

Degradation of waste water from TNT manufacturing

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Abstract

The degradation of red water from TNT waste water was studied. Three methods were employed in this study: Fenton oxidation, Photo-Fenton oxidation, and Fenton oxidation with TiO₂ photo-catalyst. Red water was decolorized by Fenton oxidation within 2 - 3 hours. The reaction rate for Fenton oxidation with TiO₂ photo-catalyst > Fenton oxidation under UV radiation > Fenton oxidation.

Organic nitrogen (nitro group) was essentially mineralized to nitrate ion and ammonium ion. The nitrate ion concentration was 2.1 times greater than the ammonium ion concentration for the photo Fenton oxidation method, and 2.3 times greater than the Fenton oxidation with TiO₂ photo-catalysis method. For the Fenton oxidation method, UV radiation appeared to be effective. This suggests that the reduction $Fe^{3+} \rightarrow Fe^{2+}$ occurs to reproduce Fe²⁺ ion under radiation.

Keywords: Red water, Degradation, TiO₂ photo-catalyst, Fenton, Photo-Fenton

1. Introduction

Degradation of dissolved TNT is a serious environmental problem^{1), 2)}. In TNT manufacturing, significant quantities of water are used for cooling, washing and re-crystallization but become contaminated with TNT in the process.

Significant quantities of waste water (known as "pink water" or "red water") are discharged³⁾. This waste water contains aromatic nitro compounds and acids, the removal of which is very difficult.

The waste water should be decontaminated by a suitable method, such as: chlorination; biological process, or distilling. The disposal of waste TNT has become an urgent problem world-wide and environmental regulations have become more stringent every year. Extensive research has been carried out to remove or decompose TNT in contaminated water and soil^{4,5,6)}. Complete degradation of TNT has been conducted by traditional bioremediation techniques⁷⁾.

Previous research on the coupled method of photo-catalytic and electrolytic degradation of TNT contaminated water and pink water using powder TiO₂ suspended in

solution using a UV lamp or black light has been published by the authors⁸⁾. In addition to the photo-oxidation of the methyl group, cleavage of nitro groups was confirmed. The degradation products were analyzed and found to consist of nitrate ion and low aliphatic carbonic acids such as malonic acid or citric acid.

The TiO₂ photo-catalytic method is not effective in the treatment of waste water having a high concentration of contaminants or in the treatment of dark colored waste water due to the high opacity of these waste waters. There is much literature on the subject of degradation of aromatic nitro compounds by the Fenton or photo-Fenton processes^{9), 10), 11)}. But most of the experiments reported in the literature have been carried out in a solution contaminated by one of these nitro-compounds. Red water contains several types of nitro-compounds.

In this report, the degradation of red water was studied by three methods of Fenton oxidation: standard Fenton oxidation, Fenton oxidation under UV radiation, and Fenton oxidation with TiO₂ photo-catalyst.

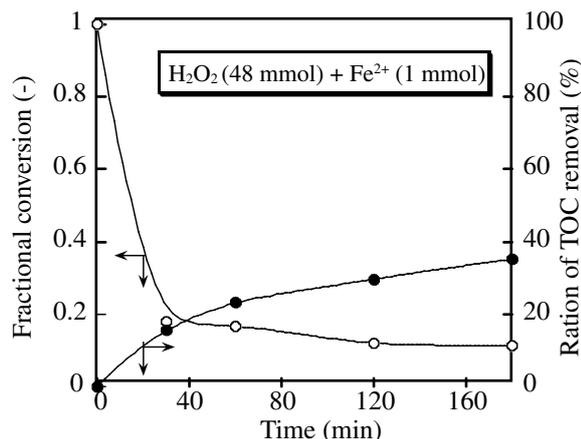


Fig. 1 Time history of the red water degradation and TOC in Fenton oxidation. (Total volume=500 mL, pH=3.2, Initial concentration of TOC=6000 ppm)

2. Experimental

2.1 Materials

Waste water (60000 ppm red water (TOC concentration)) was supplied by CHUGOKU KAYAKU Co., Ltd. The red water (containing an organic nitrogen concentration of 2000 ppm) was diluted at a ratio of 10:1 distilled water: red water. In preliminary experiments, a qualitative analysis was carried out to estimate the concentration of aromatic nitro-compounds in red water by FT/IR, $^1\text{H-NMR}$, IC, Thermal analysis, X-ray diffraction and Fluorescent X-ray diffraction methods. It was determined that in addition to TNT, red water contains: 2,4-dinitrotoluen-5-sodium sulfonate; quinine oxime; 4-amino-2,6-dinitrotoluen, and 2,4,6-trinitro-benzoate.

