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Ozone treatment of process water from a dry-mill ethanol plant

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Abstract

Fuel ethanol production in corn dry milling plants is a rapidly expanding industrial sector. Whole stillage, the residue from the distillation of the fermented corn, is centrifuged and the concentrate, thin stillage, is found to have a chemical oxygen demand (COD) of approximately 75,000 mg/L. This thin stillage is partly recycled, but much of it needs to be evaporated to concentrate the solubles for addition to the animal feed coproduct from corn dry milling. This research is an exploration into lowering COD from thin stillage using ozonation as a simple single-step unit process to facilitate a larger reusable fraction. The ozonation would usually be a pretreatment before additional flocculation or biological treatment. Also, COD removal by ozonation with and without a catalyst has been studied. Three different application rates of ozone $O_{3,1} = 7$ mg/min, $O_{3,2} = 21$ mg/min, and $O_{3,3} = 33$ mg/min were used for 8 h into samples of 2 L each of three dilutions 20×, 30× and 40×. COD removal of 85% was observed with an ozone dosage of 4000 mg/L into a 40×-diluted sample. This would correspond to about 0.5 mg COD removed per mg ozone dosed. However, at lower dosages and smaller dilutions, more than 1 mg COD removal was achieved per mg ozone dosed. Two different catalysts, Fe(II) and Fe(III), were used and the samples were ozonated for 4 h. Five different dosages of each of the two catalysts were used and better COD removal was observed compared to ozonation alone with all 5 dosages. COD removal rate was increased from 45% to 74% with Fe(III) and was increased to 77% with Fe(II). Up to 10 mg/L COD was removed per mg O_3 dosed well below the maximum dosage. Both the catalysts resulted in almost the same improved COD removal rates when compared to ozonation alone.
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Keywords: Chemical oxygen demand; Catalytic ozonation; Ozonation; Ozone; Thin stillage

1. Introduction

Ethanol is a renewable fuel made from plants. It is biodegradable, water-soluble and has a low toxicity. It provides high octane at low cost and its use as a fuel additive reduces harmful exhaust emissions. Also, it can be used in all spark ignition engines without modifications. The use of ethanol-blended fuel is increasing rapidly in the United States. Ethanol fuel is typically a 10% blend of ethanol and conventional gasoline but 85% blend is also used in flexible fuel vehicles and 95% blend is being tested.

Corn is the primary source of ethanol in the United States. Dry milling is the most common production process for ethanol from corn because of the lower costs required to build and operate. In dry milling, the corn kernel is ground into a fine powder, which is referred to in the industry as *meal*. The meal is mixed with water to form a "mash" and enzymes are added to it to convert the starch into dextrose, a simple sugar. Also, ammonia is added for pH control and as a nutrient to the yeast. The mash is then cooked at a high temperature to sterilize the bacteria prior to fermentation. The mash is cooled and transferred to the fermentation unit where yeast is added to convert sugar to ethanol and carbon dioxide (CO_2). After fermentation, the *beer* so produced is transferred to the distillation columns to separate the ethanol from the remaining *whole stillage*. Whole stillage is centrifuged to separate the distiller's

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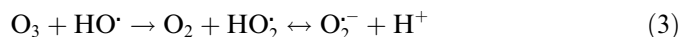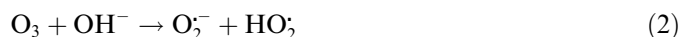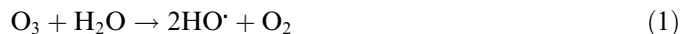*E-mail address:* mfan3@mail.gatech.edu (M. Fan).

grain from the solubles that are referred to as *thin stillage*. The distiller's grains are dried in the dryers to produce dried distillers grains with solubles (DDGS), which is a high quality and nutrient-rich livestock feed. During the fermentation process, CO_2 is released, which is collected and sold for use in carbonating beverages and the manufacture of dry ice. Some portion of the thin stillage is recycled in the ethanol plant and the rest of it is evaporated to produce syrup, which is then mixed with distiller's grains in the dryer. Laboratory COD analysis of thin stillage was done and proved that it has a very high chemical oxygen demand (COD) of 75,000 mg/L approximately. Presence of different organic compounds including acetic acid, pyruvic acid, oxalic acid, and ethanol accounts for high COD content of thin stillage. Table 1 lists the concentrations of various organic acids found in thin stillage using high-pressure liquid chromatography. There is a need to reduce the COD of thin stillage to provide cleaner recycle water to the ethanol industry.

