Catalytic Wet Oxidation of Wastewater Contaminants Using a Mn/Ce Catalyst

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The enhancement effects of a Mn/Ce catalyst were studied on the wet air oxidation (WAO) process. Tests were performed on several common wastewaters:

- Aliphatic acids mixture, which was a mixture of acetic, formic, and propionic acids
- Acrylic acid wastewater, which was a mixture of organic acids
- Acetic acid dissolved in water
- Ammonia

All tests were conducted using a one hour reaction time and a variety of pH values and temperatures. The test results indicate considerable performance enhancement from the catalyst. In brief:

- Acetic acid destruction efficiency was increased from <10% COD destruction without catalyst, to 95% destruction with catalyst at 240°C and low pH.
- Acrylic acid wastewater destruction efficiency was increased from 60% TOC destruction without catalyst to 99.5% TOC destruction with catalyst at 280°C and low pH.
- Ammonia destruction efficiency was increased from less than 10% to 80% destruction with catalyst at 280°C and at neutral pH.

Extended use tests were also performed with the acrylic acid wastewater to monitor for catalyst deactivation. No noteworthy catalyst deactivation was observed after repeat use of the same catalyst material 4 times.

Introduction

Wet Air Oxidation (WAO) is a process used for treating wastewaters containing toxic or recalcitrant contaminants[1]. In the process, dissolved or suspended contaminants are contacted with dissolved oxygen at elevated temperatures. The oxidation is a liquid phase process and the reaction chemistry requires liquid water to be present. Therefore, the system is pressurized in order to maintain water in the liquid phase. Air or oxygen is typically used as the oxygen source and is bubbled through the hot liquid.

As with any commercial process, there is a continuous desire to discover ways to improve performance or decrease the severity of operating conditions. Catalysis is one of the more popular research avenues.

Homogeneous catalysts have been tested as WAO enhancers, with copper found to be the most effective. However, copper is a toxic metal and faces discharge restrictions. Because of this, the commercial use for copper catalyzed WAO have been limited to only certain applications. One example is in the destruction of organic byproducts at an ammonium sulfate crystallization plant. In that example the liquid is recycled, so the dissolved copper does not exit the plant[2]. Other acceptable applications would be when such a low dose is used that the copper can be discharged, or cases where the copper is precipitated in a non-leaching form. These requirements limit the application range for using copper.

There has been considerable research on the use of heterogeneous catalysts, with noteworthy performance enhancements observed[1,3]. The best performing examples are usually precious metal catalysts (e.g. Pt, Ru, etc.). However, the wet oxidation process is typically used for wastewater treatment. Quality control of such streams is a low priority. As a result, heterogeneous catalysts are at high risk of being poisoned, coked, plugged, or otherwise damaged in all but the most rigorously controlled scenarios. Precious metal catalysts are also expensive. The cost savings associated with operation at less severe conditions by using such catalysts are diminished by the high cost of the catalyst. There are commercial risks with expensive catalysts due to potential unbudgeted replacement costs, should the catalyst be damaged. Commercial applications of precious metal catalysts have therefore been very limited.

Another type of catalyst, Mn/Ce, has been discussed in the literature as a highly effective heterogeneous catalyst that does not contain precious metals. Some highlights of prior research with the catalyst are tabulated in **Table 1**. This catalyst is of interest due to its potential to be affordable, environmentally acceptable, and effective.

Table 1. Summary of Research Highlights with Mn/Ce Catalyst Reported in the Literature

Compound	Catalyst Formulation (mol ratio)	Test Conditions	Performance	Ref
Acetic Acid	Mn/Ce (7/3)	247°C, 60 min, 20 mM cat	99.5% TOC destruction. (42% w/out cat)	4
ammonia	Mn/Ce (7/3)	247°C, 60 min, 20 mM cat	70% destruction. (7.7% w/out cat)	4
ethylene glycol	Mn/Ce (7/3)	200°C, 120 min, 6 g/L cat	99.3% TOC destruction. (11% w/out cat)	5
n-butylamine	Mn/Ce (7/3)	247°C, 60 min, 20 mM cat	35% TOC destruction. (3.5% w/out cat)	4
phenol	Mn/Ce (1/1) promoted with K	110°C, 20 min, 5 g/L cat	98.6% TOC destruction	6
phenol	Mn/Ce (6/4)	100°C, 60 min, 2 g/L cat	80% phenol destruction	7
phenol	Mn/Ce (6/4) promoted with K	100°C, 60 min, 2 g/L cat	87% phenol destruction	7
phenol	Mn/Ce (6/4) promoted with Cs	100°C, 60 min, 2 g/L cat	93% phenol destruction	7
phenol	Mn/Ce (6/4) promoted with Pt	100°C, 60 min, 2 g/L cat	82% phenol destruction	7
phenol	Mn/Ce (6/4) promoted with Ru	100°C, 60 min, 2 g/L cat	83% phenol destruction	7
phenol	Mn/Ce (1/1)	110°C, 20 min, 5 g/L cat	97.4% TOC destruction	6
Poly(ethylene glycol)	Mn/Ce (7/3)	247°C, 60 min, 20 mM cat	59% TOC destruction. (4.6% w/out cat)	4
pyridine	Mn/Ce (7/3)	247°C, 60 min, 20 mM cat	22% TOC destruction. (10.7% w/out cat)	4

