DEVELOPMENT OF ANALYTICAL METHOD FOR DEGRADATION OF PPCPS BY PHOTO-FENTON REACTION

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Introduction:
Pharmaceuticals and personal care products (PPCPs) have discharged into the aquatic environment, because the current sewage treatment process (e.g., activated sludge process) is not designed to remove PPCPs. Their adverse effects on the environments are concerned. In fact, diclofenac (DCF), which is used as an analgesic or anti-inflammatory, has been detected from the Yamato-gawa river in Japan (46.8 ng L^{-1})[1]. Clarithromycin (CAM) and triclosan (TCS), which are used as antimicrobial agents, have been detected at the concentrations over predicted no-effect concentration (PNEC) for aquatic life[2, 3].

Advanced oxidation processes (e.g., photo-Fenton reaction) are a promising technology to effectively remove PPCPs. Photo-Fenton reaction can continuously generate hydroxyl radicals having powerful oxidation potential by combining iron ions, hydrogen peroxide, and light energy under normal pressure and temperature. 3-Aminopyridine, which is an anti-inflammatory drug, was successfully degraded by the photo-Fenton reaction in 90 minutes (initial concentration: $10-30$ mg L^{-1})[4]. DCF was also successfully removed by the advanced oxidation process (titanium dioxide photocatalysis) (initial concentration: 30 mg L^{-1})[5]. Although the previous researches reported that the advanced oxidation processes could degrade PPCPs successfully, the initial PPCP concentrations in the removal experiments are likely to be higher than their concentrations detected in the actual environments. Given that the degradation mechanisms of PPCPs by the advanced oxidation processes can be significantly affected by the initial concentrations, the removal efficiency could be over- or under-estimated. Our previous study reported that the removal of carbamazepine (CBZ) and DCF by three different advanced oxidation processes was inhibited by co-existing substances existed in the actual wastewater, and the inhibition effects were increased with decreases in the initial concentrations of PPCPs[6]. The removal efficiencies for Reactive Orange 4 and Acid Yellow 23 by the Fenton and photo-Fenton reactions were decreased with increases in the initial concentaraions[7, 8]. Therefore, the removal experiments should be carried out in a low initial concentration (i.e., actual concentration in the environment).

In the removal experiments at low initial concentrations, the analytical method to determine the concentrations of PPCPs could be difficult due to the unintentional degradation of PPCPs during the analysis. Compared with the removal experiments at a high initial concentration, the effects of unintentional degradation on the removal efficiency could be higher. Therefore, the degradation reaction should be immediately quenched in the removal experiments at a low initial concentration to avoid overestimating the removal efficiency. However, the analytical method, especially the quenching technique, for PPCPs during the degradation experiments has not been quantitatively investigated and limited.

In this study, the effects of unintentional degradation on the removal efficiency were quantitatively investigated and the analytical method for PPCPs during the degradation experiments by the photo-Fenton reaction, including the quenching technique was developed. Using the developed analytical method, the degradation of DCF by the photo-Fenton reaction was carried out.

Materials and methods:
Degradation experiments of DCF by photo-Fenton reaction
The degradation of DCF was carried out in a 500 mL Pyrex glass beaker. The working volume was 0.25 L. The solution containing target PPCP (DCF) was adjusted to pH = 3, which is the optimum pH for the photo-Fenton reaction, using sulfuric acid. The UV-A light irradiation sources were three 6-W near-UV-A fluorescent lamps (black light blue lamps) with a radiation peak at 380 nm. The lamps were located around the reactor, and they externally irradiated the reactor. The experiment was initiated by addition of a known amounts of hydrogen peroxide and ferrous ions (iron (II) sulfate heptahydrate) to the reactor and lighting of the black lights. The solution in the reactor was thoroughly stirred with a magnetic stirrer to ensure complete mixing. Samples were withdrawn using a syringe, and various quenching techniques targeted in this study were applied. The samples were then filtered by using a membrane filter (pore size: 0.22 μL). The concentration of DCF was determined by a high performance liquid chromatograph (HPLC) (Agilent Technologies, Inc.). The hydrogen peroxide concentration was measured by the glucose oxidase method. The concentrations of ferrous ions and total iron ions (the sum of ferrous ions and ferric ions) were analyzed by the 1,10-phenanthroline method.

