# REMOVAL OF ORANGE II DYE FROM WASTEWATER BY CATALYTIC WET AIR OXIDATION-CATALYST SELECTION AND REACTION KINETICS

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## ABSTRACT

The catalytic wet air oxidation (CWAO) of Orange-II, a mono-azo dye, was investigated with different catalysts. Seven catalysts were screened for their TOC and Orange-II removal capacities with a 3-parameter 2-level half factorial experimental design with replicates. The two most efficient and economic catalysts for TOC and Orange-II abatement were determined. A lumped parameter kinetic model was proposed to describe the kinetics of oxidation of Orange-II with chosen catalysts. Within 50 minutes of reaction, 80% TOC removal and 87% Orange-II removal were observed. There was very good agreement between the developed model and the experimental data.

## INTRODUCTION

Although the art of dyeing textile materials has been practiced for nearly 5,000 years [1] , until 1856 dyes could only be extracted from natural sources like plants and minerals which made them rare and highly valuable. Colored fabrics were only reserved for royalty and noble people who could afford them. If it weren't for 18-year-old William Henry Perkin who synthesized the first organic dye "mauveine" in a laboratory in 1856 while trying to synthesize quinine as an anti-malaria medication [1], this might have still been the case today. Today, there are numerous synthetic organic dyes and pigments used for coloring everything from clothes to plastics to drugs to food. The dye manufacturing industry has certainly come a long way since the accidental discovery of the first synthetic organic dye. Whereas once it was a sign of wealth and status, today anyone can enjoy wearing colorful t-shirts, or eating cake with colorful decorations on it, thanks to the variety of dyes that are available. Unfortunately, most of the time wastewaters generated as byproducts of dyeing processes are not treatable with conventional treatment methods, are toxic to aquatic life[1], and are not as aesthetically pleasing in lakes and rivers as they are on clothing. Cooper [2] states that while the public is more ready to accept blue, green, or brown rivers, "unnatural" colors such as red and purple usually cause more concern. Most synthetic dyes cannot be removed from wastewaters by conventional methods, e.g. activated sludge systems, and end up in receiving water bodies if not treated. Even 1 mg/l of dye can lead to visible color in rivers and lakes. As discharge standards become more stringent, the need for advanced treatment systems becomes necessary for the treatment of dye containing wastewaters.

Orange II (also known as Acid Orange 7) is one of the dyes that are produced in large amounts in the United States. It is commonly used in pharmaceutical, food, and cosmetics industries as well as in the textile industry, and it is not amenable to conventional biological treatment. This research focuses on catalytic wet air oxidation (CWAO) as a treatment alternative for removing of Orange-II dye from wastewaters.

## MATERIALS AND METHODS

The experimental phase of this study focuses on the treatment of synthetically prepared Orange II containing waters by catalytic wet air oxidation. All chemicals were used as received from the manufacturer.

All experiments were carried out in an autoclave reactor equipped with gas introduction lines, vent line, sample line, a propeller for mixing, pressure control unit, and a thermocouple to monitor reaction temperature. Initially, 7 catalysts were screened for their TOC and Orange-II removal capacities. For this purpose, a two-level, 3 parameter half-factorial experimental design was constructed with replicates for each catalyst. The 3 parameters that were incorporated into the screening process were reaction temperature, total pressure, and catalyst loading. This meant that 8 experiments (including replicates) were carried out for each catalyst. The high and low level values for screening experiments can be seen in Table 1 below.

**Table 1: Half-factorial design parameter levels**

| Parameter | Low value | High value |
|---|---|---|
| Reaction Temperature, °C | 80 | 120 |
| Total Pressure, psi | 300 | 400 |
| Catalyst Loading, g | 2 | 4 |

During the catalyst screening experiments, the concentration of Orange-II dye was held constant at 100 mg/l. In a typical run, 600 ml of distilled water and 60 mg Orange II (to yield 100 mg/l) were placed in the reactor with required amount of catalyst according to the design matrix. The reactor was closed and purged with nitrogen gas for a few minutes. The furnace was turned on and the reactor was heated up to the desired temperature under nitrogen atmosphere. This ensured that there was no oxygen to initiate the oxidation reaction in the reactor until desired reaction temperature was reached. When the desired reaction temperature was reached, oxygen was introduced into the reactor, and the stirrer was turned on. This time was marked as the starting time for the experiment. Experiments were run for 120 minutes and a final sample was collected at this time. Control experiments were also run without catalyst under nitrogen atmosphere to confirm that thermal degradation of the dye was not taking place during reactor heat-up.