Experimental Section

Catalyst Preparation

At the time of this research, there were no commercial providers of Mn/Ce catalyst. So it was made in the laboratory. Reagent grade chemicals from Sigma-Aldrich were used and Imamura's recipe was followed, as described below[8].

An aqueous solution of manganese (II) chloride and cerium (III) chloride was prepared by dissolving $MnCl_2 \cdot 4H_2O$ and $CeCl_3 \cdot 7H_2O$ in deionized water. The resulting metal salts solution was poured into a caustic solution to precipitate an intimate mixture of $Mn(OH)_2$ and $Ce(OH)_3$. The precipitate was rinsed and dried. It was then calcined at 350°C. The catalyst was crushed into a powder using a mortar and pestle. Based upon the starting materials, the catalyst was calculated to contain manganese oxide and cerium oxide in a ratio of about 70:30 mole % Mn:Ce.

Laboratory Equipment and Procedures Description

The wet air oxidation tests were performed in laboratory autoclaves fabricated from titanium or nickel 200, each having a capacity of 500 mL. An illustration of the bench scale shaking autoclaves used in the tests is shown in **Figure 1**. The autoclaves were charged with a known amount of catalyst and wastewater solution. The autoclaves were sealed and charged with sufficient compressed air or oxygen to yield residual oxygen after the oxidation reaction is completed. The charged autoclaves were then placed in a heater/shaker unit as shown in **Figure 2**, heated to the desired temperature and held at temperature for the reaction time. Immediately following oxidation, the autoclaves were removed from the heater/shaker unit and cooled to room temperature using tap water. After cooling, the off-gas in the headspace of the autoclave was analyzed for oxygen, nitrogen, carbon monoxide, carbon dioxide, hydrogen, methane and total volatile organic compounds and the volume of the off-gas was measured. Subsequent to the analysis of the off-gas, the autoclave was depressurized and opened. The oxidized effluent was removed from the autoclave, placed into a 500 mL plastic bottle, and was then submitted for analysis.

All of the analyses included as a part of the wet oxidation testing were performed by Zimpro personnel or by Zimpro's analytical laboratory, Enviroscan, according to:

1. Standard Methods[9]
2. EPA Methods for the Chemical Analysis of Water and Wastewater[10]

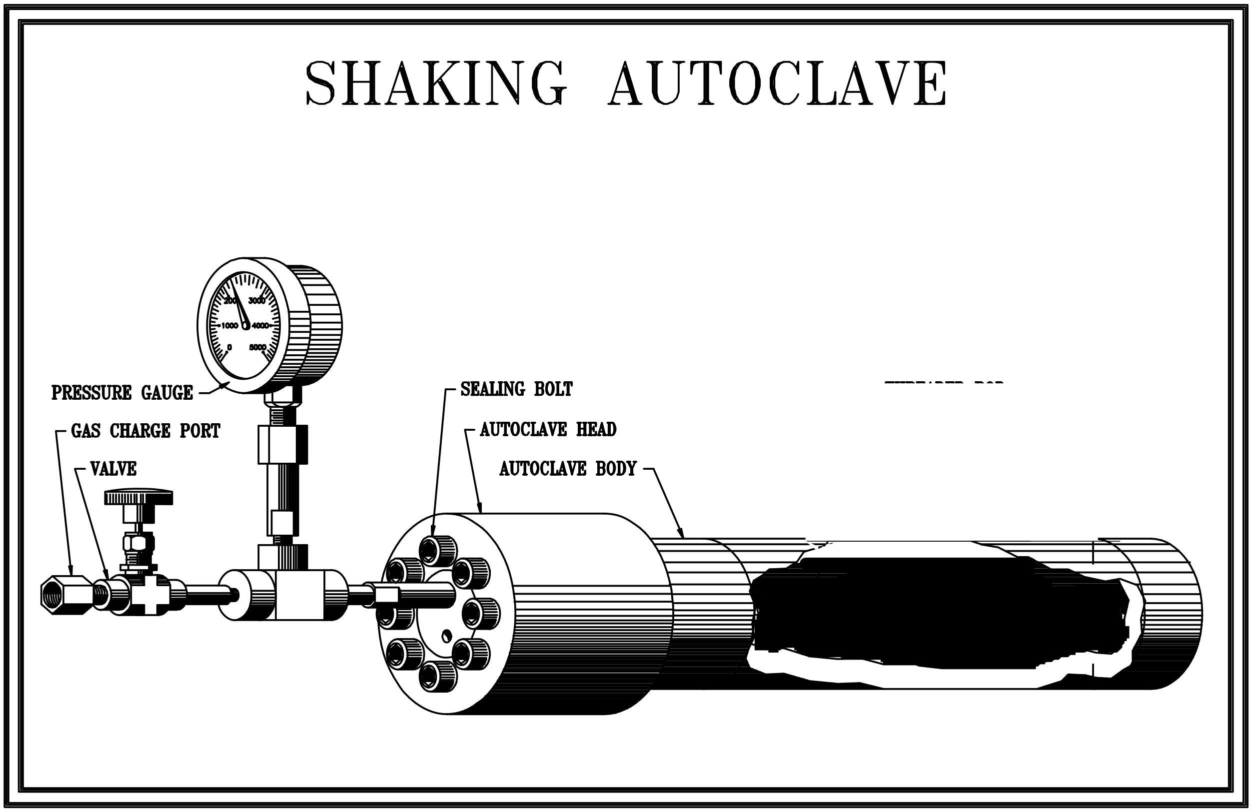

Figure 1. Laboratory Shaking Autoclave

Figure 2. Heater/shaker unit

Experiments were conducted on the following feed solutions

- Aliphatic acids mixture, which is
    - 30 g/L acetic acid,
    - 2 g/L propionic acid,
    - 40 g/L formic acid.
- Synthetic acrylic acid wastewater mixture, which wass:
    - 1 g/L acrylic acid,
    - 10 g/L acetic acid,
    - 15 g/L maleic acid,
    - 1 g/L acrolein
    - 1 g/L formaldehyde
    - 1.5 g/L n-butyl acrylate
    - 4 g/L n-butanol
- 10 g/L acetic acid
- 20 g/L ammonium sulfate

Unless otherwise stated, all tests were performed with 5 g/L catalyst and for 60 minutes at reaction temperature. In some tests, pH was varied in order to observe its effect. This was done be adding NaOH or $NaHCO_3$ to the feed, such that after the reaction, the effluent pH was in the desired range.

Dissolved Mn was detected in some of the oxidized effluents, an indication of catalyst leaching. One test was performed with $MnSO_4$ salt, instead of Mn/Ce catalyst, in order to observe if the dissolved Mn was the active catalyst. This test was performed with the synthetic acrylic acid wastewater, and is discussed in that results section.

Catalyst longevity tests were conducted during the synthetic acrylic acid wastewater tests. Tests were done by recycling the catalyst and 4 cycles were performed. The recycle was accomplished by decanting the oxidized effluent from the catalyst. Some catalyst attrition was expected due to the handling of the material between runs, so 10 g/L Mn/Ce was used for the initial cycle, and 5 g/L for the recycle runs. For each cycle, the recovered catalyst was dried and recharged with fresh feed into the autoclave.

Experimental Results and Discussion

Aliphatic Acids Test Results

Catalytic and non-catalytic results are shown comparatively in **Figure 3**. The effluent pH was neutral for the three tests that showed noteworthy COD destruction, but was acidic for the 200°C non-catalytic test, since none of the organic acids were destroyed at that condition. The effluents were not analyzed for leaching. It is apparent the catalyst enhanced the destruction of the organic acids.