Reagent grade 30 % H_2O_2 and $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (from Wako pure Chemicals Co.) and Anatase-type TiO_2 (from FUJI TITAN INDUSTRY Co.Ltd.) were employed for Fenton oxidation.

2.2 Experimental procedure

A series of Fenton oxidation reactions were initiated by adding 5 mL of 30 % H_2O_2 (48 mmol), and 10 mL of Fe^{2+} ion solution containing 3 g $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ per 100 mL distilled water into 1 L- flask containing 500 mL of 10 % red water.

In the photo-Fenton procedure and Fenton procedure combined with photo-catalyst, the light source was a 200 W high pressure mercury lamp or 6 sets of 20 W black light lamps. Samples were taken at predefined times and the reaction was quenched by adding 10 mL of 10 N H_2SO_4 solution to permit rapid H_2O_2 consumption.

2.3 Analytical methods

It was observed that waste water changed color from dark red to light red, as the reaction proceeded. In the UV spectrum, the shoulder was observed at a wave length of 240 nm which originated from the aromatic nitro group⁷.

The absorbance at the shoulder became smaller as the reaction proceeded. Absorbance at 240 nm was measured to determine the time history of decolorization and degradation⁸. Quantitative determination of nitrate and ammonium ions were carried out under UV spectrometry with an Ubest V560 UV/Vis spectrophotometer from JASCO Corporation.

An analysis of reaction products was performed via HPLC from JASCO Corporation (Shodex model KC 811) under the following Analytical Conditions: Eluent: 0.1 % H_3PO_4 , Flow rate:1.0mL/min, Oven Temp.: 60°C, Detector: UV at 210 nm). Decarbonation of red water was monitored by measuring the decrease in Total Organic Carbon (TOC) content using the YANACO brand total organic carbon hardware (TOC-800). Chemical Oxygen Demand (COD) was also monitored by the COD_{Cr} method¹².

3. Results and Discussion

3.1 Decomposition and degradation of red water

Decolorization and degradation reactions were initiated by mixing red water with Fenton reagent (a mixture of H_2O_2 and Fe^{2+} solution) at room temperature, and the reaction was monitored by UV absorbance and TOC measurements. As the reaction proceeded, the color of the red water was observed to change from dark red to a faint orange color. In Fig. 1, the time history of the concentration of the aromatic nitro group was determined from UV absorbance at 240 nm. TOC concentration as a function of time is also shown when red water was mixed with Fenton reagent. This figure shows a decrease in concentration corresponding to TOC removal as was previously reported for pink water degradation⁸. It was confirmed that Fenton reagent can decolorize and degrade red water. It is also known that Fenton reagent can produce highly reactive intermediate oxidants, such as the OH radical. Walling¹³ proposed a mechanism for OH radical formation as follows:

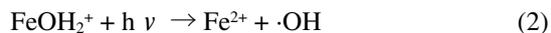


The OH radical extracts the π -electrons of aromatic nitro-compounds to break the aromatic ring, resulting in degradation.

In photo-Fenton oxidation and Fenton oxidation combined with photo-catalyst, two types of light sources were employed; a 200 W high pressure mercury lamp, or six sets of 20 W black lights. Figure 2 shows the time history of red water degradation as a function of time under various conditions. In both cases, the degradation of red water decreases rapidly in the first 30 minutes, which suggests that the degradation is efficiently promoted by employment of a light source. This result coincides with other experiments^{14, 15}.

The degradation with black lights (20 W \times 6) is nearly equal in efficiency to the mercury lamp (200 W). It should be noted that as a UV light source, the mercury lamp may be replaced with a black light which has a lower operation cost.

It is known that a UV light source enhances the photo-reduction of hydroxylated ferric ion to ferrous ion resulting in a continuous supply of hydroxyl radical as expressed by equation (2) ¹⁶.



