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# Pretreatment laundry wastewater for removing organic surfactant

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## 1. Introduction

Radioactive laundry wastewater is one of low-level radioactive waste (LLW) derived from showering and washing of worker's clothing during nuclear power plants (NPPs) operations. It contains radionuclides such as Cs, Sr, and Co and non-radioactive species such as non-ionic surfactant, electrolytes and fiber particles [1]. Typical activities range from $10^{-7}$ to $10^{-4}$ μCi/cc and its annual generation volume can reach up to 4,000 $m^3$ per unit NPP in Korea [1], highlighting the need for effective treatment and volume minimization. The primary objective of radioactive laundry waste treatment is the removal of radionuclides. However, this waste also contains refractory surfactants that cannot be effectively treated using conventional technologies such as evaporation or membrane filtration [2]. To enhance the surfactant removal of laundry wastewater, a pretreatment process for non-ionic surfactant is necessary.

Laundry wastewater in Korean NPPs is treated by filtration. In Korean NPPs, if the radioactivity is below the regulation limits, then the total organic content (TOC) concentration of surfactant is diluted to 25 mg/L or less and discharged into the sea so that it is below the discharge standard of the Water Quality and Environment Conservation Act [1,3]. If it exceeds regulatory limits, laundry wastewater is treated by a conventional treatment such as an evaporation. However, the foam generated out of the surfactant can form bubble and cause radionuclide leakage, which significantly impact the treatment performance, operating costs, and equipment lifespan. This approach does not achieve zero-release and sustainable management of radionuclides. On the other hand, in Russia, the Kursk NPP used ozonation, microfiltration, and ion exchange resin to selectively adsorb Cs and other remaining ions in the laundry waste [4]. Ozone is known to have a high removal rate, but the huge facility scale results in high maintenance and operational costs. The ozone system, consisting of a generator, auxiliary facilities, and an ozone chamber, can cost more than 275,000 USD, not including its high maintenance expenses [1]. Ion exchange resin also shows high removal efficiency. However, it requires a large quantity of resin and generates a large volume of secondary waste that needs pretreatment process before solidifying of spent resins.

In this study, more appropriate treatment process is proposed to reach zero-release of radioactive waste to environment, enabling to reuse the treated water in the next process. This study investigated the pretreatment effect combining a precipitation reaction involving copper and/or calcium ions at basic pH an advanced oxidation process (AOP) using peroxydisulfate (PDS) to remove non-ionic surfactants. This method used $Cu^{2+}$ not only to make complexes with surfactant but also to activate PDS to generate sulfate radicals ($SO4^{-}\bullet$) and/or hydroxyl radicals (•OH) [4-6]. Compared to conventional technology, the refractory non-ionic surfactant can be degraded into $CO_2$ and $H_2O$ by radical oxidation, and other radionuclides in wastewater can be precipitated as metal hydroxides by injection of $Ca(OH)_2$, so zero-release of radioactive waste can be achieved. This approach is also cost-effective, since most of the expenses are associated with the reagents used. Moreover, at the end of the process, sludge is expected to be produced, consisting of the hydroxide precipitants from copper/calcium and other radionuclides. Although radionuclides were not addressed in this study, according to an IAEA report, radionuclides present in wastewater can be precipitated at pH 11 by forming hydroxides [9]. Therefore, only liquid–solid separation process is expected to be installed to separate the sludge. The sludge will subsequently be treated by plasma, and physicochemical characteristics of the treated sludge are anticipated to comply with disposal standards. This study focused on the precipitation and radical oxidation od non-ionic surfactants to pretreat laundry wastewater.