Biological treatment is the most widely used process for industrial process and wastewater containing organic compounds. Some of the organics are not easily biodegradable. In such cases, chemical oxidation technologies help oxidizing the refractory organic compounds. Ozone is a strong oxidizing agent, with a redox potential of 2.07 V used frequently in drinking water and wastewater treatment. Ozone treatment is specifically suitable for partial or complete oxidation of non-biodegradable components (Beltran et al., 1999; Jochimsen and Jekel, 1997). Ozone oxidation can be used as a pretreatment step to improve biodegradability or a post-treatment step to remove remaining COD. The disadvantage of ozone in wastewater treatment is the high-energy cost required for its production. Catalytic ozonation is a good extension of ozonation developed in recent years. Studies have been conducted to show that ozone oxidation and its efficacy can be improved by using catalysts (Beltran, 2003; Brillas et al., 2003, 2004; Ernst et al., 2004; Legube and Leitner, 1999; Oh et al., 2004; Syroezhko et al., 2004; Zaror et al., 2001). The application of ozonation and catalytic ozonation on thin stillage for COD removal is a new approach. Moreover, it also investigates the catalytic effects of Fe^{2+} and Fe^{3+} on the removal of COD with O_3 from thin stillage.

Ozone is a strong oxidizing agent. Ozone reacts directly with constituents found in solution and is also capable of forming highly reactive chemical agents that can contribute to additional oxidizing reactions. The most common of these reactive agents is the hydroxyl free radical. Molecular ozone can serve as a dipole, an electrophilic or a nucleophilic agent. Its high reactivity accounts for its high unstability in water. Ozone decomposition follows the following chain reaction (Kasprzyk-Hordem et al., 2003):

$$O_3 + H_2O \rightarrow 2HO^{\cdot} + O_2 \quad (1)$$

$$O_3 + OH^- \rightarrow O_2^- + HO_2^{\cdot} \quad (2)$$

$$O_3 + HO^{\cdot} \rightarrow O_2 + HO_2^{\cdot} \leftrightarrow O_2^- + H^+ \quad (3)$$

$$O_3 + HO_2^{\cdot} \leftrightarrow 2O_2 + HO^{\cdot} \quad (4)$$

$$2HO_2^{\cdot} \rightarrow O_2 + H_2O_2 \quad (5)$$

The above chain reaction clearly shows that OH^- plays a significant role in initiating the ozone decomposition process in water. Also, there are several organic compounds that can initiate ($OH-$, H_2O_2/HO_2^-, Fe^{2+}), propagate (R_2–CH–OH, formate, humic substances) and inhibit (CH_3–COO^-, alkyl-(R), HCO_3^-/CO_3^-) the chain reaction.

Organic matter or COD removal only occurs when ozone reacts with organic compounds to produce carbon dioxide and water. Ozone can react with organic compounds in aqueous solution either directly through selective reactions with specific functional groups (double bonds, nucleophilic positions) or through a radical reaction like hydroxyl radicals that are produced by the decomposition of ozone in water (Beltran et al., 2002). For instance, oxalic acid does not have the specific functional groups favorable for direct ozone reaction and hence the suggested mechanism is through hydroxyl radicals.

Catalytic ozonation can be of two types: homogeneous catalytic ozonation and heterogeneous catalytic ozonation. In homogeneous catalytic ozonation, ozone is activated by metals ions particularly transition metals like Fe(II), Mn(II), Co(II) while heterogeneous catalytic ozonation takes place in the presence of metals or metal oxides on supports such as Cu–Al_2O_3, Cu–TiO_2, TiO_2/Al_2O_3. The use of Fe(II) and Fe(III) in our experiments supports it being an example of homogeneous catalytic ozonation.

