



## Mn(II) OXIDATION BY OZONE IN THE PRESENCE OF ACTIVATED CARBON

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### ABSTRACT

In previous studies manganese dioxide has been produced through the oxidation of Mn(II) by ozone (OMD), and this manganese dioxide has exhibited good characteristics of ion exchange. Ozone dissociation in aqueous solution in the presence of activated carbon (AC) has been studied by other authors and AC has been shown to have a positive influence on ozone dissociation over a large range of pH. In this study, oxidation of manganese ions by ozone in the presence of AC was investigated.

Batch experiments on a laboratory scale were conducted by contacting solutions of manganese sulfate with ozone in the presence of AC under various conditions. Variables studied during the oxidation process were stirring speed, temperature, pH, ozone concentration, AC particle size and AC concentration. The Mn(II) concentration of samples were monitored by ICP.

Increasing stirring speed, temperature and ozone concentration all cause an increase in the oxidation reaction rate. AC particle size and AC concentration did not have a significant influence on the Mn(II) oxidation. When the pH was decreased the oxidation reaction was retarded. The oxidation rate was observed to follow a (negative) first-order expression with respect to the addition of the sulfuric acid. The oxidation rate followed a zero-order rate law with regard to both activated carbon and manganese concentrations. Also, at lower ozone concentrations a zero-order rate was observed; but the oxidation rate increased according to a second-order rate expression as the concentration of ozone was increased.

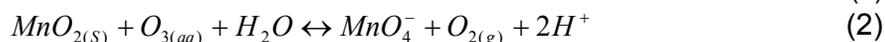
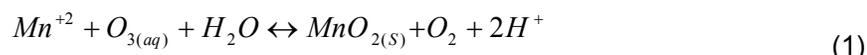
### INTRODUCTION

Ozone is a strong oxidizer of organic and inorganic materials. As an oxidant, Ozone has several benefits. It does not pollute the system, it can be used in acidic and basic solutions and it has a greater potential than other oxidants (Contreras, 1999).

In a previous study the decomposition of ozone in aqueous solutions in presence of activated carbon (AC) has been evaluated. The decomposition of ozone without the presence of AC occurred only at a pH>7. On the other hand, decomposition of ozone in the presence of AC was observed for a range of pH of 2-12 (Rodriguez-Santillán *et al*, 2005).

In other studies, manganese dioxide has been precipitated from slightly and strongly acidic solutions of manganese sulfate by ozone oxidation. Ozone was found to very effective in producing manganese dioxide even at acid concentration as high as 5M

(Nishimura & Umetsu, 1991). The  $Mn^{+2}$  oxidation reaction can be expressed with the following :



Reaction 1 was found to be zero order with respect to concentration of  $Mn^{+2}$  when the acid concentration was 1M (Contreras, 1999). In the current work, oxidation of manganese ions by ozone in the presence of AC was investigated.

## **MATERIALS AND METHODS**

Manganese dioxide was precipitated by ozone oxidation in the presence of AC in acidified solutions using sulfuric acid concentration ranging from 1 to 3 M. Temperature was varied from 25 to 70 °C, ozone concentration ranged from 0.35 to 1.36 M and at the stirring speed ranged from 200 to 800 rpm. In addition, the AC particle size and the concentration of AC were varied from 0.56 to 1.6 mm and 0.5 to 5 g/L respectively.

Ozone was generated from dry oxygen in an electrical ozone generator. The concentration of ozone in the acid solution was determined. The  $O_2$ - $O_3$  mixture was fed into the reactor and put in contact with the manganese sulfate solution for two hours. Samples for analysis were withdrawn at selected time intervals. The precipitated was filtered at vacuum conditions and the filtrate was analyzed for  $Mn^{+2}$  by inductively coupled plasma (ICP) spectrometry.