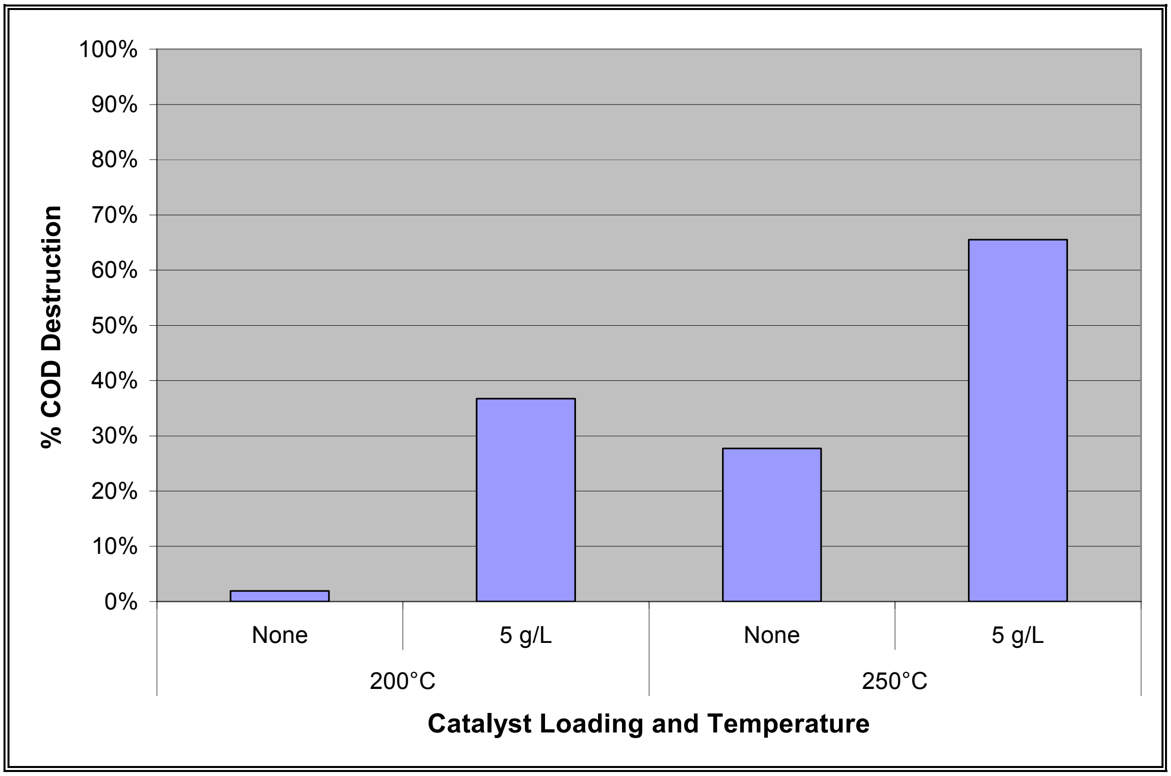

Figure 3. COD Destruction of Aliphatic Acids with 5 g/L Mn/Ce Catalyst, 60 min reaction time.

Synthetic Acrylic Acid Wastewater Test Results

Catalytic and non-catalytic test results are shown in **Figure 4**. No pH adjustments were made, and for all tests, the effluent pH was between 2 and 3. The non-catalytic test was at 280°C. A test was also made using a soluble Mn salt, which was added as $MnSO_4$, rather than using the heterogeneous Mn/Ce catalyst. This test was conducted at 280°C.

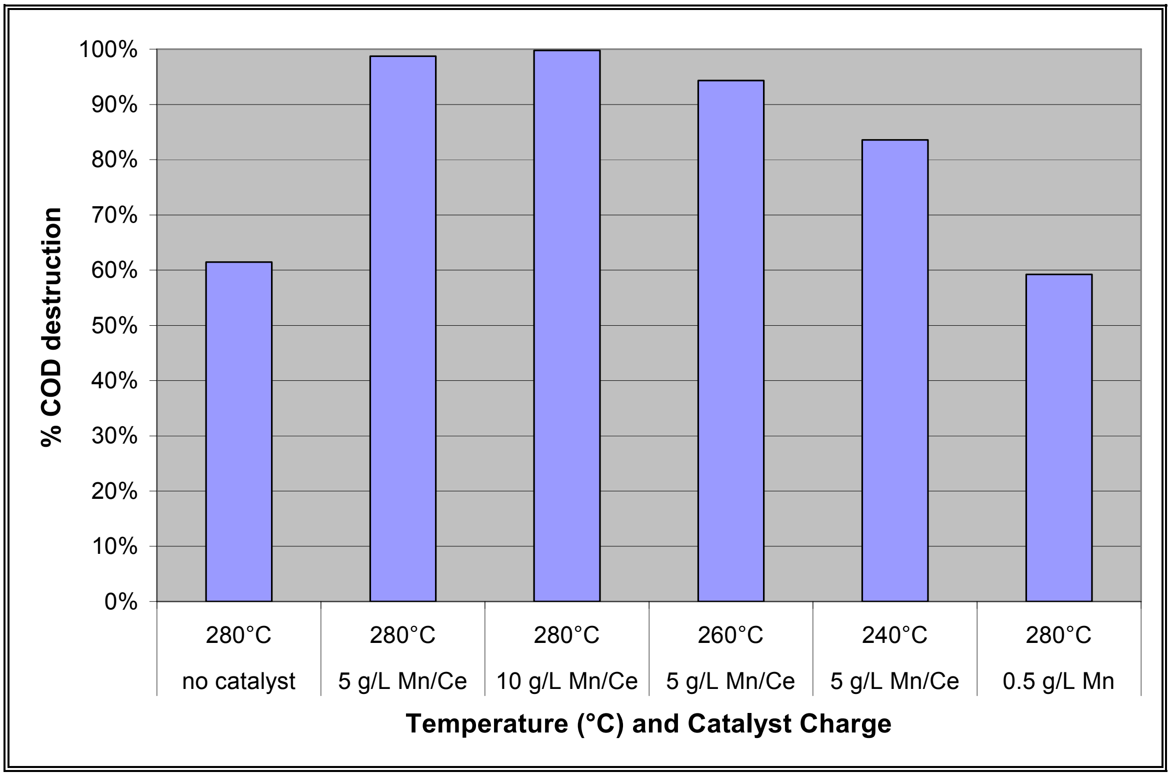

Figure 4. COD Destruction of Synthetic Acrylic Acid Wastewater, 60 min reaction time.

