Improving the Biodegradability of Non-Biodegradable Compounds Using Photo-Fenton Reaction

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ABSTRACT

The feasibility of using the photo-Fenton reaction to improve the biodegradability of non-biodegradable compounds that originated from sewage was examined. Non-biodegradable compounds are degraded by hydroxyl (OH) radicals generated by the photo-Fenton reaction. During the degradation of non-biodegradable compounds, biodegradable intermediates such as organic acids are produced, resulting in improved biodegradability. The results of an experiment, in which a filtered supernatant solution of activated sludge from a sewage treatment plant was used, confirmed that the 5-day biochemical oxygen demand (BOD₅) increased with decreasing total organic carbon (TOC) concentration as a result of the photo-Fenton reaction. This increased the ratio of BOD₅ to TOC, which indicated that the biodegradability was improved. Although many non-biodegradable compounds have electron-dense structures, many biodegradable compounds have electron-lucent structures. Hydroxyl radicals, which are an oxidant in the photo-Fenton reaction, act as an electrophilic agent. In the degradation experiments using a mixture of biodegradable and non-biodegradable compounds, OH radicals preferentially attacked non-biodegradable compounds, and biodegradable compounds accumulated in the solution. As a result, the biodegradability was improved.

Keywords: biodegradability, non-biodegradable compound, photo-Fenton reaction

INTRODUCTION

The activated sludge process has been widely used for cost-effective wastewater treatment because it has advantages such as low running costs and high degradation efficiency (Lapertot *et al.*, 2006). In the activated sludge process, biodegradable compounds are decomposed by microorganisms in the activated sludge, and non-biodegradable compounds are removed by adsorption onto the surface of the activated sludge (Wilén *et al.*, 2003). Excess sludge is produced with increased biological degradation of biodegradable compounds. In order to reduce the sludge volume, sludge treatment processes such as dewatering, digestion, and burning are carried out (Chu *et al.*, 2009). In the dewatering process, adsorbed non-biodegradable compounds on the sludge desorb and transfer into the liquid phase. As a result, wastewater that includes a large amount of non-biodegradable compounds is produced. Moreover, the digestion process also produces wastewater that includes high concentrations of phosphorus and nitrogen (Ivanov *et al.*, 2009). These wastewaters are returned upstream of the activated sludge process, and are treated along with the raw wastewater (Guo *et al.*, 2010). These wastewaters are called returned water. High loads of non-biodegradable compounds in returned water could inhibit the activated sludge process. This leads to the addition of non-biodegradable compounds into the treated water, and these compounds are discharged into aquatic environments. In fact, some pharmaceuticals, which are classified as non-biodegradable compounds, can be found in aquatic environments (Klavarioti *et al.*, 2009).

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Received August 20, 2012, Accepted October 30, 2012.

Various techniques for degrading non-biodegradable compounds, such as ozonation and TiO_2 or ZnO photocatalytic oxidations, have been examined (Matsumura *et al.*, 2007; Nishio *et al.*, 2006; Pophali *et al.*, 2011). Among these techniques, the photo-Fenton reaction may be a promising technology because of its high oxidation performance (Feng *et al.*, 2005). The photo-Fenton reaction consists of two reactions. The first reaction is the decomposition of H_2O_2 , catalyzed by Fe^{2+} (Reaction 1), which generates highly reactive hydroxyl (OH) radicals and oxidizes Fe^{2+} to Fe^{3+} .

The second reaction is the photoreduction of Fe^{3+} , which occurs on irradiation with ultraviolet (UV) or adequate visible light (Reaction 2).

In this reaction, OH radicals are also generated and Fe^{3+} is reduced to Fe^{2+} . In these two oxidation–reduction reactions of Fe ions, OH radicals are continuously produced. Hydroxyl radicals attack pollutants in wastewater, resulting in degradation and mineralization of pollutants via production of intermediates such as organic acids (Katsumata *et al.*, 2006; Wu *et al.*, 2007) (Reaction 3). Because most organic acids are biodegradable (Suarez-Ojeda *et al.*, 2007), the photo-Fenton reaction can decompose non-biodegradable compounds to biodegradable compounds.