## **RESULTS AND DISCUSSION**

The tendency in the increasing of  $Mn^{+2}$  oxidation rate was similar for all curves of temperature as shown in Figure 1 . At the highest temperature, the oxidation rate was slower for short time. However, a faster oxidation rate was observed when the time was increased which is consistent with the literature. The rate constant at each temperature was determined and was applied to calculate the activation energy following the Arrhenius equation. Figure 2 shows the Arrhenius plot for the oxidation reaction. The activation energy was calculated to be 6.779 Kcal/mol.

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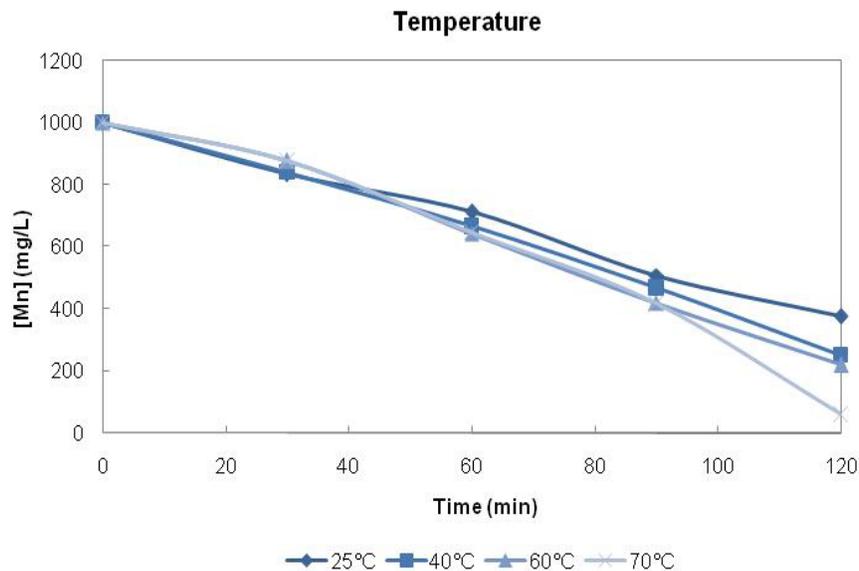


Figure 1.  $Mn^{+2}$  oxidation rate with respect to the temperature

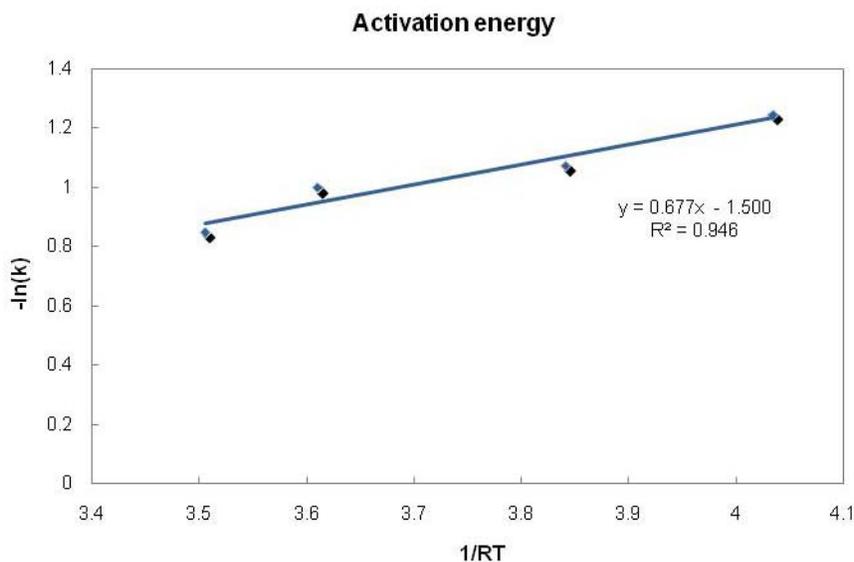


Figure 2.. Arrhenius plot for the  $Mn^{+2}$  oxidation.