The test results indicate that the catalyst enhanced the WAO performance. COD destruction that was achieved at 280°C without catalyst was exceeded by using the catalyst at 240°C.

The effluent from the test that was at 280°C with 10 g/L Mn/Ce was analyzed for Mn and Ce. No Ce was detected, but 220 mg/L of Mn was detected in the effluent. A test was then made at 280°C with dissolved Mn, from $MnSO_4$, rather than use the Mn/Ce. The comparison shown in **Figure 4** shows that dissolved Mn had no catalytic effect.

Longevity tests were also performed to determine the effectiveness of the catalyst upon successive reuse. COD destruction and leach results are summarized in **Figures 5** and **6**. From **Figure 5**, it is apparent that catalyst remained active in each cycle. From **Figure 6**, it is shown that the most Mn leaching occurred in the first cycle. The continued high performance of the catalyst in the recycle tests, even without as much Mn leaching indicates that the catalytic enhancement was from the Mn/Ce, and not the leached Mn.

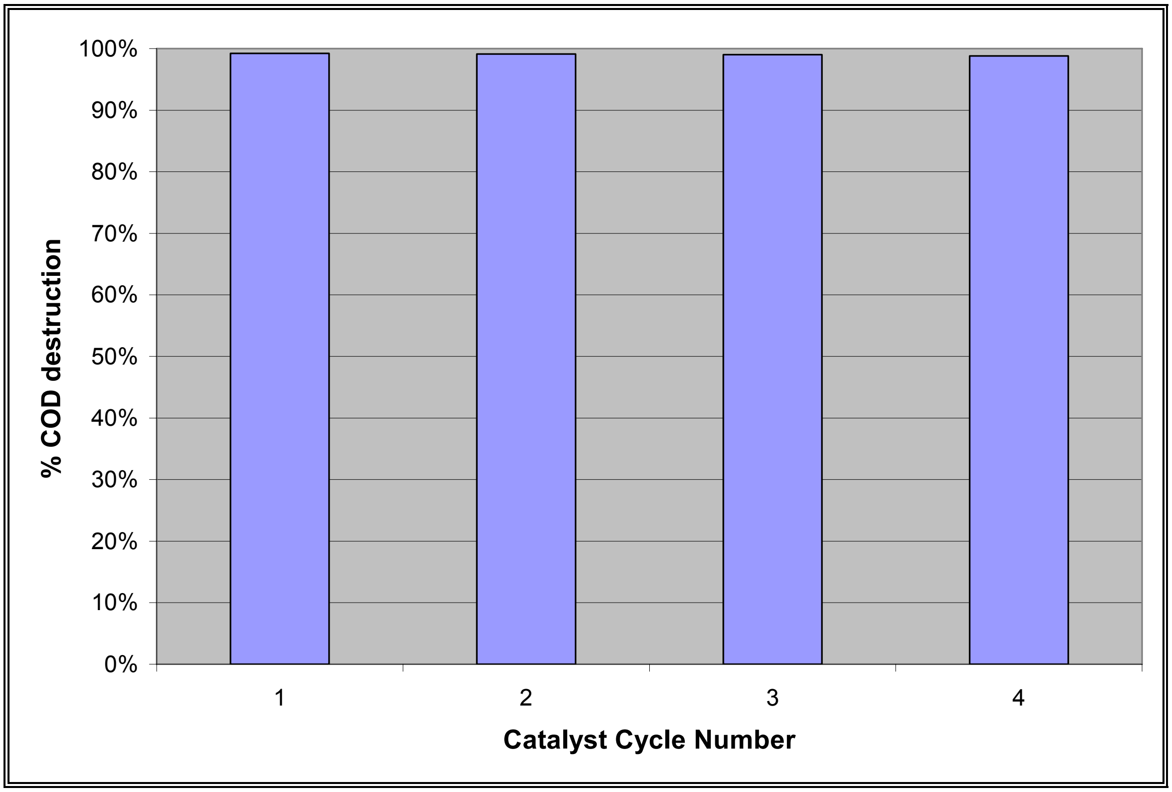

Figure 5. COD Destruction Using Recycled Catalyst. 280°C, 60 min reaction time per cycle, 10 g/L Mn/Ce for cycle 1, 5 g/L Mn/Ce for recycles.