All collected samples were analyzed for Total Organic Carbon (TOC) and Orange-II concentrations. For measuring Orange-II concentrations, a dye solution of 50 mg/l was scanned with a UV-VIS spectrophotometer. Orange-II displayed maximum absorbance at 486 nm, which agrees with values mentioned in literature. UV absorbance of all collected samples was measured and the corresponding dye concentrations were calculated with a calibration curve constructed with dye standards up to 50 mg/l. The efficiencies of the different catalysts were determined by comparing TOC removal capacities per gram of active metal in the catalyst. Table 2 lists catalysts that were screened during this study.

**Table 2: List of catalysts screened for Orange-II oxidation efficiency**

| Catalyst # | Composition | % Active Metal in Catalyst |
|---|---|---|
| 1 | CuO/ZnO | 100 |
| 2 | $CuO/Al_2O_3$ | 10 |
| 3 | $CuO/(Fe, Mg)Cr_2O_4$ | 100 |
| 4 | $Pt/SnO_2/CeO_2$ | 0.5 |
| 5 | $CuO/CeO_2$ | 2.5 |
| 6 | $Mn/CeO_2$ | 70 |
| 7 | Mn/CuO | 100 |

In order to choose the best catalyst, a number of factors were considered including the price of metals that make up the catalyst and the efficiencies for Orange-II and TOC removal. The best two catalysts were chosen to be modeled. These two catalysts were further investigated for reaction kinetics and rate expression.

A theoretical triangular lumped parameter kinetic model was developed to explain the reaction kinetics. This model assumes that Orange-II, which accounts for all of the initial TOC concentration, breaks down via two pathways; one to complete oxidation to carbon dioxide and water, and a second path into intermediates because of partial oxidation. The intermediates formed are then oxidized into final products, carbon dioxide and water. Figure 1 depicts this triangular lumped model. According to this model, at any given time, the total TOC concentration in solution would be equal to concentrations A and B added together, $[TOC]_t=[A]+[B]$

Assuming that each step is first-order, we get:

$$\frac{d[A]}{dt} = -(k_1 + k_2)[A] \quad \text{and} \quad \frac{dB}{dt} = k_2[A] - k_3[B].$$

Solving these equations and rearranging, the model becomes:

$$\frac{[TOC]}{[TOC]_0} = \frac{[A]+[B]}{[A]_0} = e^{-(k_1+k_2)t} + \frac{k_2\left(e^{-(k_1+k_2)t} - e^{-k_3 t}\right)}{-k_1 - k_2 + k_3}$$

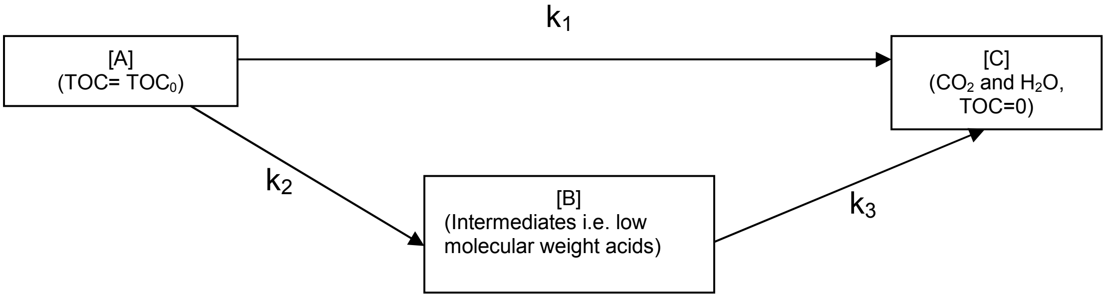

**Figure 1: Triangular lumped kinetic model**

For the kinetics experiments, the catalyst concentration was fixed at 3 g/l, the initial Orange-II concentration was fixed at 100 mg/l and the total pressure was fixed at 400 psi. Samples were taken at different intervals, and analyzed for TOC and Orange-II concentrations. The results were analyzed with non-linear regression to determine the reaction rate constants $k_1$, $k_2$, and $k_3$ at different temperatures, and to determine whether the theoretical model explained the actual reaction kinetics. The results are discussed in the next section.

## RESULTS AND DISCUSSION

Figures 2 and 3 summarize the results of the catalyst screening experiments. It is evident without a doubt that the 0.5 % Pt/$SnO_2$/$CeO_2$ is the best catalyst in terms of oxidation capacity. Its TOC removal per gram metal was about 20 times more than the SOR 10-IV catalyst, which was the second best. Unfortunately, platinum is a very expensive metal and costs about 6,000 times more per gram than copper as of September 2008. For this reason alone, a large scale industrial application of platinum catalyst would not be feasible in this case.