When the acid concentration was increased the oxidation reaction was retarded. (Figure 3). The oxidation rate was observed to follow a negative first-order relationship with respect to the addition of the sulfuric acid (Figure 4).

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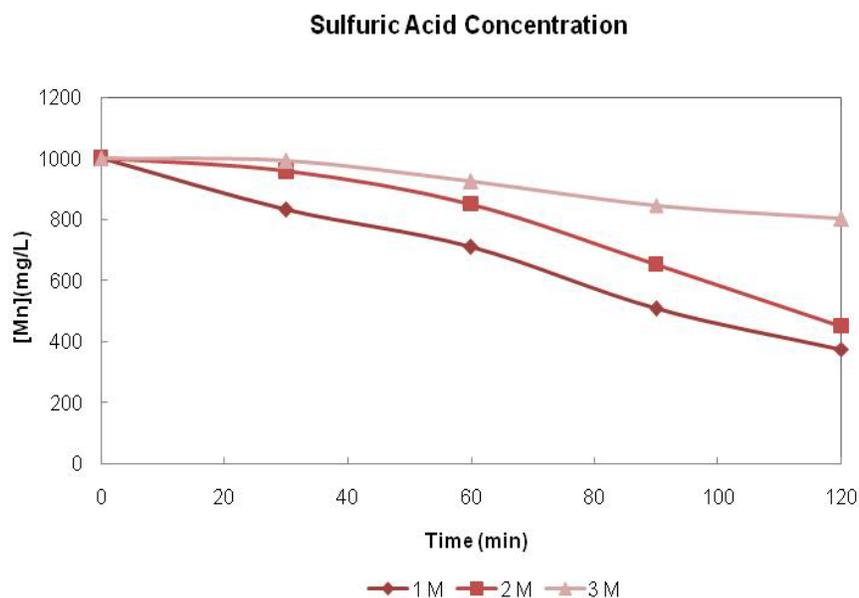


Figure 3. Mn<sup>2+</sup> oxidation rate with respect to the sulfuric acid concentration

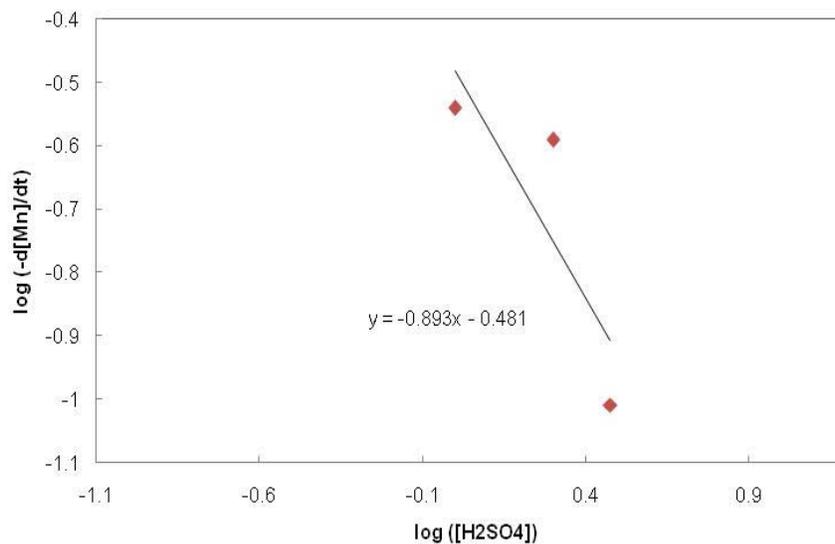


Figure 4. Oxidation reaction with respect acid sulfuric concentration

Figure 5 shows the Mn<sup>2+</sup> with respect to ozone concentration. The Mn<sup>2+</sup> in solution decreased proportionally with the increasing ozone concentration. The decreasing tendency is different in the curve representing 1.36 M of ozone. The minimum Mn<sup>2+</sup> in solution were observed at 90 minutes.