2. Methods

2.1. Thin stillage

Thin stillage samples were obtained from a dry-mill ethanol plant in Lakota, Iowa, owned and operated by Midwest Grain Processors (MGP). The sample was refrigerated as soon as it was obtained from the dry-mill ethanol plant. Before the ozonation/catalytic ozonation experiments, thin stillage was centrifuged for 30 min at 4500 revolutions per minute (rpm) using laboratory scale (IEC Model K) centrifuge. After centrifuging, it was filtered through 0.22 μm pore size (Glass Microfiber Filter, Whatman) filter. COD of thin stillage was measured using Standard Methods 522 °C (Clesceri et al., 1998). Also, thin stillage was found to contain various organic acids including lactic acid, acetic acid and oxalic acid. High-pressure

Table 1

Characterization of filtered thin stillage, process water from dry-mill ethanol plant used in this study

Constituents	Unit	Value
Acetic acid	ppm	3500
Butyric acid	ppm	100
Lactic acid	ppm	6000
Oxalic acid	ppm	5500
Propionic acid	ppm	5000
Pyruvic acid	ppm	800

liquid chromatography (HPLC) was conducted on thin stillage to find the concentration of the organic acids present in thin stillage, the results of which are listed in Table 1.

2.2. Ozonation

Ozone was generated using a laboratory-scale corona-discharge ozone generator (Ozat Compact Ozone Unit, Ozonia) and oxygen from a gas cylinder with a purity of 99%. The output of the ozone generator was determined by passing the ozone gas through a potassium iodide trap and titrating with standardized sodium thiosulfate as per standard method 2350 E (Clesceri et al., 1998). Three different ozone dosages were used for COD determination including $O_{3,1} = 7$ mg/min, $O_{3,2} = 21$ mg/min, and $O_{3,3} = 33$ mg/min. Samples were collected at regular intervals corresponding to know applied ozone dosages for COD analysis.

2.3. Ozone losses

The experiments were conducted in an open 3 L Pyrex cell and ozone losses occurred from the cell. To calculate the actual ozone consumption, the output of the ozone generator was passed through a 200 mL volume of the 40 times diluted sample for 45 min. The off-gas from the sample trap was passed through a 200 mL potassium iodide trap for 15 s. The process of passing the off-gas through the potassium iodide trap was repeated every 15 min and total ozone loss from the system was calculated to be about 50%.

2.4. Catalysts

Ferric(III) chloride ($FeCl_3 \cdot 6H_2O$ certified A.C.S. Fisher Scientific) and ferrous(II) chloride ($FeCl_2 \cdot 4H_2O$, ARCOS organics) were used as catalysts to speed up the oxidation process. Five different dosages of each of the two catalysts were tested including 100 ppm, 200 ppm, 300 ppm, 400 ppm, and 500 ppm.

2.5. Experimental design

All the experiments were done in a 2 L Pyrex cell in a batch mode (Fig. 1) at room temperature. Ozone was bubbled into the reactor by means of a diffuser. A mixer with a
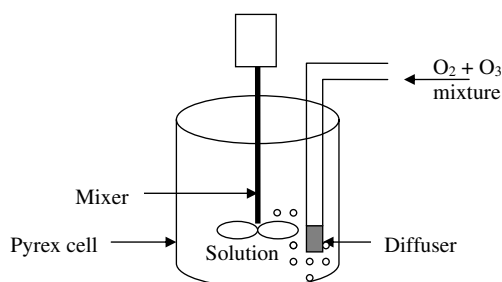
mixing speed of 200 rpm was used to provide good contact between the diluted sample and ozone. Run times of 8 h and 4 h were used for ozonation alone and catalytic ozonation experiments, respectively. In each run; a sample volume of 2 L was used. Three different dilutions, $D_1 = 20$, $D_2 = 30$, and $D_3 = 40$ were investigated. Samples each of size 7 ml were taken at different time intervals for determination of COD. The collected samples were filtered through a 0.45 μm filter. The collected sample was further diluted 5 times for D_1 and D_2 and 10 times for D_3 before performing the COD analysis.