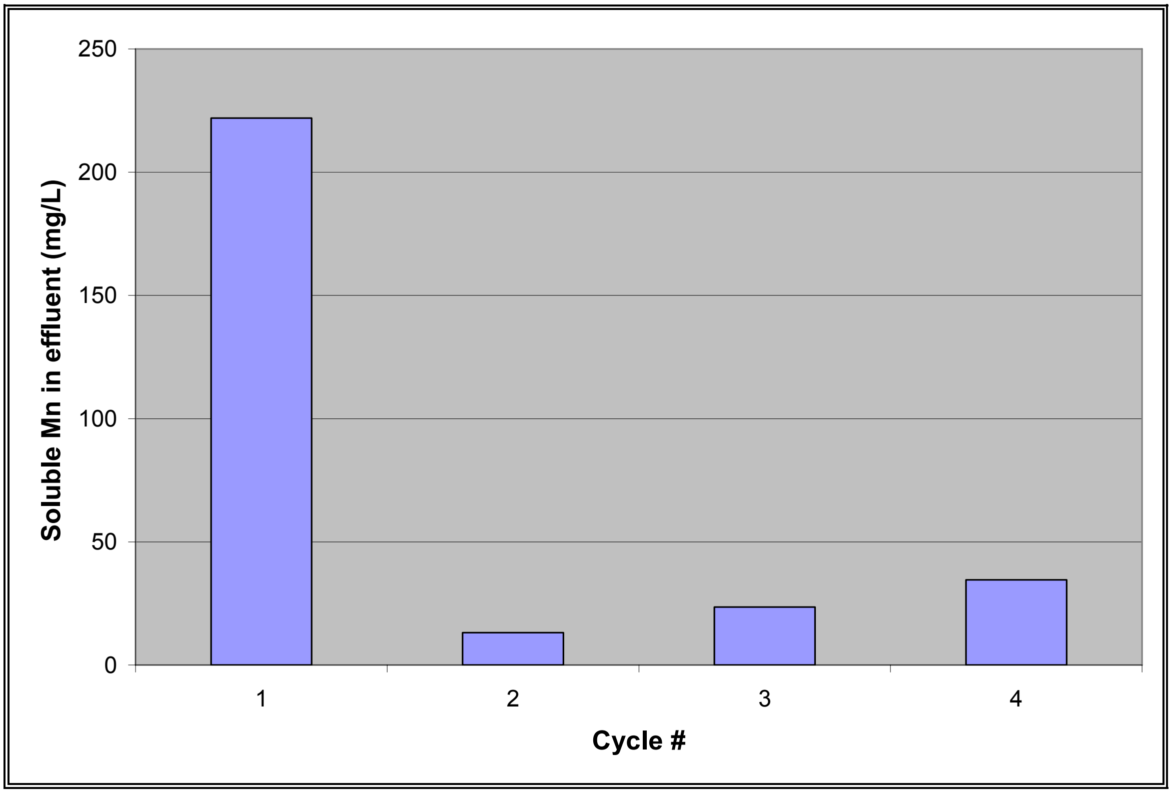

Figure 6. Dissolved Mn in the effluent from oxidation runs using recycled catalyst, 280°C, 60 min reaction time per cycle,10 g/L Mn/Ce for cycle 1, 5 g/L Mn/Ce for recycles.

Acetic acid test results

Oxidation tests were performed without catalyst at low, neutral, and high pH. These baseline tests were performed at up to 260°C. In all cases, less than 10% Chemical Oxidation Demand (COD) destruction was observed without catalyst. Imamura had reported 42% TOC destruction at 250°C (**Table 1**) however this could not be repeated.

Tests were then performed with 5 g/L of catalyst. Test results are summarized in **Figure 7**. Results show that the catalyst greatly enhanced acetate destruction, particularly at low pH and at high temperature.

Catalyst leaching was monitored by analyzing the liquid effluent for dissolved Mn and Ce. No soluble Ce was detected in any effluent. The soluble Mn results are shown in **Figure 8**. There was no catalyst leaching at high pH. At neutral and low pH, there was a trend of decreasing Mn leaching with increasing process temperature.

