Advanced Oxidation Process to Decompose Oils & Greases

Danielle Miousse & Fabienne Biasotto, CÉPROCQ, Montreal, Canada

Oils and greases can be degraded using a clean technology combining ozone, hydrogen peroxide and UV irradiation. The final degradation products expected if the reaction goes to completion are carbon dioxide and water. The influence of different parameters on the degradation process was observed (ozone, hydrogen peroxide, UV irradiation, recirculation, turbidity, pH, temperature). Flocculation was introduced in the process to reduce the reaction time. Total organic carbon concentrations as high as 3000 ppm could be reduced to the expected level of 30 ppm and lower in less than 24 hr. A pilot scale unit has been built and 300 gal/day are expected to be treated on a regular basis.

For more information, contact:
Danielle Miousse, Ph.D., CEF
Project manager
CEPROCQ
6220 Sherbrooke East
Montreal, Quebec, Canada
H1N 1C1
dmiousse@ceprocq.com

Introduction

Advanced oxidation processes make use of oxidants to reduce COD/BOD levels, and to remove both organic and oxidisable inorganic components. The process should be able to completely oxidize organic materials to carbon dioxide and water, although it is often not necessary or not possible to operate the processes to this level of treatment. A wide variety of advanced oxidation processes are available: a) chemical oxidation processes using ozone (O_3), hydrogen peroxide (H_2O_2), the combination of ozone and peroxide, catalytic ozonation, Fenton's reagent (Fe^{2+}/H_2O_2); b) ultraviolet enhanced oxidation such as UV/ozone, UV/H_2O_2, UV/air; c) wet air oxidation and catalytic wet air oxidation.

Advanced oxidation processes are particularly appropriate for effluents containing refractory, toxic or non-biodegradable materials. The processes offer several advantages over biological or physical processes including: process operability, unattended operation, the absence of secondary wastes, the ability to handle fluctuating flow rates and compositions.

Background of the technology

A system has been developed to decrease the concentration of BTEX in wastewater (see figure 1). Total removal of as much as 99% could be achieved using a combination of UV irradiation using 185 nm or 254 nm lamps combined with ozone. A Venturi injector was used to favor dissolution of ozone in water.

Best results were obtained using shorter wavelength UV lamps emitting their spectral output at 185 nm. These shorter wavelength lamps emit more energy than the standard 254 nm lamps producing hydroxyl free radicals ($OH^\bullet$), which in turn oxidizes most organics into carbon dioxide (CO_2) and water (H_2O). Both TOC reduction and microbial reduction occur with the same 185 nm UV lamp.

Fig. 1. Lab scale advanced oxidation system.

Results and discussion

The solution tested is the liquid used in the non-destructive inspection process. It is a green fluorescent water emulsifiable liquid. The colored compound is most probably the fluorescein that is present in very low concentration. Its structure is shown in figure 2. The remaining composition of the solution is not well known. The main component is an alkyloxypolyethylene-oxyethanol, a polymer with alcohol and ether functions.

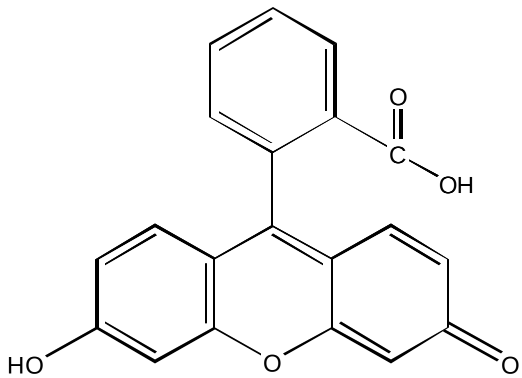

Fig.2. Chemical structure of the fluorescein.

When that solution is rejected to waste, it causes oils and greases concentration higher than the value permitted by the regulation. Degradation of the organic content can be achieved using an advanced oxidation process. The final expected products are carbon dioxide and water. The measure of the total organic carbon was selected as the easiest and most accurate technique to follow the degradation efficiency.

The total organic carbon (TOC) is the organic carbon content of a sample. Inorganic carbon (CO_2, HCO_3^- and CO_3^{2-}) must be purged from the sample under acidic conditions or alternatively it may be assessed through an acidity analysis. A sample is injected into the TOC analyzer that uses a catalyst and heat while supplying oxygen to convert organic carbon into CO_2. The amount of CO_2 produced is measured for the known volume of sample.

Some parameters are expected to influence the process: ozone, hydrogen peroxide, UV irradiation, circulation rate, pH and temperature. Many experiments were conducted to verify the importance and the effects of these parameters on the degradation process. The following observations can be reported:

- Hydrogen peroxide, ozone or UV irradiation at 185 nm alone does not decrease the organic concentration of the solution.
- The combination of hydrogen peroxide and UV irradiation at 185 nm can reduce the concentration of organic contaminants.
- The ozone is essential to remove the colored component. That coloration has to be removed before the degradation can start. The TOC level will not change significantly as long as the color is present.

- The color removal by ozone is easier at lower pH.
- Homogeneity of the solution is essential to allow degradation. Circulation rate must be high enough to avoid phase separation within the reactor.
- Too high concentrations of hydrogen peroxide do not promote or increase the degradation rate or efficiency.
- Hydrogen peroxide must be added all along the decomposition process to achieve complete degradation of the organic matter.
- The temperature of the solution must not be too high because the UV irradiation efficiency will be lost. Constant circulation of the solution permits an easy control of that parameter.

