozonation process (Table 1), while the ratio of Mn³⁺ and Mn⁴⁺ increased. This was possibly due to a portion of Mn²⁺ being oxidized by O₃.

The O 1s spectra before and after ozonation were deconvoluted into the peaks at 531.7–531.8 eV that were assigned to surface chemisorbed oxygen (O_ads) and at 530.8–530.9 eV that were ascribed to lattice oxygen (O_latt) (Fig. 5d) (Garcia et al. 2013; Jiang et al. 2019). Due to the high reaction activity, surface chemisorbed oxygen played an important role in a series of organic substances oxidation reactions. Obviously, the O_ads species accounted for a much higher ratio than the O_latt species at the surface of the 1.0wt.% MnO₂/γ-Al₂O₃ catalyst. The peak area ratio of O_ads/(O_ads+ O_latt) decreased from 77.9% before ozonation to 74.4% after ozonation (Table 1).
Fig. 5 (a): The X-ray diffraction (XRD) patterns of the MnO$_2$/γ-Al$_2$O$_3$ catalysts. (i) γ-Al$_2$O$_3$; (ii) 1.0wt.% MnO$_2$/γ-Al$_2$O$_3$; (iii) 0.5wt.% MnO$_2$/γ-Al$_2$O$_3$; and (iv) 10wt.% MnO$_2$/γ-Al$_2$O$_3$. (b): The SEM images of the MnO$_2$/γ-Al$_2$O$_3$ catalyst and the corresponding energy-dispersive X-ray spectroscopy (EDS) mappings of the Al, Mn, and O elements. XPS spectra of Mn2p (c) and O1s (d) of the 1.0wt.% MnO$_2$/Al$_2$O$_3$ before and after acetic acid ozonation reaction

Table 1 Peak area ratios of Mn and O at the 1.0wt.% MnO$_2$/Al$_2$O$_3$ surface before and after acetic acid ozonation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mn 2p$_{2/3}$ (%)</th>
<th>O 1s (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn$^{2+}$</td>
<td>Mn$^{3+}$</td>
</tr>
<tr>
<td>Before ozonation</td>
<td>27.5</td>
<td>28.7</td>
</tr>
<tr>
<td>After ozonation</td>
<td>16.2</td>
<td>35.7</td>
</tr>
</tbody>
</table>

Mechanism of acetic acid ozonation over the MnO$_2$/γ-Al$_2$O$_3$ catalyst

To study the mechanism of acetic acid ozonation on the surface of the MnO$_2$/γ-Al$_2$O$_3$ catalyst, in-situ DRIFTS was used to identify the functional groups on the catalyst surface. An acetic acid/water bubbler and O$_3$ generator were used to feed the in-situ cell with a gas mixture of acetic acid, water, and O$_3$ and to simulate the gas-liquid-solid reaction on the MnO$_2$/γ-Al$_2$O$_3$ catalyst surface. Figs. 6a, 6b, and 6c show the DRIFT spectra of acetic acid ozonation within different durations on 0.5wt.%, 1.0wt.%, and 10wt.% MnO$_2$/γ-Al$_2$O$_3$ catalysts at room temperature (25°C). The absorption in the υOH region (3200 cm$^{-1}$) is attributed to the surface hydroxyl group, and the adsorption peak at 3460 cm$^{-1}$ was attributed to
H₂O (Zaki and Knözinger 1987). This corresponded to the reactive oxygen species of the ·OH group investigated above. The absorption peak at 1345 cm⁻¹ is caused by the δCH₃ vibration of the CH₃C=O fraction, while the absorption peak at 1640 cm⁻¹ is caused by the δ(H₂O) vibration in liquid water phase on MnO₂/γ-Al₂O₃ surface. The absorption peak at 1563 cm⁻¹ is attributed to υCOO from acetic acid (Nakamoto 1970). The absorption peak at 982 cm⁻¹ is due to superoxide O₂⁻ on the metal oxide (M²⁺-O₂⁻) (Li et al. 1990).