However, biodegradable compounds such as organic acids have electron-lucent structures (Sakurai and Ikai, 1999). Because OH radicals act as an electrophilic agent, they are not suitable for the degradation of biodegradable compounds. In contrast, because many non-biodegradable compounds have electron-dense structures, OH radicals are suitable for the degradation of non-biodegradable compounds. A combination of the photo-Fenton reaction and the activated sludge process could therefore be a cost-effective wastewater treatment process. In the combination process, the photo-Fenton reaction is used as a returned water treatment process to improve the biodegradability of non-biodegradable compounds in returned water. As a result of the photo-Fenton reaction, non-biodegradable compounds in the returned water are degraded to biodegradable compounds in the returned water treatment process. Subsequently, biodegradable compounds are degraded by microorganisms in the aeration tank. A schematic diagram of the activated sludge process combined with the photo-Fenton reaction is shown in Fig. 1.

Returned water generally contains high concentrations of phosphorus and nitrogen, originating from the digestion of excess sludge (Ivanov *et al.*, 2009; Guo *et al.*, 2010). High concentrations of phosphorus and nitrogen may affect the photo-Fenton reaction (Wells and Salam, 1968; Fytianos *et al.*, 1998). Because this study is the first step in determining the feasibility of a returned water treatment process using the photo-Fenton reaction, the returned water sample used in the experiment was a filtered supernatant

Fig. 1 - Schematic diagram of the activated sludge process combined with photo-Fenton reaction.

solution of activated sludge taken from a secondary clarifier of an effluent treatment plant (Kawagoe City, Saitama, Japan). The samples, therefore, do not contain high concentrations of phosphorus and nitrogen, but include non-biodegradable compounds originating mainly from raw wastewater. The phosphorus and nitrogen concentrations of the supernatant were 2.8 mg-P/L and 11 mg-N/L, respectively. Incidentally, the phosphorus and nitrogen concentrations of the returned water were 68 mg-P/L and 537 mg-N/L, respectively (Guo *et al.*, 2010).

MATERIALS AND METHODS

Chemicals

Hydrogen peroxide (30 wt%) and Iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were used as Fenton reagents. Sulfuric acid was used for pH control before the experiments. All chemicals were reagent grade and purchased from Kanto Chemical Co., Inc. (Tokyo, Japan).

Methods

The experiments were carried out in a Pyrex glass cylindrical reactor of 0.10 m diameter and 0.20 m height. The working volume was 1 L. All experiments were conducted in batch mode at room temperature. A schematic diagram of the experimental setup is shown in Fig. 2. A motor-driven disk-turbine impeller (impeller diameter: 65 mm) installed at 0.005 m above the photoreactor bottom was used at 400 rpm to ensure complete mixing. The UV light irradiation sources were three 15 W near-UV (black light) fluorescent lamps (FL15T8BLB, Sankyo Electronics, Co., Japan) with a radiation peak at 352 nm. The lamps were located around the cylindrical photoreactor and irradiated the solution externally, as shown in Fig. 2. The distance between the photoreactor wall and the lamps was 0.025 m.

Using sulfuric acid, the solution pH was adjusted to 3.0, which is the optimal value for photo-Fenton reactions (Tokumura *et al.*, 2006). All experiments were carried out without adding any buffers for pH adjustments during the degradation process. The pH monitoring of the initial solution and the samples was performed using a pH meter (Toa Denpa, Japan).

Samples from the liquid phase were withdrawn using a syringe at predetermined time intervals. In order to remove the fine solids (Fe^{3+} oxyhydroxides, Fe complexes, etc.), the samples were filtered with a polytetrafluoroethylene-membrane filter with a pore

Fig. 2 - Experimental setup (1. photoreactor; 2. magnetic stirrer; 3. stir bar; 4. sampling point; 5. pH meter and thermometer; and 6. ultraviolet lamps).

size of 0.45 μm (Advantec Toyo, Tokyo, Japan). The soluble total organic carbon (TOC) was measured using a TOC analyzer (TOC-VE, Shimadzu, Kyoto, Japan).