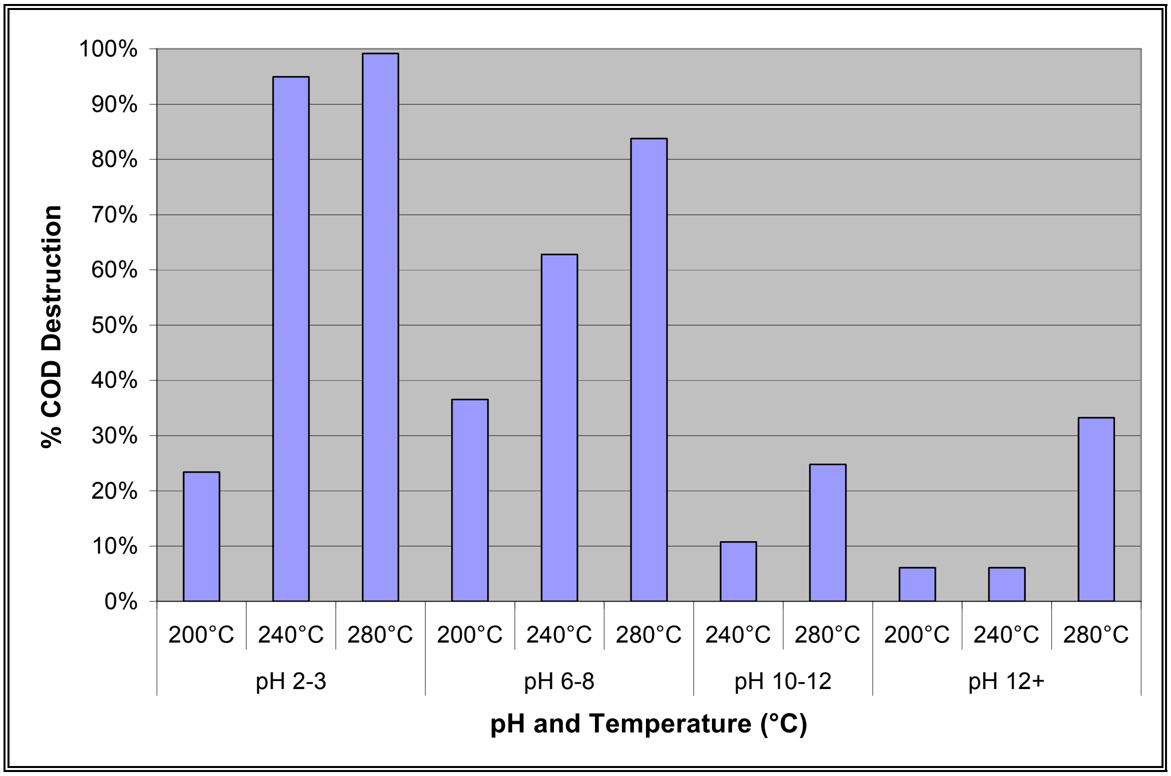

Figure 7. COD Destruction of Acetate, 5 g/L Mn/Ce Catalyst, 60 minutes reaction time.

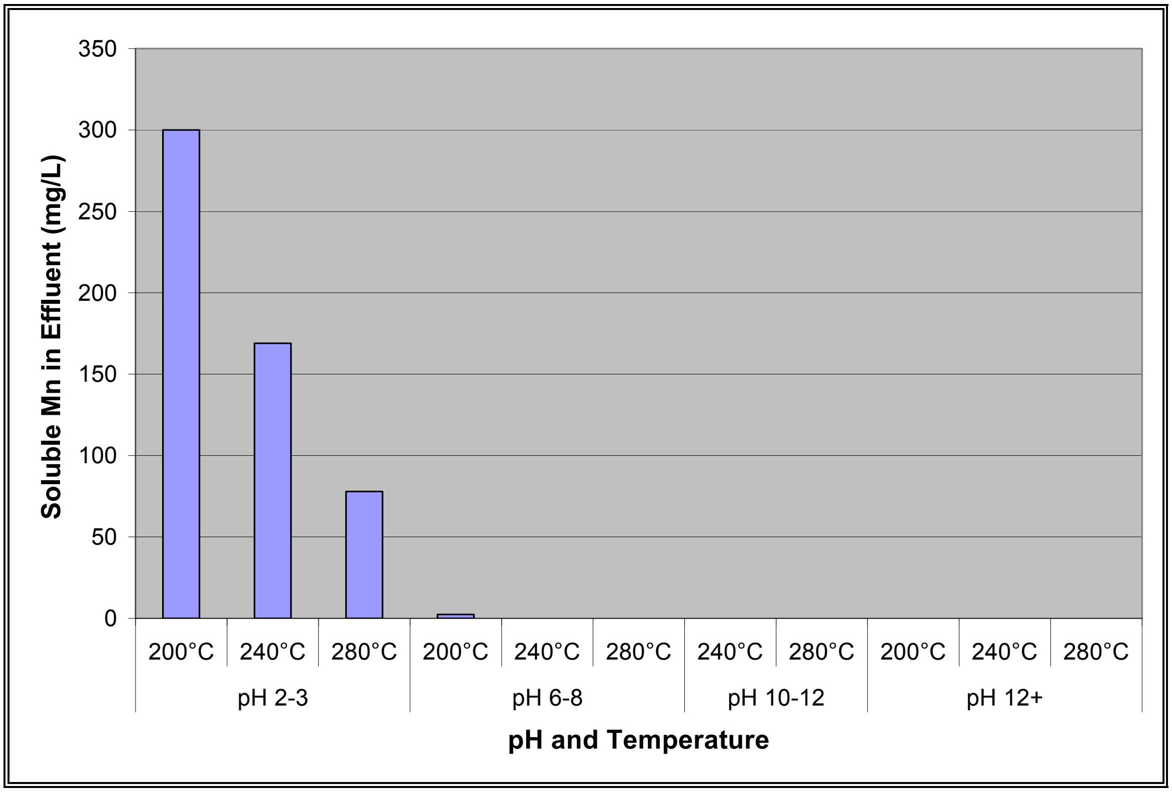

Figure 8. Mn concentration in WAO effluent from acetate oxidation tests, 5 g/L Mn/Ce, 60 minutes reaction time.