Figure 1 Scheme of precipitation and radical oxidation pretreatment process for laundry wastewater

## 2. Methods and Results

### 2.1 *Materials and Experiments*

All chemicals used in this study were analytical grade. Synthetic laundry wastewater was prepared using non-ionic surfactant (EM-100 from LG Household and Health Care Co., Korea). $CuSO_4$ (97.5% assay) was purchased from Junsei Chemical Co., Japan. $Na_2S_2O_8$ (PDS $\geq$ 98% assay) was obtained from Daejung Chemicals & Metals Co., Korea. $Ca(OH)_2$ (0.3% assay) was purchased from Samchun Chemical Co., Korea.

The synthetic wastewater was prepared as 0.1% (v/v) non-ionic surfactant in deionized water, with an initial TOC of around 200 mg/L. Batch experiments were performed to study the effectiveness of treating laundry wastewater using PDS as an oxidant and $Ca(OH)_2$ as a precipitant, with varying concentrations of $Cu^{2+}$, PDS, and different amounts of $Ca(OH)_2$ injected. Three batch tests were conducted for the pretreatment of non-ionic surfactants. In the first experiment, non-ionic surfactant was treated with varying concentrations of $CuSO_4$ (0, 1, 2, 4, 6, and 8 mM), followed by a 60 mM of PDS concentration and 44 mL of $Ca(OH)_2$. The second experiment employed 2 mM of $CuSO_4$, PDS concentrations ranging from 10 to 60 mM, and 44 mL of $Ca(OH)_2$. In the final experiment, the injected volume of $Ca(OH)_2$ was varied between 0 and 110 mL, while maintaining 2 mM of $CuSO_4$ and 20 mM of PDS. Radical oxidation and precipitation reactions were carried out for 6 and 4 minutes, respectively. Following a 15-minutes sedimentation period, the supernatant was filtered through a 0.45 µm syringe filter. The TOC removal efficiency of laundry wastewater was estimated using a total organic carbon analyzer (TOC-L CPH/CPN, Shimadzu, Japan).

### 2.2 *Effect of $Cu^{2+}$and PDS concentration on laundry wastewater treatment*

To activate PDS for surfactant degradation, the effects of $Cu^{2+}$ concentration were investigated in the first batch test. As depicted in Fig. 1, the TOC removal efficiency increased up to 2 mM and then decreased with further increases in $Cu^{2+}$ concentration. The TOC removal efficiency reached as high as 61.6% after 0.45 µm filtration at 2 mM $Cu^{2+}$. Previous studies have shown that Cu is the most effective catalyst for generating sulfate radicals from PDS among Fe, Co, Cu, and Mn [5], [8].

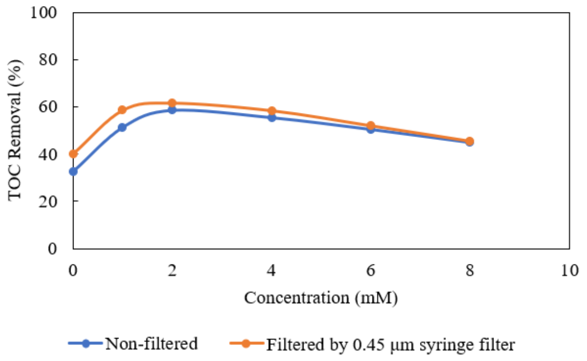

Figure 2 Effects of $Cu^{2+}$ concentrations on TOC removal of laundry wastewater

As presented in Fig. 2, TOC removal efficiency was 63.53% at 10 mM PDS and rose to 65.70% at 20 mM. However, further increases in PDS concentration led to a decline in removal efficiency. The TOC removal efficiency decreased as the PDS concentration increased. This decrease may occur because a higher PDS concentrations generate an excess of radicals, which reduces TOC removal. According to Chanikya, when persulfate concentration increases, sulfate radicals tend to recombine, thereby lowering removal efficiency [10].