3. Results

3.1. Ozonation

The objective of this research was to evaluate the efficiency of ozonation alone in the removal of organics from thin stillage. Comparisons of COD removals between three different dilutions $D_1 = 20$, $D_2 = 30$, and $D_3 = 40$ using ozone application rates of 7 mg/min, 21 mg/min and 33 min/min, respectively are shown in Figs. 2–4. All the
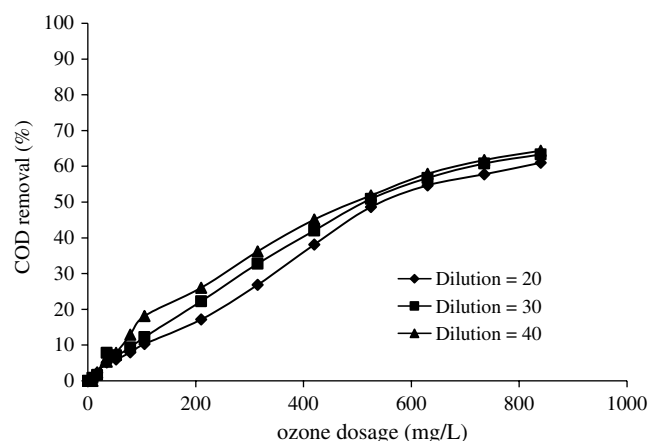
Fig. 2. Comparison of COD removal using ozone application rate of 7 m g/min on different dilutions.
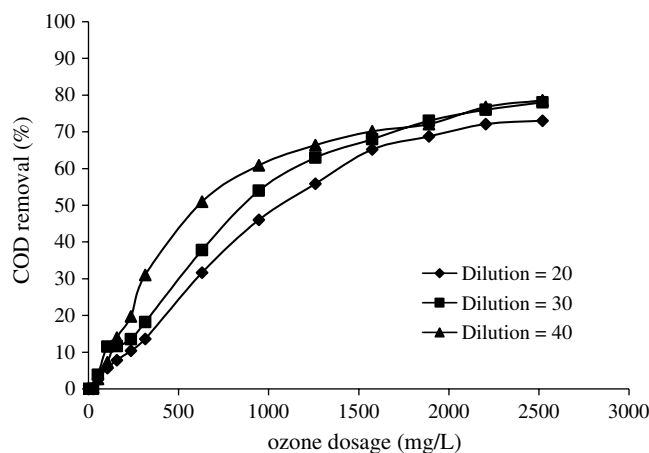
Fig. 3. Comparison of COD removal using ozone application rate of 21 mg/min on different dilutions.

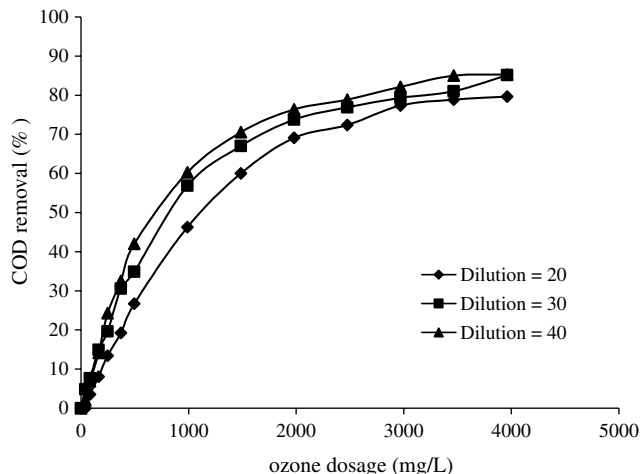Fig. 1. Line diagram of experimental set-up of ozonation.

Fig. 4. Comparison of COD removal using ozone application rate of 33 mg/min on different dilutions.

experiments were conducted at room temperature with an ozonation time of 8 h. For each of the three ozone application rates, it was found that the COD removal increased with increased dilution. Also, improved COD removal was observed with an application of a higher ozone dosage. For the lowest ozone application rate, $O_{3,1} = 7$ mg/min, the lowest dilution, $D_1 = 20$, and ozonation time of 8 h, 61% COD removal was achieved while the maximum COD removal of 85% was observed with the highest ozone application rate, $O_{3,3} = 33$ mg/min and the highest dilution, $D_3 = 40$. However, the removal efficiency dropped in terms of g COD removed per g ozone applied, at the higher dilutions and higher ozone applications.