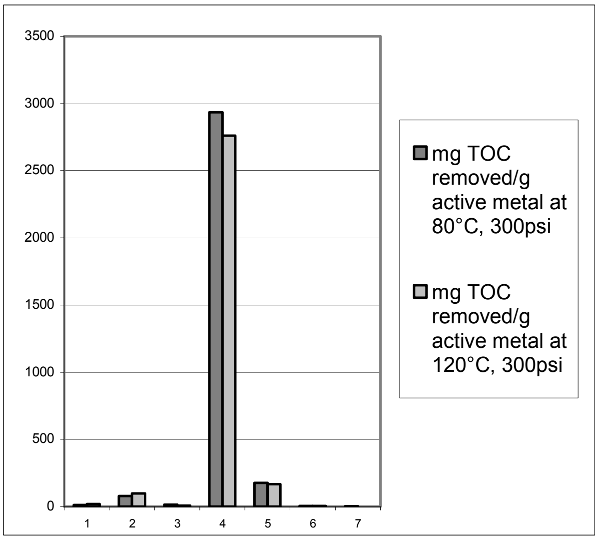

**Figure 2: mg TOC removed/g active metal at 300 psi**

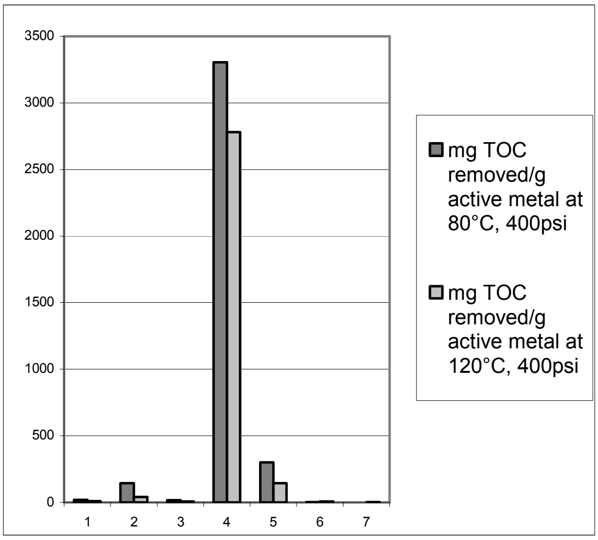

**Figure 3: mg TOC removed/g active metal at 400 psi**

In the following figures 4 and 5, Pt/$SnO_2$-$CeO_2$ catalyst was removed from the graphs so that the other catalyst results can be viewed better. From these graphs, CuO/$CeO_2$ has the second highest TOC removal per gram active metal.