The peak heights of the primary functional groups M²⁺-O₂⁻ at 982 cm⁻¹ and COO at 1563 cm⁻¹ are illustrated in Figs. 6d and 6e. As shown in Fig. 6d, the peak height of the reactive species M²⁺-O₂⁻ generated on the 1.0wt.% MnO₂/γ-Al₂O₃ after 80 min was greater than that on the 0.5wt.% and 10wt.% MnO₂/γ-Al₂O₃. It happened to verify once again that superoxide radicals are involved in the degradation process of acetic acid. In addition, the COO peak height on the 0.5wt.% MnO₂/γ-Al₂O₃ increased with time, while that of the 1.0wt.% MnO₂/γ-Al₂O₃ was relatively stable at a low level (Fig. 6e). This suggested that the COO species accumulated on the 0.5wt.% MnO₂/γ-Al₂O₃ surface and could not be further oxidized due to a lack of reactive oxygen species, leading to an undesirable catalytic ozonation performance. The M²⁺-O₂⁻ peak was ascribed to an oxygen molecule adsorbed on the surface of MnO₂ that was associated with oxygen vacancies and would play an important role in catalytic oxidation reactions of acetic acid (Sun et al. 2020). Thus, the peak height ratio of COO to M²⁺-O₂⁻ (COO/O₂⁻) is an index to show the ability of a catalyst to inhibit the accumulation of COO (acetic acid). Fig. 6f shows that the 1.0wt.% MnO₂/γ-Al₂O₃ had the lowest COO/O₂⁻ ratio. This fact implies that the best performance of the 1.0wt.% MnO₂/γ-Al₂O₃ was enhanced by the surface O₂⁻ superoxide.
Fig. 6 DRIFT spectra of the acetic acid catalytic O₃ oxidation at various ozonation times on the (a) 1.0wt.% MnO₂/γ-Al₂O₃, (b) 0.5wt.% MnO₂/γ-Al₂O₃, and (c) 10wt.% MnO₂/γ-Al₂O₃; peak heights of M²⁺-O₂⁻ (d) and COO (e); and the peak height ratio of COO/O₂⁻ (f) at various ozonation times.

To determine the main active species during acetic acid ozonation, TBA and PBQ radical quenchers were added to the acetic acid solution, and the results are shown in Fig. 7. It was noted that when the hydroxyl radical (·OH) quencher TBA (362 mM) was added, the degradation of acetic acid decreased from 88.1% to 15.7%. When the superoxide radical (O₂⁻) quencher PBQ (1.1 mmol/L) was added, the degradation decreased from 88.1% to 63.2%. This finding suggests that the hydroxyl radical (·OH) and superoxide radical (O₂⁻) species contributed to acetic acid degradation, and the ·OH species played a more
important role than the $O_2^\cdot$ species. This result was consistent with the results in the section (Effect of pH) where the high energy efficiency was obtained at a low pH.

![Graph (a)](image1)

![Graph (b)](image2)

**Fig. 7** Effect of the 1.0 wt.% MnO$_2$/$\gamma$-Al$_2$O$_3$ on the degradation rate of acetic acid after adding the free radical scavenger. Experimental condition: 1.0 g L$^{-1}$ acetic acid concentration, 3.42 initial pH, 3.0 g 1.0 wt.% MnO$_2$/$\gamma$-Al$_2$O$_3$ dosage, 30.0–40.0 g Nm$^{-3}$ O$_3$ concentration. 25 °C ozonation temperature, 362 mM TBA, and 1.1 mM PBQ. The acetic acid solution after ozonation in the presence of MnO$_2$/$\gamma$-Al$_2$O$_3$ was analyzed using the HPLC. At 120 min of ozonation time, only oxalic acid could be found as the by-product of acetic acid oxidation (Fig. S5). The acetic acid ozonation was related to the adsorption of O$_3$ and acetic acid on the surface of the MnO$_2$/$\gamma$-Al$_2$O$_3$ catalyst. This result was similar to that of the experimental and theoretical research on the decomposition of acetic acid by pulsed DBD plasma reported by Matsui et al. (2011). It should be noted that the adsorption configuration of acetic acid on metal oxides is in a bidentate state (Almutairi et al. 2018).

The breakings of the C-H and C-C bands are the primary steps in acetic acid oxidation that produce oxalic acid and formic acid (Partenheimer et al. 2011). By combining the results of this study with the research on catalytic O$_3$ decomposition (Li et al. 2020; Zhu et al. 2017) and acetic acid oxidation
(Almutairi et al. 2018; Samskruthi et al. 2021) over an MnO₂ catalyst, the mechanism of acetic acid catalytic ozonation is illustrated in Fig. 8. Eqs. 5-6 and 8-9 are O₃-related surface reactions to produce reactive species O_{surf} such as surface M-O and M^{2+}-O_{2}⁻ (Anpo et al. 2021; Che and Sojka 2001). O_{surf} is then supplied to acetic acid oxidation. Furthermore, O₃ reacts with adsorbed water to form surface OH (Eqs. 8 and 9) and ·OH radicals (Eq. 10) (Zhu et al. 2017), which also contributes to acetic acid oxidation (Eq. 11). The surface oxygen species from the M^{2+}-O_{2}⁻ group and ·OH radicals played an important role in the oxidation of acetic acid into CO₂ and H₂O.