Liou¹⁷) suggests that the mechanism of photochemical reduction is explained by the stability of Fe^{2+} ion rather than Fe^{3+} ion on the basis of crystal field theory.

Figure 3 (a) and 3(b) show the TOC change after the reaction proceeded for 60 and 180 minutes in order to show the effect of H_2O_2 and Fe^{2+} concentration on the degradation of red water by Fenton oxidation as a function of time. From this figure, the optimal ratio of $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}]$ for treatment of red water with Fenton reagent, is 12:1 as reported in the literature¹⁸). In this experiment, the optimal

quantity of H_2O_2 and Fe^{2+} is 50 mmol and 1 mmol, respectively, a ratio of 50:1. This difference of a factor of over 4 may be caused by the fact that in the literature, model waste water contains only a single contaminant, while in this experiment, the red water contained numerous contaminants as described in section 2.1.

3.2 Decomposition products and TOC

Figure 4(a) and 4(b) show the removal of organic nitrogen, nitrate and ammonium ions produced during the oxidation associated with the Fenton procedure as well as the Fenton procedure combined with a photo-catalyst. Organic nitrogen (found in red water as a nitro group) decreases in concentration rapidly for first the 30 minutes along with an increase in inorganic nitrogen such as nitrate and ammonium ions. Analysis of nitrite ion was not conducted. Rapid formation of nitrate and ammonium ions from the

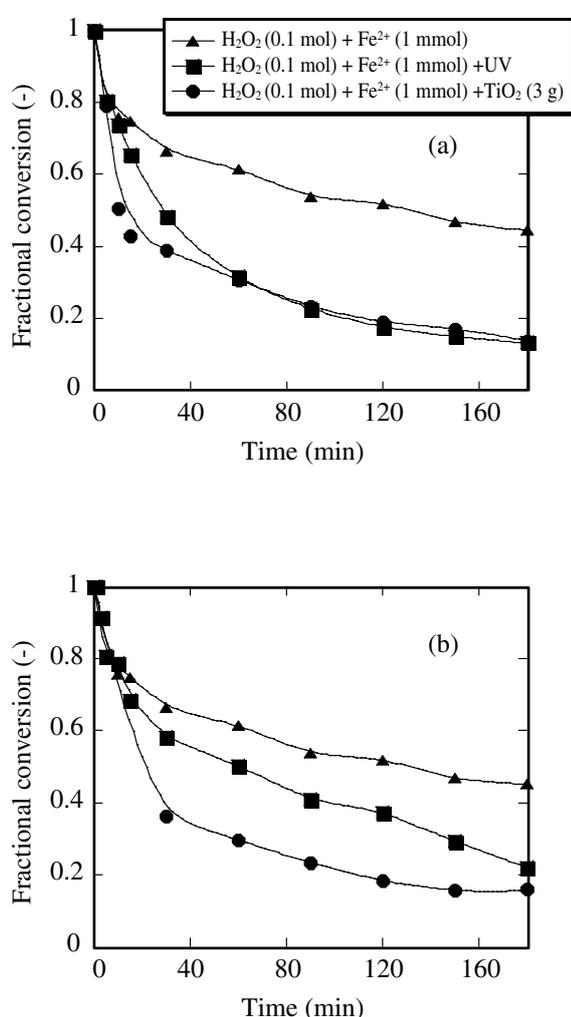


Fig. 2 Time history of the red water degradation in Fenton oxidation, photo-Fenton oxidation and Fenton oxidation with TiO_2 photo-catalyst irradiated by (a) UV high pressure mercury lamp(200W) and (b) Six sets of Black light lamp. (Total volume=500 mL, pH=3.2, Initial concentration of TOC=6000 ppm)