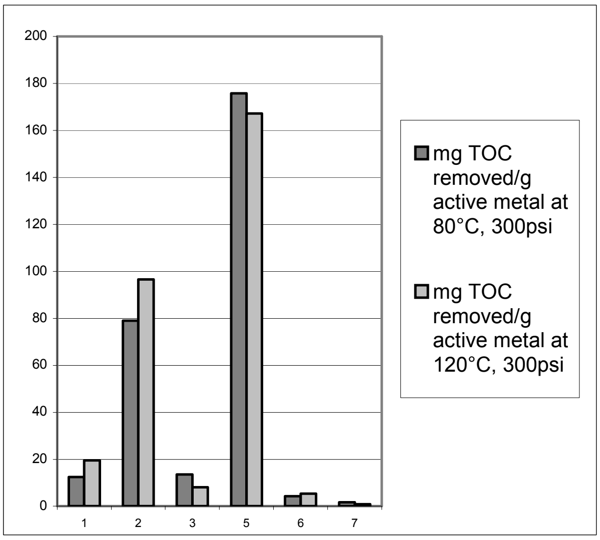

**Figure 4:** **mg TOC removed/g active metal at 300 psi**

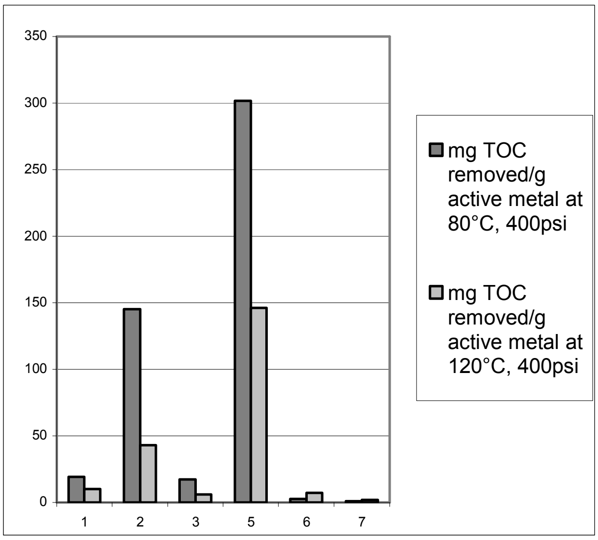

**Figure 5** **: mg TOC removed/g active metal at 400 psi**

**Table 3: %TOC and Orange-II removals at 120 minutes**

| **Catalyst** | **% TOC removal at 120 min.** | **% Orange-II removal at 120 min.** |
|---|---|---|
| CuO+ZnO | 77 | 85 |
| CuO+$Al_2O_3$ | 80 | 87 |
| CuO+ (Fe, Mg)$Cr_2O_4$ | 47 | 99 |
| Pt/$SnO_2$/$CeO_2$ | 91 | 100 |
| CuO+$CeO_2$ | 46 | 55 |
| Mn/$CeO_2$ | 22 | 75 |
| Mn/CuO | 5 | 35 |

Table 3 shows the TOC and Orange-II removal percentages for all the catalysts with 2 grams of catalyst, at 80°C and 400 psi. One of the most important observations from the results is that TOC removal and dye removal are not correlated. For example, the Cu-Chromite catalyst removed only 47% of the total TOC, but Orange-II removal was 99%. This is due to the fact that there are intermediates formed during the reaction, which account for the TOC. However, the double nitrogen bond of Orange-II is broken, so the color is not there anymore. When all factors are considered including TOC removed per gram active metal and the prices of the metals, along with the percent of TOC and dye removed per gram catalyst, the catalysts that perform the best are the CuO+ $Al_2O_3$ catalyst and the CuO+$CeO_2$ catalyst.

A graph of TOC concentrations of samples taken at different time intervals for CuO/ $Al_2O_3$ at different temperatures can be seen in Figure 6. From this graph, it is clear that there are two distinct reaction steps taking place, one fast and the other slow. Once oxygen is introduced into the reactor, the oxidation reaction proceeds very rapidly and within the first 10 minutes TOC is reduced by almost 75%. Then the reaction proceeds relatively slower.

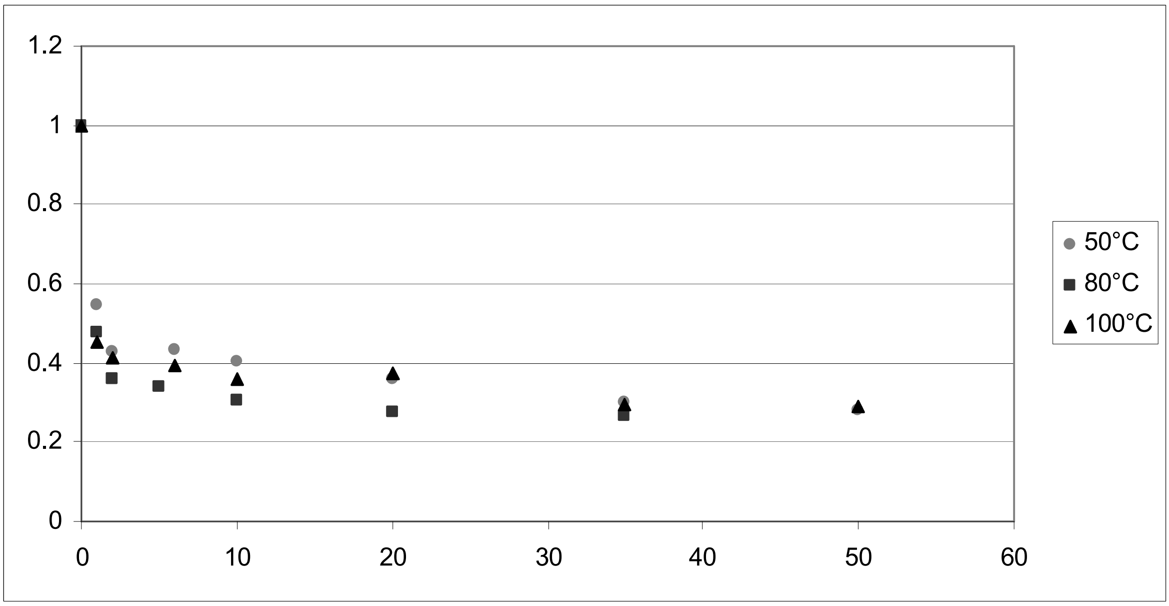

**Figure 6: TOC removal with CuO/ $Al_2O_3$ at different temperatures**

The reaction rate constants computed with non-linear regression for different temperatures are given in Table 4. The theoretical model that was constructed fits the experimental data very closely. A graph of actual versus model predicted $TOC/TOC_0$ values with the catalyst CuO/ $Al_2O_3$ at 80°C can be seen in Figure 7.