3.2. Catalytic ozonation

In order to quantify the catalytic effects of Fe(II) and Fe(III) when compared to ozonation alone, an ozone application rate of 7 mg/min was applied to 40 times diluted sample for 4 h. Organic acids can also adsorb to the surface of iron. To check for the possible adsorption on the surface of the ferric chloride, separate experiments were conducted by adding the highest dose of 500 ppm of ferric chloride to the 40 times diluted sample without passing any ozone. Similar experiments were done for ferrous chloride. No adsorption was observed with any of the catalysts. This showed that most of the removal in the Fe-catalyzed ozonation experiments was due to oxidation.

The comparison of COD removal efficiencies for ozonation alone to Fe^{3+}/O_3 and Fe^{2+}/O_3 systems, respectively is given in Figs. 5 and 6. The results indicate that catalytic ozonation in the presence of Fe(II) and Fe(III) improved COD removal in comparison to the standard ozone experiments. For 500 ppm of ferrous chloride added to the diluted sample, a removal efficiency of 77% was observed when compared to 45% efficiency of ozonation alone. However, catalytic ozonation resulted in more than 40% improvement in the final COD removal efficiencies for each
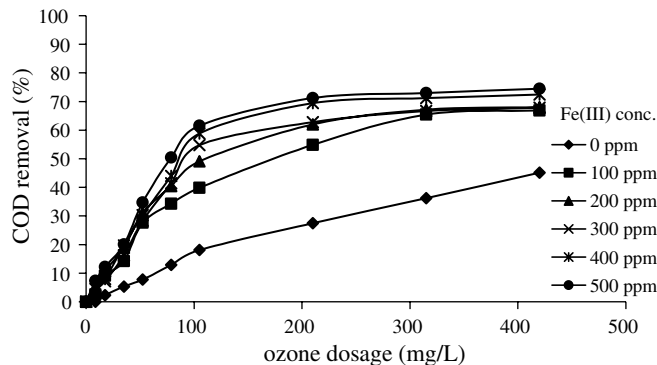

Fig. 5. COD removal results for thin stillage from Fe(III) catalyzed ozonation experiments using the ozone application rate of 7 mg/min and 40 times dilution.
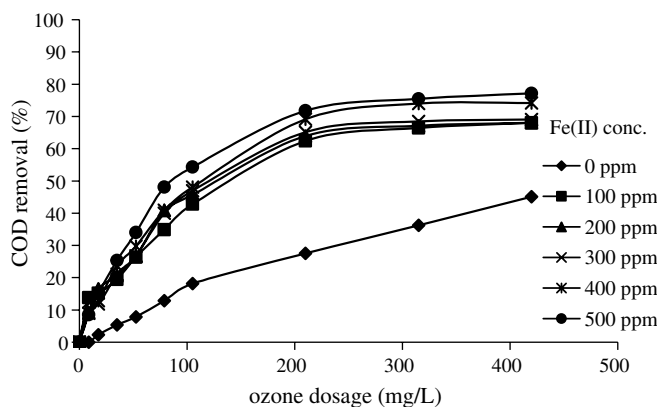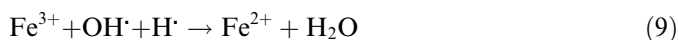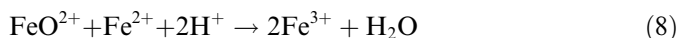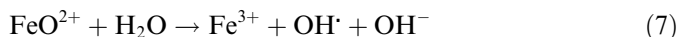

Fig. 6. COD removal results for thin stillage from Fe(II) catalyzed ozonation experiments using the ozone application rate of 7 mg/min and 40 times dilution.

of the catalysts and their dosages when compared to ozonation alone. No significant difference was observed between the two catalysts. Also, COD removal efficiency was only increased slightly on the application of higher catalyst dosage.