The Fenton reactions were initiated by the addition of a known amount of H_2O_2 to a solution containing Fe(II) sulfate heptahydrate as a source of Fe ion. The starting point of the experiments was set to be the time at which the UV light was turned on and H_2O_2 was added to the photoreactor. The H_2O_2 concentration was measured using the enzyme method (Sundstrom *et al.*, 1986). The concentrations of Fe ions (Fe^{2+} and Fe^{3+}) dissolved in the solution were measured using the 1,10-phenanthroline method (Sibata Scientific Technology, Ltd., Saitama, Japan) (Tokumura *et al.*, 2006). In the measurement of Fe concentration, Fe^{3+} was reduced by ascorbic acid before the reaction with 1, 10-phenanthroline. Then, the total concentration of Fe^{2+} and Fe^{3+} was measured. The 5-day biochemical oxygen demand (BOD_5) was measured according to a standard method (APHA/AWWA/WEF, 1995). Microorganisms present in activated sludge were used as inoculum. Bottles containing the sample solution, mineral nutrition, and inoculum were incubated at $20 \pm 1^\circ\text{C}$ in the dark. Five days later, the depletion of dissolved oxygen was measured. A control experiment without a sample solution was conducted in parallel.

Degradation of a mixture of biodegradable and non-biodegradable compounds was carried out to compare their degradation tendencies. In this study, Orange II was used as the non-biodegradable compound and acetic acid was used as the biodegradable compound. Orange II is an azo dye and is used as a typical non-biodegradable compound (Gumy *et al.*, 2005). The initial molar concentrations were adjusted to be equal.

RESULTS AND DISCUSSION

Figure 3 shows the typical experimental results for the returned water treatment process using the photo-Fenton reaction. It can be seen from Fig. 3 that the TOC decreases with time; 35% of the initial TOC was mineralized in 400 min, and thereafter remained constant. During the mineralization of non-biodegradable compounds, organic acids such as acetic acid and oxalic acid are produced. Because organic acids have low electron density structures, they are not adequately degraded by OH radicals. As a result, organic acids gradually accumulated in the solution with time, and the TOC did not change after 400 min. However, organic acids are classified as biodegradable compounds, and can be degraded using biological treatments. Consequently, the biodegradability of the non-biodegradable compounds in the returned water was improved. The improvement in biodegradability is demonstrated experimentally later in this section.

The H_2O_2 concentration decreased linearly with time. As shown in Reaction 1, H_2O_2 was consumed. In general, the decomposition rate of H_2O_2 in the photo-Fenton reaction obeys pseudo-zero-order kinetics (Lee *et al.*, 2003; Tokumura *et al.*, 2011a). This result is in good agreement with the literature.

Although the initial Fe ion concentration was adjusted to 1.3 mg/L, the measured value for the initial Fe ion concentration was 0.6 mg/L. This may be the result of precipitation of insoluble Fe complexes. Iron ions can easily form complexes with inorganic and organic compounds. Iron hydroxide, which is one of the inorganic Fe complexes, is insoluble. On the other hand, complexes of Fe ions and organic compounds could be degraded by light irradiation (Perez *et al.*, 2006; Tokumura *et al.*, 2011b). Irradiation

Fig. 3 - Typical experimental results for returned water treatment process using the photo-Fenton reaction (initial Fe ion concentration = 1.3 mg/L; initial H_2O_2 concentration = 500 mg/L).

with UV light started when the experiment started, and the complexes formed were subsequently degraded. Consequently, Fe ion concentration increased with time and the final Fe ion concentration reached 1.3 mg/L.

In the photo-Fenton reaction, Fe^{3+} is reduced by Reaction 2, but the oxidation rate of Reaction 1 is significantly faster than the reduction rate. The Fe^{2+} produced by Reaction 2 was, therefore, immediately oxidized to Fe^{3+} by Reaction 1. As a result, the Fe^{2+} concentration was very low during the reaction.

Improvement in Biodegradability Using Photo-Fenton Reaction

In order to avoid the effects of residual H_2O_2 on the BOD_5 measurements, other experiments to measure the changes in BOD_5 during the photo-Fenton reaction were carried out. In these experiments, the initial H_2O_2 concentrations were varied from 0 mg/L to 500 mg/L. The BOD_5 and TOC of each sample were measured after the H_2O_2 was exhausted. The duration of each experiment was less than 12 h. The experimental results are shown in Fig. 4.

