Study on the Ozonation of Organic Wastes (1)

Ki Hong Kim*, Il Sik Kang, Dae Seok Hong
Korea Atomic Energy Research Institute, 150 Deokjin-dong, Yuseong-gu, Daejeon
**Corresponding author: nkhkim@kaeri.re.kr*

1. Introduction

Ozone is considered to be an attractive agent in the chemical oxidation process due to its high oxidant capacity (E_o = 2.07 V, Table 1) and the hydroxyl radicals produced during the ozonation process are a highly reactive transient that can rapidly oxidize most organic substances. But Ozone has a disadvantage that the reaction of ozone with some organic matters is slow or does not respond to it.

Table 1. Standard Redox Potential of Oxidant Species

Oxidant Species	E^o, Volts	Relative Potential of Ozone
Fluorine	3.06	1.48
Hydroxyl radical	2.80	1.35
Atomic oxygen	2.42	1.17
Ozone	2.07	1.00
Hydrogen peroxide	1.77	0.85
Hydroperoxide radical	1.70	0.82
Permanganate	1.67	0.81
Chlorine dioxide	1.50	0.72

Therefore, to compensate for these disadvantages, ozone is often used in combination with H_2O_2, UV, peroxides, and the catalyst. These combined processes have the purpose to increase OH radicals, so this combination process is called the advanced oxidation process (AOP, Advanced Oxidation Process). In this study, the possibility of the oxidation treatment of LSC Cocktail solution by using a combination of ozone and hydrogen peroxide was investigated.

The addition of a suitable amount of hydrogen peroxide increases the efficiency of the oxidation process during ozonation of the organic materials. But on the contrary, the excess addition of hydrogen peroxide decreases the ozonation efficiency because they can play a role as a scavenger consuming the hydroxyl radicals generated during the ozonation process. So it is very important to find the amount of volume of hydrogen peroxide. The efficiency of oxidation treatment of organic materials is greatly depended on the properties of liquid waste (pH, concentration and chemical type of organics), the process temperature, the flow rate (waste and ozone gas), the ozone concentration, the hydrogen peroxide concentration and the presence or absence of scavengers. In this study, by using an ozone contactor (hydrophobic hollow fiber membrane type), the basic experiments were carried out to evaluate the applicability of ozonation to the organic wastes. First of all, the oxidation treatment was evaluated by ozone alone, and secondly was evaluated according to the changes of the amount of hydrogen peroxide and a pH of wastes. Through the basic experiments, we tried to obtain basic data for further processing and to establish the direction of treatment for the actual radioactive organic wastes.

2. Methods and Results

Hydrophobic PTFE membrane contactor was used to dissolve ozone into the pure water (Table 2), and the flow diagram of ozonation process was shown in Fig. 1. Ozone gas (IN USA Inc. AC-2025, 25 g/hr) generated outside was supplied into the tube side of the membrane contactor, and the pure water was supplied to the shell side (inside of the hollow fiber membrane module). So the concentration of dissolved ozone (IN USA Inc. dFFOZ, ~ 150 ppm) in water and ozone gas (IN USA Inc. gFFOZ, ~ 900 g/m^3) according to the reaction time is shown in Fig. 2. As a result, Fig. 2 shows the concentration of dissolved ozone was about 29 ~ 31 ppm.

LSC Cocktail solution selected as a target material was Scint-A XF (Packard Company). For this study, LSC Cocktail solution was diluted to 1/100 times to evaluate the possibility of the oxidation treatment by ozone. At this time, their TC (Total Carbon) was about 5,835 ppm.

Table 2. Membrane Contactor Module Characteristics

Membrane material	Pore size(μm)	Membrane Porosity (%)	Fiber i.d./o.d (mm)	Effective module length(mm)	Internal specific area(m^2)	Number of fiber
PTFE	0.1	25	1.0/2.0	30	0.21	100

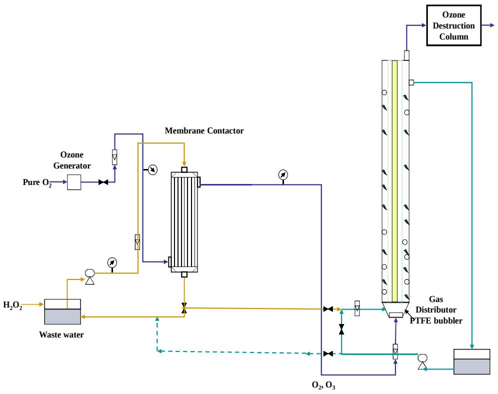

Fig. 1. Experimental setup for ozonation in a membrane contactor

In general, the LSC Cocktail solution was composed of aromatic solvent, scintillators (Fluorescing agent) and surfactants (detergents), and his total carbon content is known to be 80 - 90%.