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Ozone concentration

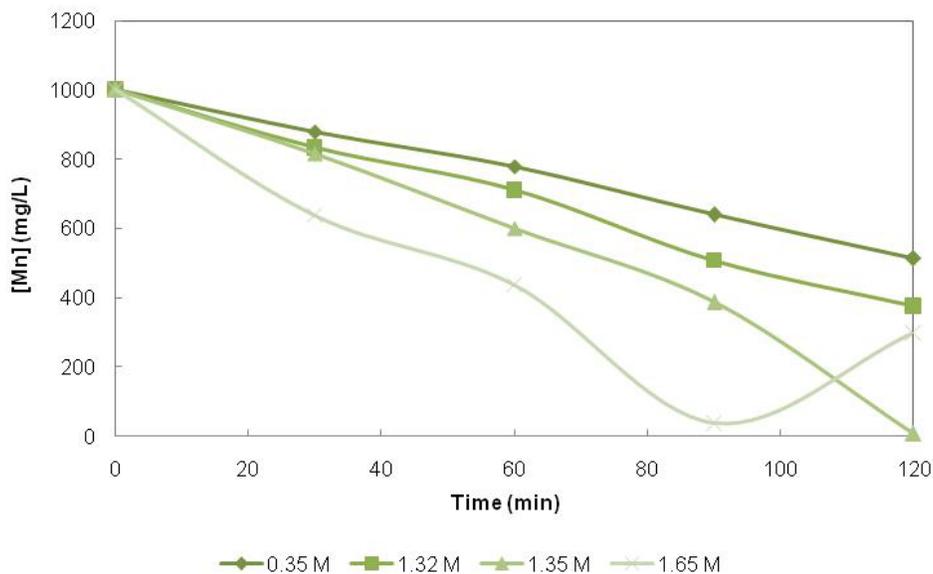


Figure 5. Mn<sup>2+</sup> oxidation rate with respect to ozone concentration

The oxidation at lower ozone concentrations a zero-order rate was observed but the oxidation rate increased according to a second-order rate relationship as the concentration of ozone was increased. It is believed that the mass transport at low ozone concentration is the most important phenomena (Figure 6).

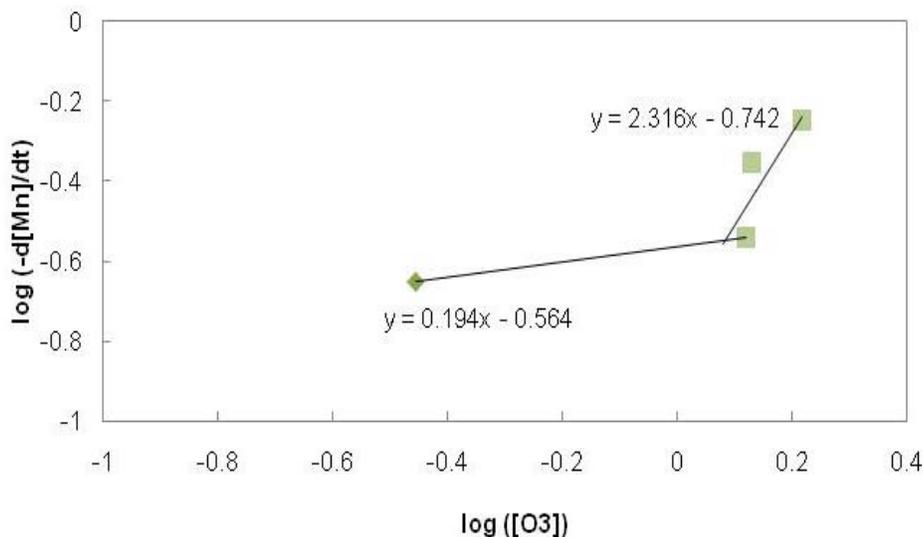


Figure 6. Oxidation reaction with respect ozone concentration

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