4. Discussion

The mechanism of homogeneous catalytic ozonation is mainly a two-step process. Ozone is decomposed by the active metal species followed by the generation of free radicals. Then complex formation takes place between catalyst and organic acids followed by a final oxidation step. Our system is slightly acidic with a pH of 5.0. For Fe^{2+}/O_3 system, the following mechanism is suggested for free radical generation in an acidic medium (Brillas et al., 2004):

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \tag{6}$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + OH^{\cdot} + OH^- \tag{7}$$

$$FeO^{2+} + Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2O \tag{8}$$

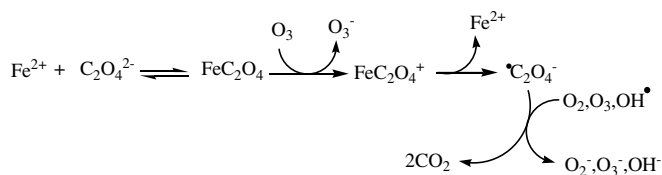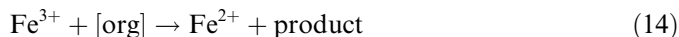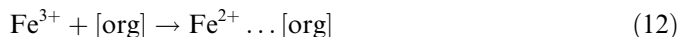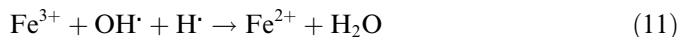$$Fe^{3+} + OH^{\cdot} + H^{\cdot} \rightarrow Fe^{2+} + H_2O \tag{9}$$

Fig. 7. Suggested mechanism for catalytic ozonation of oxalic acid by Fe(II)/O$_3$ system (Kasprzyk-Hordem et al., 2003).

Fe^{2+} reacts with ozone in the acidic medium to produce FeO^{2+}. Hydroxyl radical is generated from the reaction of FeO^{2+} with water. Hydroxyl radical thus produced helps in the oxidation of organic acids. For instance, the oxidation of oxalic acid in the Fe(II)/O$_3$ first takes place with Fe(II)-oxalate complex formation, which is then oxidized by ozone to Fe(III)-oxalate (Fig. 7). In the second step, the decomposition of Fe(III)-complex takes place with the formation of an oxalate radical and Fe(II). For Fe^{3+}/O$_3$ system, the suggested mechanism for free radical generation and oxidation of organic acids is as follows (Ni et al., 2003):

$$Fe^{3+} + O_3 + H^+ \rightarrow Fe^{2+} + OH^· + O_2 \tag{10}$$

$$Fe^{3+} + OH^· + H^· \rightarrow Fe^{2+} + H_2O \tag{11}$$

$$Fe^{3+} + [org] \rightarrow Fe^{2+} \ldots [org] \tag{12}$$

$$Fe^{3+} \ldots + [org] \rightarrow Fe^{2+} + [org]^+ \tag{13}$$

$$Fe^{3+} + [org] \rightarrow Fe^{2+} + product \tag{14}$$

$$OH^· + [org] \rightarrow product \tag{15}$$

5. Conclusions

It is possible to remove most of the COD (85%) from thin stillage using ozonation alone. Addition of catalysts results in more efficient and quicker COD removal for the same experimental conditions because of the generation of hydroxyl radicals. For an ozonation time of 4 h with $O_{3,1} = 7$ mg/min, dilution, $D_3 = 40$, COD removal efficiency was increased from 45% in case of ozonation alone to 74% in Fe(III)/O$_3$ system and increased to 77% in Fe(II)/O$_3$ system. Fe(II) and Fe(III) were found to have almost the same COD removal efficiencies. In the Fe(II)/O$_3$, the reaction proceeds by the oxidation of Fe(II) to Fe(III) and thus competes with the oxidation of organics, which suggests that Fe(III) is a better alternative to Fe(II). Ozonation demands are high and probably uneconomical for complete oxidation. Considering the high cost of ozone production, catalytic ozonation is the preferred alternative. Also, this study provides a baseline for further study on partial oxidation with O$_3$ and AOPs as a pretreatment step to improve the biodegradability or a post-treatment step for removing residual COD.

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