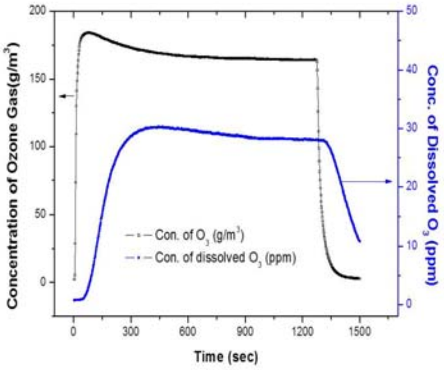

Fig. 2. Concentration of O_3 gas (g/m^3) and dissolved O_3 in water (ppm)

Fig. 3 shows the oxidation ratio according to the changes of the addition of hydrogen peroxide, and Fig. 4 shows the oxidation ratio of the pH of wastes, 4 and 12. These graphs showed a certain oxidation pattern. The oxidation ratio was calculated with TC results analyzed by the TOC analyzer (Lachat, IL 550 TOC-TN). All samples were analyzed after 24 hours for the phase separation and the extinction of ozone. As shown in figures, the oxidation ratios were about 81 ~ 83% at the beginning of the oxidation, and then decreased about 40%, and after increased to about 45%. It was reason that the aromatic solvents of the initial samples were separated and precipitated for 24 hours, and then solvents were oxidized gradually and partially while increasing the reaction time. In fact, it is well known that the aromatic compounds were very hard to oxidize by any kind of oxidants due to their chemical stabilization. This study also found that the overall oxidation ratio was low due to their slow oxidation after the oxidation of surfactants. But at the end parts of oxidation, the oxidation ratio was increase somewhat due to the conversion from compounds of high molecular weight to that of low molecular weight according to their partial oxidation. And the oxidation pattern at pH=12 was clear and the oxidation ratio was higher than at pH=4 because of the rapid degradation of ozone in the alkali solution.

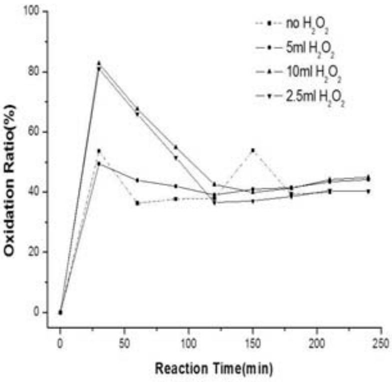

Fig. 3. Oxidation ratio (%) of LSC Cocktail solution according to the changes of volume of H_2O_2

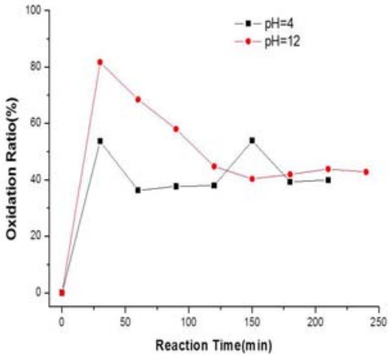

Fig. 4. Oxidation ratio (%) of LSC Cocktail solution according to the changes of pH

3. Conclusions

We investigated the possibility of the chemical oxidation of LSC Cocktail solution by using ozone. The surfactants could be oxidized easily than the aromatic solvent. But we thought that the solvent, aromatic compounds, could be oxidized under the conditions like the maximum utilization of ozone gas, the optimum amount of hydrogen peroxide, the optimum pH of wastes. For the purpose of the volume reduction of liquid organic wastes, it is desirable to oxidize the surfactants firstly, and then to extract the aromatic solvents which is hard to oxidize because the solvent can be separated easily from the wastes treated by ozone.