Using the best experimental conditions, degradation of TOC levels as high as 3300 ppm could be degraded to less than 30 ppm within 24 hours using a combination of ozone/hydrogen peroxide/UV irradiation (figure 3).

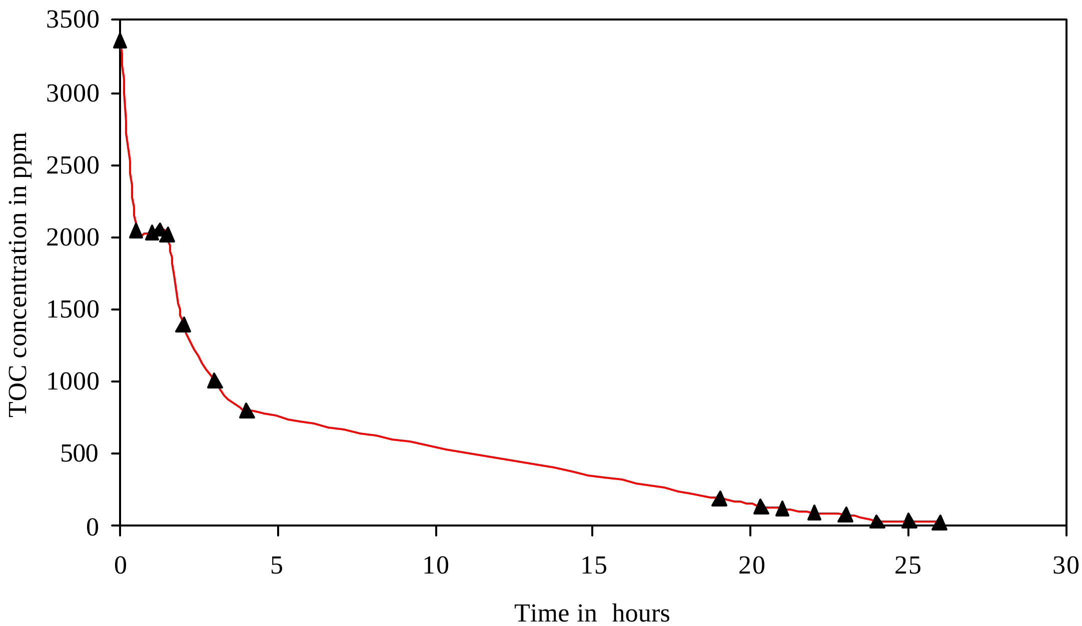

Fig. 3. Example of a degradation curve obtained using O_3 + UV/H_2O_2

Unfortunately that time was not acceptable on an industrial point of view. A way to increase the reduction speed was to introduction flocculation and coagulation in the process. These new parameters help reduce the total process time to about 10 hours. The coagulation and flocculation remove the colored compound and about 75% of the total organic matter. The remaining solution is then treated using combined hydrogen peroxide/UV irradiation technology. Table 1 describes an example of the results obtained using that process. The concentration of oils and greases analyzed after that process was under the detection limit.

Table 1
Degradation of the liquid penetrant using the combination of O_3 + Fenton reagent + coagulation + UV/H_2O_2

Description of the process	Time Hours	TOC concentration ppm	Aspect of the solution
Initial sample	0	1373	Yellow
After ozonation	1	1349	Milky
After addition of $FeSO_4$ + coagulant aid + pH adjustment	2	497	Slightly yellow
After UV/H_2O_2	7	14	Clear

Conclusions

Degradation of high concentrations of organic contaminants can be degraded using a combination of clean technologies. TOC levels as high as 3300 ppm could be reduced to less that 30 ppm in one day and respect the oils and greases limitations. Introduction of flocculation and coagulation decreased the process time to about 10 hours. Three processes proved to be equivalent considering their efficiency in TOC removal:

- **O_3 + UV/H_2O_2**: The removal of the color is done by the ozone followed by the TOC reduction using the combination UV/H_2O_2.
- **O_3 + Fenton reagent + coagulation + UV/H_2O_2**: The color is removed by the ozone. Then most of the organic content is removed by the combination Fenton reagent and coagulation. The remaining TOC is degraded using UV/H_2O_2.
- **Fenton reagent + coagulation + UV/H_2O_2**: The color and most of the organic content is removed by the combination Fenton reagent and coagulation. The remaining TOC is degraded using UV/H_2O_2.

The difference in time consumption and waste generation can help in the selection of the most appropriate process depending on the industry and regulation requirements.

Turbidity cannot be used to control the process. Its value could not be related to the concentration of the organic matter to be degraded. On the other hand, TOC level is a very reliable measure of the organic concentration.

References

1. M. Doré, *Chimie des oxydants et traitement des eaux*, Technique et Documentation-Lavoisier, Paris, France, 1989.

2. W. J. Masschelein, *Ozone et ozonation des eaux*, Technique et Documentation-Lavoisier, Paris, France, 1991.

3. R. L. Droste, *Theory and Practice of Water and Wastewater Treatment*, John Wiley & Sons Inc., New York, NY, 1997.

4. J. Dallan, *Ultraviolet Light in TOC reduction*, Water Conditioning & Purification, 36-37, June 2002.

5. Yabe et al., *Dissociation Energies for Interatomic Bonds in Organic Substances*, http://www.trojanuvlogic.com/UV_Applications/diss_toc.html

6. *Municipal Water Disinfection and Destruction of Toxic Organic Compounds in Wastewater*, http://www3.sympatico.ca/csatari/index5.htm