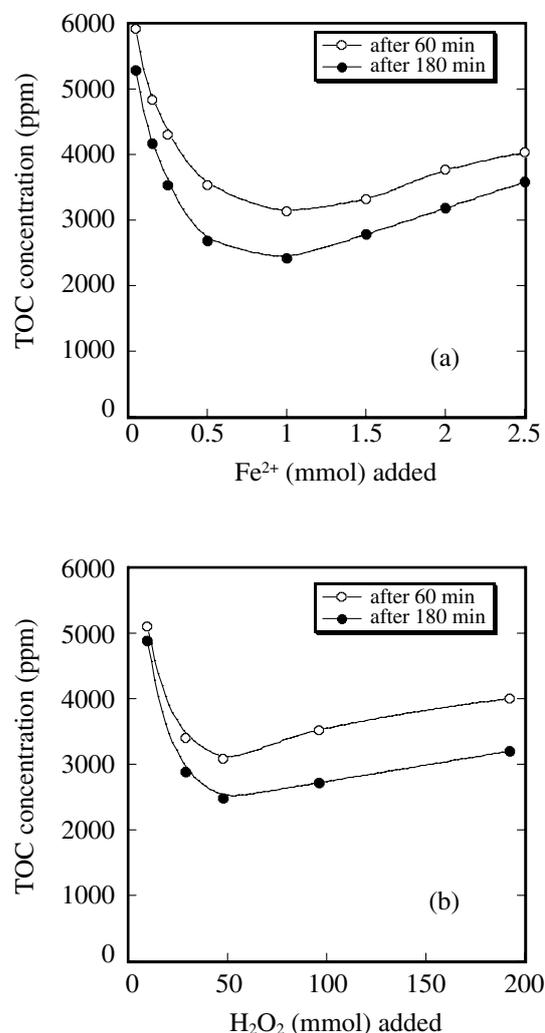


Fig. 3 Effect of (a) Fe^{2+} and (b) H_2O_2 of Fenton reagent on the red water degradation by Fenton oxidation. (Total volume=500 mL, pH=3.2, Initial concentration of TOC=6000 ppm)

initiation of Fenton oxidation may suggest the possibility of direct attack by the OH radical on the nitro group in the aromatic ring. Total nitrogen mass balance is insufficient to verify this because the nitrite ion was not analyzed as nitrogen gas could have been formed during the reaction. Organic nitrogen (nitro group) was almost mineralized to nitrate ion and ammonium ion. The amount of nitrate ion was 2.1 times greater (under photo Fenton oxidation) and 2.3 times greater (under Fenton oxidation with TiO_2 photocatalysis) than that of ammonium ion.

The organic degradation products were determined by HPLC and determined to consist of low aliphatic carbonic acids (including malonic, succinic, acetic and formic acids) as shown in Fig. 5. In this experiment, we could not separate and quantify oxalic acid. As the oxidation reaction proceeds, malonic, succinic and acetic acids decrease and formic acid tends to increase. Kavitha⁸⁾ reported the

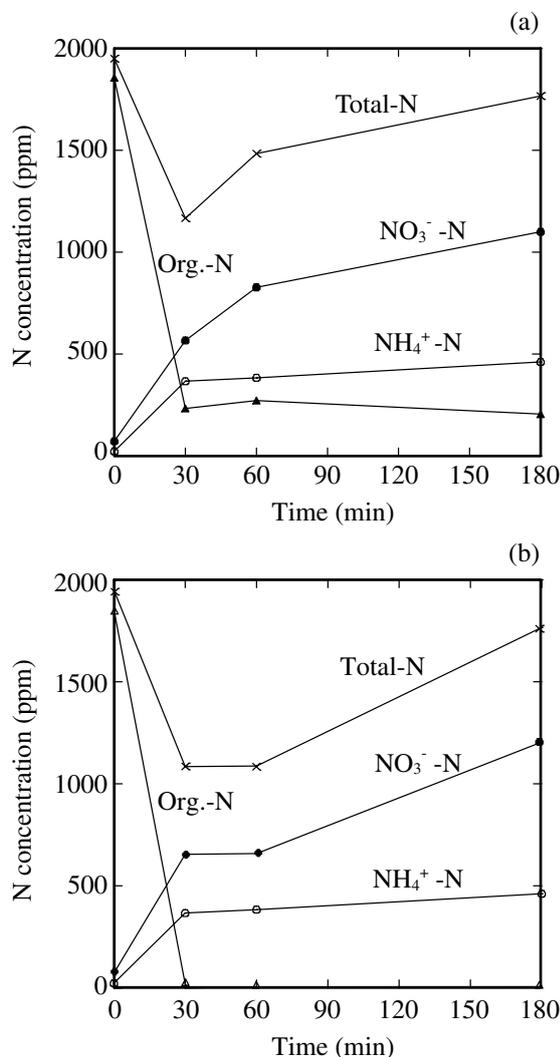


Fig. 4 Concentration of total N, organic N, NO_3^- and NH_4^+ during photo-Fenton oxidation.
 (a) Photo-Fenton oxidation
 (b) Fenton oxidation with TiO_2 photo-catalyst
 (Total volume=500 mL, pH=3.2)