As seen in Fig. 4, the TOC concentration decreases with increasing initial H_2O_2 concentration. The BOD_5 decreased with increasing initial H_2O_2 concentration up to 77 mg/L of H_2O_2 . When the initial H_2O_2 concentration was lower than 77 mg/L, compounds that could be easily degraded by OH radicals would be preferentially degraded by OH radicals. The BOD_5 and TOC, therefore, decreased significantly at low initial H_2O_2 concentrations. At initial H_2O_2 concentrations above 77 mg/L, although the

Fig. 4 - Effects of H_2O_2 concentration on the improvement in biodegradability (initial Fe ion concentration: 1.3 mg/L).

TOC decreased slightly with increasing initial H_2O_2 concentration, the BOD_5 increased gradually. One reason may be due to the accumulation of intermediates that are not adequately degraded by OH radicals, for example, organic acids such as acetic acid and oxalic acid, which have molecular structures of low electron density. As mentioned before, organic acids are classified as biodegradable compounds, therefore, the BOD_5 increased with increasing initial H_2O_2 concentration. This led to an increase in the BOD_5/TOC ratio, i.e., the ratio of biodegradable compounds to total organic compounds. This indicates that non-biodegradable compounds were degraded to biodegradable compounds by reaction with OH radicals.

The value of BOD_5/TOC obtained in this study was relatively high. This may be attributed to the procedure for the measurement of BOD_5 . In this study, the value of BOD_5 included nitrogenous BOD, as mentioned before. Because a filtered supernatant solution of activated sludge contains a nitrogen component, BOD_5 may become higher compared to the value of TOC. Higher nitrogenous BOD value may overestimate the BOD_5/TOC ratio. Thus, further experiments for the estimation of the effects of nitrogenous BOD value on the BOD_5/TOC ratio are required.

Comparison of Degradation Tendencies of Biodegradable and Non-Biodegradable Compounds

Some non-biodegradable compounds have unsaturated bonds, which have high electron densities. Hydroxyl radicals act as an electrophilic agent and preferentially attack non-biodegradable compounds. Figure 5 displays the experimental results for the

Fig. 5 - Comparison of the degradation tendencies of biodegradable and non-biodegradable compounds [initial Fe ion concentration = 1.3 mg/L; initial H_2O_2 concentration = 500 mg/L; initial concentration of biodegradable compound (acetic acid) = 30 mg/L (0.5 mM); initial concentration of non-biodegradable compound (Orange II) = 175 mg/L (0.5 mM)].

comparison of the degradation tendencies of a non-biodegradable compound and a biodegradable compound. It can be seen from the figure that although the concentration of the non-biodegradable compound gradually decreases with time, the concentration of the biodegradable compound does not. After the degradation of the non-biodegradable compound was largely complete, the concentration of the biodegradable compound started to decrease. These results were attributed to the different reactivities of the compounds with OH radicals. The reactivity of Orange II with an OH radical is 10^9 L/(mol·s) (Yuranova *et al.*, 2004), whereas that of acetic acid is 1.6×10^7 L/(mol·s) (Stefan *et al.*, 1996).

CONCLUSIONS

This study focused on the enhancement of the biodegradability of non-biodegradable compounds using the photo-Fenton reaction for the effective use of an activated sludge system. The experimental results revealed the following facts.

1. Hydroxyl radicals generated by the photo-Fenton reaction have the ability to convert non-biodegradable compounds into biodegradable compounds. The OH radicals could also degrade non-biodegradable compounds to CO₂ and H₂O.
2. During the photo-Fenton reaction, biodegradable compounds accumulated in the solution. This is attributed to the differences between the reactivities of non-biodegradable compounds and biodegradable compounds with OH radicals.

This investigation has demonstrated the potential of applying the photo-Fenton reaction to the treatment of returned water. This study was undertaken as a starting point. More verification studies for practical use, such as the effects of phosphorus and nitrogen on the process, are required.

ACKNOWLEDGEMENT

The authors would like to thank the JSPS Research Fellowships for Young Scientists (23·5773).

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