Step 1: Mn-O + O₃ → Mn-O-O₃
Step 2: Mn-O-O₃ → Mn-O₂ + O₂
Step 3: Mn^{−}O₂⁻ + Mn^{−}O₂⁻ → Mn₂^{−}O₂⁻ + O_{surf}
Step 4: Mn − OH₂ + O₃ → Mn − OH₂ − O₃
Step 5: Mn − OH₂O₃ → Mn − OH + HO₃
Step 6: HO₃ → ·OH + O₂
Step 7: Mn − OH + H₃CCOOH → Mn − OH₂ + H₂CCOOH
Step 8: CH₃COOH + OH and O_{surf} → CO₂ + H₂O

Fig. 8 Mechanism of acetic acid ozonation over MnO₂/γ-Al₂O₃

**Symbol notification:**
- \( \text{Mn}^{2+} - O₂⁻ \)
- \( \text{Mn}^+ - O₂⁻ \)

**Kinetic study of acetic acid ozonation over the MnO₂/γ-Al₂O₃ catalyst**

Catalytic ozonation can be described as a first order reaction (Cihanoğlu et al. 2015). According to the experimental results of acetic acid ozonation on 1.0wt.% MnO₂/γ-Al₂O₃ catalyst at different ozonation temperatures (Fig. 4), we fitted the degradation (X) data using the first-order reaction. As shown in Fig. 9, ln(1−X) was linear to ozonation time t, and the linear coefficient R² were between 0.95−0.99. This finding implied that the acetic acid ozonation is exactly first order reaction (Eq. 13).

\[
\ln(1 - X) = kt + b
\]
Where \( k \) and \( b \) are constant.

The activation energy \( (E_a) \) of acetic acid ozonation on 1.0wt.% MnO\(_2\)/\(\gamma\)-Al\(_2\)O\(_3\) catalyst was calculated to be 16.1 kJ mol\(^{-1}\) using Arrhenius equation. This activation energy level is close to 15.9 kJ mol\(^{-1}\) for acetic acid ozonation without a catalyst. This fact suggested that the acetic acid ozonation with or without catalyst may be controlled by the same kinetic step, perhaps the transformation of O\(_3\) from gas phase to liquid or on to catalyst surface.

**Fig. 9** The relations of \( \ln(1-X) \) with ozonation time \( t \) at various ozonation temperatures (a-e) and \(-\ln k\) with \( 1/T \) in the presence of 1 wt%MnO\(_2\)/\(\gamma\)-Al\(_2\)O\(_3\) catalyst. Experimental condition is as per Fig. 4g

**Conclusions**

The mineralization of acetic acid by catalytic ozonation was studied, the primary results are summarized as follows.

1. Among the four metal oxides (MnO\(_2\), Fe\(_2\)O\(_3\), Co\(_3\)O\(_4\), and CeO\(_2\)), MnO\(_2\) had the best catalytic performance for acetic acid degradation.

2. Using 3.0 g of the 1.0wt.% Mn/\(\gamma\)-Al\(_2\)O\(_3\) catalyst at 25°C to treat 100 mL of acetic acid at a concentration of 1.0 g L\(^{-1}\), the degradation and mineralization of acetic acid reached as high as 88.4% at 300 min, with an average energy efficiency of approximately 14.9 g kWh\(^{-1}\). However, without a catalyst, the degradation and mineralization of acetic acid were only 45.3% and 33.2%, respectively, and the energy efficiency was only 5.1 g kWh\(^{-1}\).

3. •OH radicals and surface-active oxygen species (such as O and Mn-O\(^{2-}\)) due to the O\(_3\) reaction played an important role in acetic acid ozonation to CO\(_2\) and H\(_2\)O.

4. The reaction temperature had a positive effect on improving the degradation, mineralization, and energy efficiency.

5. A low pH favored acetic acid ozonation since •OH radicals could be effectively produced from O\(_3\) and H\(_2\)O.
(6) The mechanism of acetic acid ozonation on the 1.0wt.% MnO$_2$/γ-Al$_2$O$_3$ surface was proposed. The adsorbed acetic acid was completely oxidized to CO$_2$ and H$_2$O by reactive oxygen species such as •OH and O$_2^-$ in the solution and O$_2^-$ on the catalyst surface.

(7) Only an approximate 1-20 g Nm$^{-3}$ O$_3$ concentration was used for acetic acid oxidation, and most of the O$_3$ was not used. A further study is required to effectively utilize O$_3$.

Further studies should focus on the modification of catalyst morphology from powder to sphere or honeycomb and to treat the real wastewater.

**Ethical Approval** This manuscript is the original work and has not been submitted to more than one journal for simultaneous consideration and has not been published elsewhere in any form or language (partially or in full).

**Consent to Participate, Consent to Publish and Authors Contributions** Shuiliang Yao contributed to the study conception and design. Material preparation, data collection and analysis were performed by Ruiyun Meng. The first draft of the manuscript was written by Ruiyun Meng and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript for publication.

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**Competing Interests** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Availability of Data and Materials** The data and materials used or analysed during the current study are available from the corresponding author on reasonable request.

**References**


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