primary products are acetic acid and oxalic acid, but these products disappeared during photo-Fenton oxidation due to the formation of an unstable metal complex between ferric ion and oxalic ion which formed as a result of UV radiation. A time history of COD is shown in Fig. 6. As the oxidation reaction proceeds, COD decreases to one third of initial concentration within 60 minutes. There is

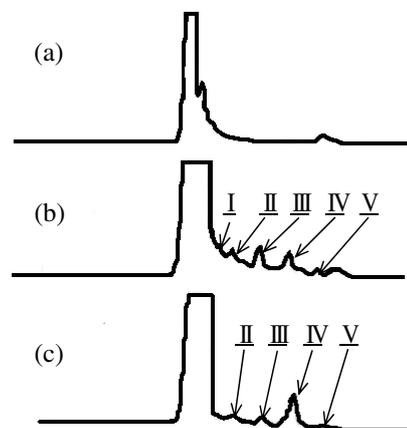


Fig. 5 Oxidation products analyzed by HPLC chromatogram for Fenton oxidation.
 (a) 0 hour (b) after 90 minutes (c) after 180 minutes
 I: Citric acid II: Malonic acid III: Succinic acid
 IV: Formic acid V: Acetic acid
 [Shodex KC 811 column : Analytical conditions;
 Eluent: 0.1 % H_3PO_4 , Flow rate: 1.0 mL/min,
 Oven temp.: 60 °C, Detector: UV at 210 nm]

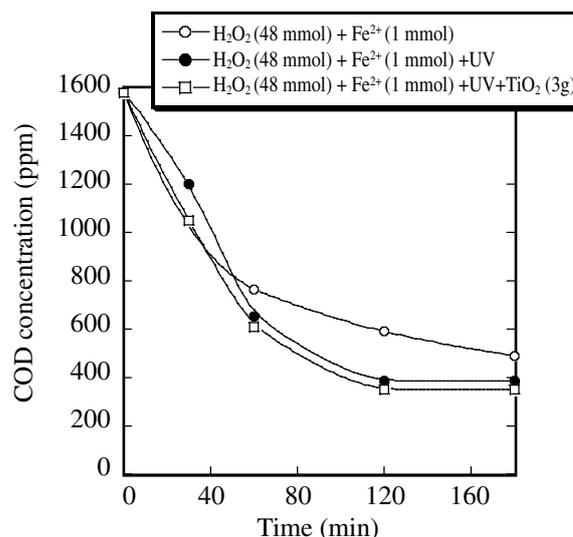


Fig. 6 Concentration of COD for Fenton oxidation with three methods of Fenton oxidation, photo-Fenton oxidation and Fenton oxidation with TiO_2 photo-catalyst.
 (Total volume=500 ml, pH=3.2)

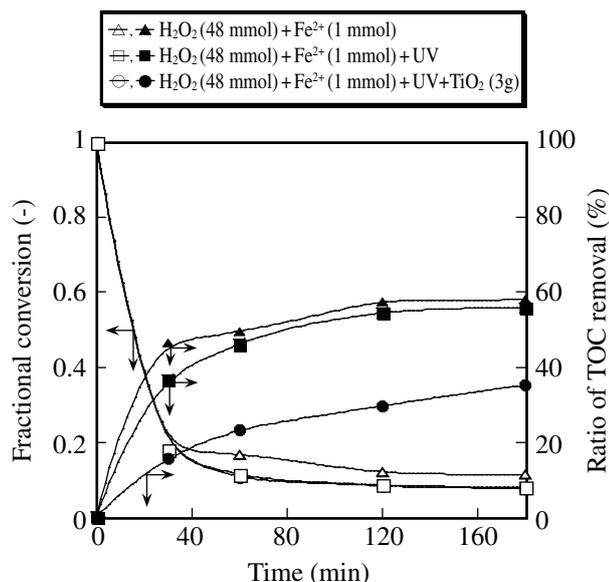


Fig. 7 Comparison of the red water degradation by Fenton oxidation with three methods of Fenton oxidation, photo-Fenton oxidation and Fenton oxidation with TiO_2 photo-catalyst (Total volume = 500 mL, pH = 3.2, Initial concentration of TOC=6000 ppm)