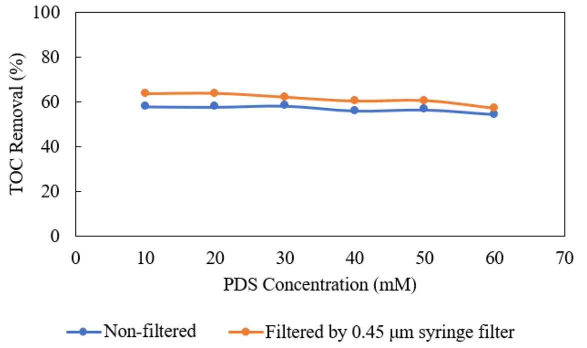

Figure 3 Effects of PDS concentrations on TOC removal of laundry wastewater

### 2.3 *Effect of $Ca(OH)_2$ injection on laundry wastewater treatment*

The effects of $Ca(OH)_2$ injection on treating laundry wastewater was evaluated. The experimental conditions were established based on the optimal parameters obtained from previous tests. As shown in Fig. 4, increasing the injection volume of $Ca(OH)_2$ resulted in higher removal efficiency. The results indicated that the TOC removal efficiency was minimized without $Ca(OH)_2$, reaching 1.5% in the non-filtered sample. This showed the importance of precipitation by $Ca(OH)_2$ addition. The highest TOC removal efficiency achieved was 77.9% within 10 minutes of total reaction time, with 110 mL $Ca(OH)_2$, followed by filtration through a 0.45 µm syringe filter.

The $Ca(OH)_2$ facilitated not only the formation of transition metal hydroxides for radionuclide removal, but aslo reacted with the surfactant to produce calcium-surfactant ligand complex precipitates. Surfactant decomposition by radicals may break down the surfactant into smaller size molecules, subsequently may be removed by generating ligand complex. This mechanism was observed on Ma's research where divalent metal (M(II)) influenced the morphology of gypsum coprecipitates at pH 10, forming stubby rod-lid particles with a small number of fine particles on their surfaces. The concentration of $Cu^{2+}$ incorporated into gypsum was about 32 times more than that at pH 4. Furthermore, with the consecutive addition of $OH^-$, the $Cu(OH)_4^{2-}$ complex could form and then subsequently coprecipitated by $SO_4^{2-}$ [11]. Therefore, the incorporation mechanism may be described by:

$$Ca^{2+} + xCu(OH)_4^{2-} + (1-x)SO_4^{2-} + 2H_2O \rightarrow Ca(Cu(OH)_4)_x(SO_4)_{(1-x)}.2H_2O \qquad (1)$$

The experiment showed that $Cu^{2+}$ achieved better coprecipitation under basic conditions. Similarly, in this PS system, $Cu^{2+}$ improved the TOC removal efficiency at 2 mM, suggesting a optimal range of $Cu^{2+}$ for coprecipitation. Therefore, coprecipitation likely occurred in this experiment and further analysis should be conducted soon to investigate it in more detail.

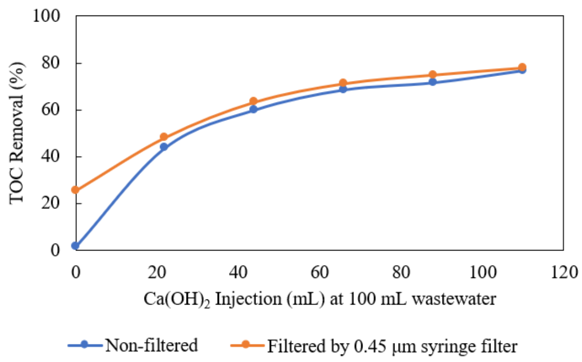

Figure 4 Effects of $Ca(OH)_2$ injection on TOC removal of laundry wastewater

## 3. Conclusions

In conclusion, this study showed that combined effects of radical oxidation and precipitation reactions in removing organic surfactants from laundry wastewater. The optimal use of $Cu^{2+}$ to activate PDS enhanced the efficiency of surfactant removal, which subsequently coprecipitated with calcium in the supernatant. The high performance of TOC removal in laundry wastewater can be obtained within 10 minutes, indicating its potential for full-scale applications.

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