Ammonia Test Results

A non-catalytic oxidation test was performed at 280°C and pH 11 for 60 minutes. Less than 10% Ammonia destruction was observed. The enhancement effect of the catalyst was then tested by performing oxidations at 280°C with 5 g/L of catalyst. Test results are summarized in **Figure 9**.

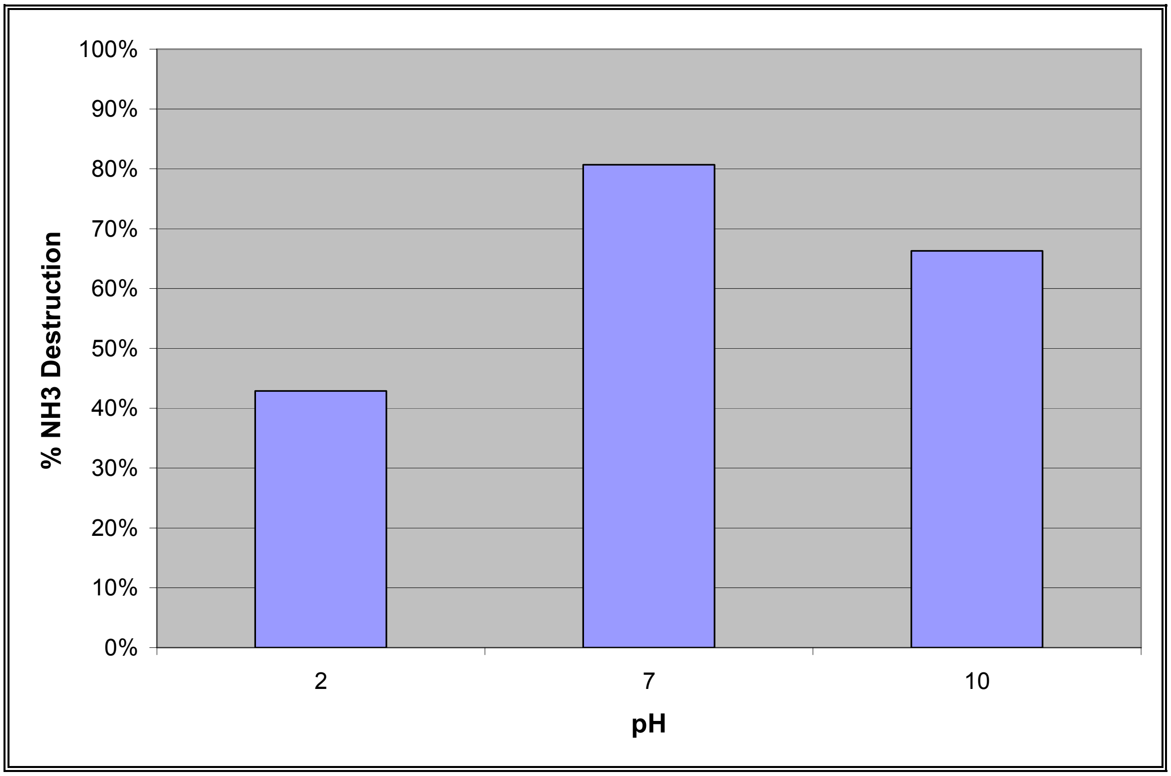

Figure 9. COD Destruction of Ammonia at 280°C with 5 g/L Mn/Ce Catalyst and 60 minutes reaction time.

The results show a significant enhancement due to the catalyst. The best performance was achieved at neutral pH. This differed from non-catalytic oxidation, where it is known that ammonia destruction increases with increasing pH[8].

To monitor for leaching, the effluent was analyzed for dissolved Mn and Ce. No Ce was detected at any condition. Mn was only detected at the low pH, where 48 mg/L was found.

Conclusions

- Mn/Ce catalyst enhanced the oxidation of the tested organic compounds, particularly at neutral and low pH.
- Mn/Ce catalyst enhanced ammonia oxidation, particularly at neutral and high pH.
- Catalyst leaching was strongest initially, and continues to occur only at a reduced leach rate. Only Mn leaches, the Ce remains insoluble. The immediate affect this has on the catalyst effectiveness is not great, though the long term effect (e.g. over several weeks) is unknown.
- The heterogeneous Mn/Ce catalyst is the active catalyst, not the homogeneous Mn.
- Leaching of Mn was observed to occur predominately at low pH.

Needed Future Work

- Longer term longevity tests, preferably in a continuous flow environment.
- Tests for more stable forms of Mn/Ce catalyst by adding enhancements.

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