no difference in the COD removal rate due to either Fenton reagent, photo-Fenton reagent or Fenton reagent combined with photo-catalyst in the early stages of the oxidation reaction. After 3 hours, the efficiency is slightly better for the photo-Fenton reagent and the Fenton reagent combined with photo-catalyst than for the Fenton reagent alone.

3.3 Degradation process and comparison of degradation method

Figure 7 shows the time history of degradation of red water and TOC under Fenton oxidation, photo-Fenton oxidation and Fenton oxidation combined with photo-catalyst. The removal rate of TOC is maximum at the initial stage (at $t=0$) and then gradually decreased for the first 30 minutes.

After 30 minutes, the rate becomes very slow. The descending order of efficiency of removal of TOC is:

Fenton procedure < photo-Fenton procedure < Fenton procedure combined with photo-catalyst.

The TOC concentration decreases rapidly and then gradually decreases at the same rate regardless of the procedure. It is suggested that the rapid removal of TOC or rapid decrease in concentration during the first 30 minutes is due to the possibility that the aromatic nitro compounds contained in red water are oxidized to low aliphatic carbonic acids in the early stages of oxidation and subsequent mineralization of low aliphatic carbonic acids are difficult with just the Fenton reagent.

There exist several types of aromatic nitro-compounds in

red water, as previously stated. There are numerous reports regarding the mechanism of waste water degradation containing only one type of aromatic nitro-compound as the contaminant^{15), 17), 18)}. From our results, Fenton oxidation in red water proceeded as well as experiments containing only one type of aromatic nitro compound. A similar mechanism of degradation may be applied to red water. The first step is the ring breakage attack by the OH radical which was formed by Fenton reagent. Next, low aliphatic aromatic acids are produced. The nitro group may be changed to nitrite, nitrate and ammonium ions. Organic carbon is partly mineralized to carbon dioxide and partly changed to low aliphatic carbonic acids which causes the COD reduction. Though the total nitrogen mass balance analysis method is insufficient to verify this supposition, organic N may be almost completely mineralized to nitrogen gas, nitrite, nitrate and ammonium ions.

4. Conclusion

TNT red water was decolorized by Fenton oxidation in 2 or 3 hours. The order of reaction rate was:

Fenton oxidation with TiO_2 photo-catalysis > Fenton oxidation with UV > Fenton oxidation.

Organic nitrogen (nitro group) was almost completely mineralized to nitrate ion and ammonium ion. The amount of nitrate ion was 2.1 times greater under photo Fenton oxidation, and 2.3 times greater under Fenton oxidation with TiO_2 photo-catalyst than that of ammonium ion. In Fenton oxidation, UV radiation seemed to be effective. It is suggested that the reduction of $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ occurs to produce Fe^{2+} ion under radiation.

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TNT製造過程で排出される廃液(赤水)の処理について

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永易伸生**, 原田洋一郎**

TNT 製造過程で排出される廃液である赤水の処理について検討を行った。フェントン試薬を使うことにより 2~3 時間で廃液の脱色が可能であった。フェントン, 光フェントン, TiO₂ 光触媒とフェントンの組み合わせの 3 種類の方法で処理効果を比較したところ, フェントン<光フェントン< TiO₂ 光触媒とフェントンの組み合わせ, の順になった。

有機体窒素はほとんど硝酸イオンおよびアンモニウムイオンなどの無機体窒素に変化した。硝酸イオンはアンモニウムイオンに比べて光フェントン法で約 2.1 倍, TiO₂ 光触媒とフェントンの組み合わせ法で約 2.3 倍ほど大きかった。また, フェントン試薬を使うとき UV の照射は廃液処理に有効であることが確認できた。これは, UV 光照射により 3 価の鉄イオンが 2 価の鉄イオンに再生されることによると考えられる。

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