**Table 4: Reaction rate constants at different temperatures**

| Temperature, °C | $k_1$ ($min^{-1}$) | $k_2$ ($min^{-1}$) | $k_3$ ($min^{-1}$) |
|---|---|---|---|
| 50 | 0.948285 | 0.232279 | 0.009507 |
| 80 | 1.021212 | 0.518596 | 0.007806 |
| 100 | 1.473231 | 1.006182 | 0.007306 |

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The formation of intermediates is slow compared to the complete oxidation of Orange-II, but the slowest step of the reaction is the oxidation of formed intermediates into carbon dioxide and water. This is expected, because the formed intermediates are most probably low molecular weight acids which are very hard to completely oxidize at such low temperatures. This also explains why the $k_3$ values are almost the same and very small at these temperatures.

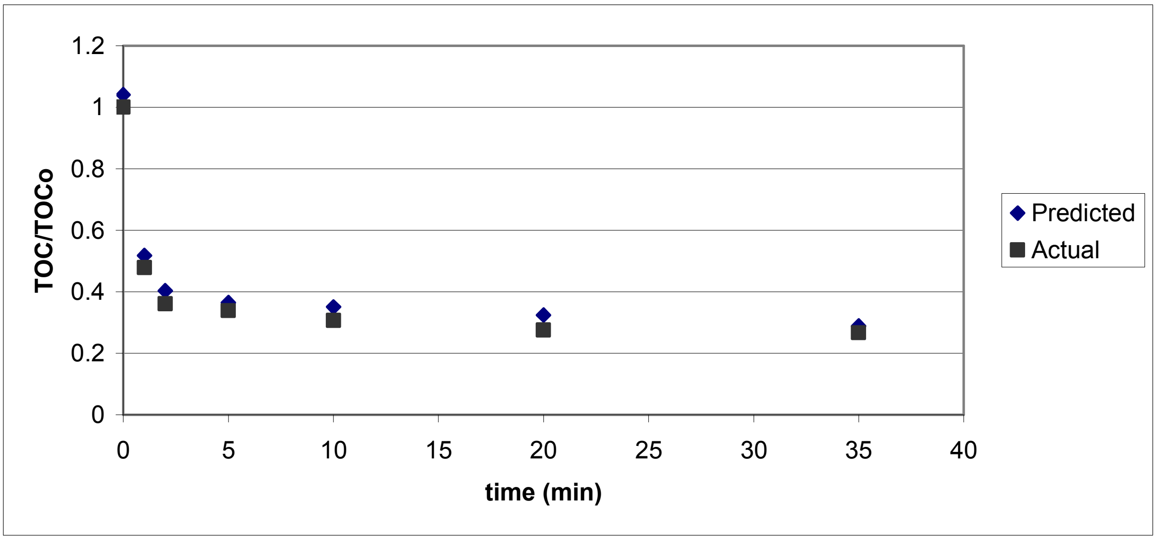

**Figure 7: Actual vs. model predicted TOC/TOC$_0$ at 80°C with CuO/ $Al_2O_3$**

## CONCLUSIONS

The compound studied, Orange-II, is oxidized by the CWAO process. Among the different catalysts that were tested, CuO/$CeO_2$ and CuO/ $Al_2O_3$ were found to be the most economic and efficient catalysts. The degradation of Orange-II was found to be partial with the formation of some byproducts; however, during the first 50 minutes of reaction, almost 80% of the total TOC was completely oxidized. A lumped parameter kinetic model was constructed to explain the reaction kinetics. There was very good agreement between the experimental data and the model predicted values.

## REFERENCES

1. Zollinger, H., *Color Chemistry-Synthesis, Properties, and Applications of Organic Dyes and Pigments*. 2003, Zurich: Wiley-VCH.
2. Cooper, P., ed. *Colour in Dyehouse Effluent*. 1995, Oxford-The Alden Press.