Analytical method for DCF
Samples, in which the degradation reaction was quenched, were directly introduced to HPLC. The injection volume was 10 µL and the flow rate was set at 0.4 mL min^{-1}. SB-C18 column (2.1 mm × 150 mm, 2.7 µm, Agilent Technologies, Inc.) was used, and the column temperature was maintained at 50°C. The mobile phase A and B consisted of 0.1% or 0.01% (v/v) formic acid in water and 0.1% (v/v) formic acid in methanol, respectively. The gradient program was started with 30% the mobile phase B, kept isocratic for 1 min, rose to 100% in 4 min, kept isocratic for 5 min, and fell to 30% in 5 min. A diode array detector (DAD) was used for the detection. Full spectra were recorded in the range of 190–400 nm. Detection wavelength for DCF was set at 283 nm.

Results and discussion:
Development of quenching technique
The photo-Fenton reaction consists of two reactions. The first reaction is the Fenton reaction (Eq. 1).

$$Fe^{2+} + H_2O_2 \rightarrow \cdot OH + Fe^{3+} + OH^- \tag{1}$$

In this reaction, a ferrous ion reacts with a hydrogen peroxide to produce a ferric ion and a hydroxyl radical. The second reaction is the photo-reduction reaction (Eq. 2).

$$FeOH^{2+} + h\nu \rightarrow \cdot OH + Fe^{2+} \tag{2}$$

The ferric ion is exposed to light energy (wavelength is less than 540 nm), which results in the production of a ferrous ion and a hydroxyl radical. Under no irradiation of light energy, the Fenton like reaction is occurred instead of the photo-reduction reaction (Eq. 3).

$$Fe^{3+} + H_2O_2 \rightarrow \cdot OOH + Fe^{2+} + H^+ \tag{3}$$

The reactions in Eqs. 1−3 are successively occurred, hydroxyl radicals are continuously produced. Therefore, to quench the degradation reaction, iron ions (ferrous and ferric ions) and hydrogen peroxide should be removed immediately.

To remove iron ions, a phosphate buffer was used. By adding the phosphate buffer (phosphate buffer : sample = 1 : 5) to the sample (pH = 3), the pH of the sample was increased and neutralized (pH = 6.86). The ferric ions in the sample were then precipitated as ferric hydroxide. In addition, phosphate ion in the phosphate buffer makes a complex with a ferric ion (insoluble iron phosphate). As a result, iron ions could be removed.

To remove hydrogen peroxide, the powder of manganese dioxide was added to the sample. To determine the optimum concentration of the powder of manganese dioxide, the pre-experiment was carried out. A various concentrations of manganese dioxide powder (0.005-0.1 g mL^{-1}) were added to the solution, which contained 500 mg L^{-1} hydrogen peroxide. The sample was vortexed for 1 min, and then the concertation of residual hydrogen peroxide was measured. A higher concentration of manganese dioxide powder led to a lower concentration of residual hydrogen peroxide. However, the concentrations of residual hydrogen peroxide were increased above the optimum concentration of manganese dioxide powder. A higher concentration of manganese dioxide powder has a larger reaction surface area to catalytically remove the hydrogen peroxide, which improved the removal of hydrogen peroxide. However, at a very high concentration (above the optimum concentration), manganese dioxide powder was sedimented and covered the surface, which inhibited the removal of hydrogen peroxide. Consequently, the optimum concentration of manganese dioxide powder was existed. According to the pre-experiment, 0.01 g mL^{-1} was the optimum concentration and 98% hydrogen peroxide was removed within 1 min.

In addition to two quenching techniques as mentioned above, methanol (radical scavenger) was added to remove hydroxyl radicals produced by the Fenton and Fenton like reactions. The effects of three quenching techniques on the unintentional degradation of DCF during the analysis were quantitatively measured. The DCF concentrations at 10 min after starting the degradation were determined after the quenching techniques were applied. After 2 and 20 h, the DCF concentrations were repeatedly measured. The ratios of DCF concentrations measured immediately and after 2 or 20 h (change rates) were shown in Figure 1. Without any quenching techniques, the change rate was 64%, which means DCF could be unintentionally degraded during the analysis. By using the combination of three quenching techniques (simultaneously adding phosphate buffer, methanol, and manganese dioxide into the sample), the concentrations of DCF was not changed for 20 h (0.64%). From these

results, the unintentional degradation reaction during the analysis could be successfully quenched by adding three reaction terminators.
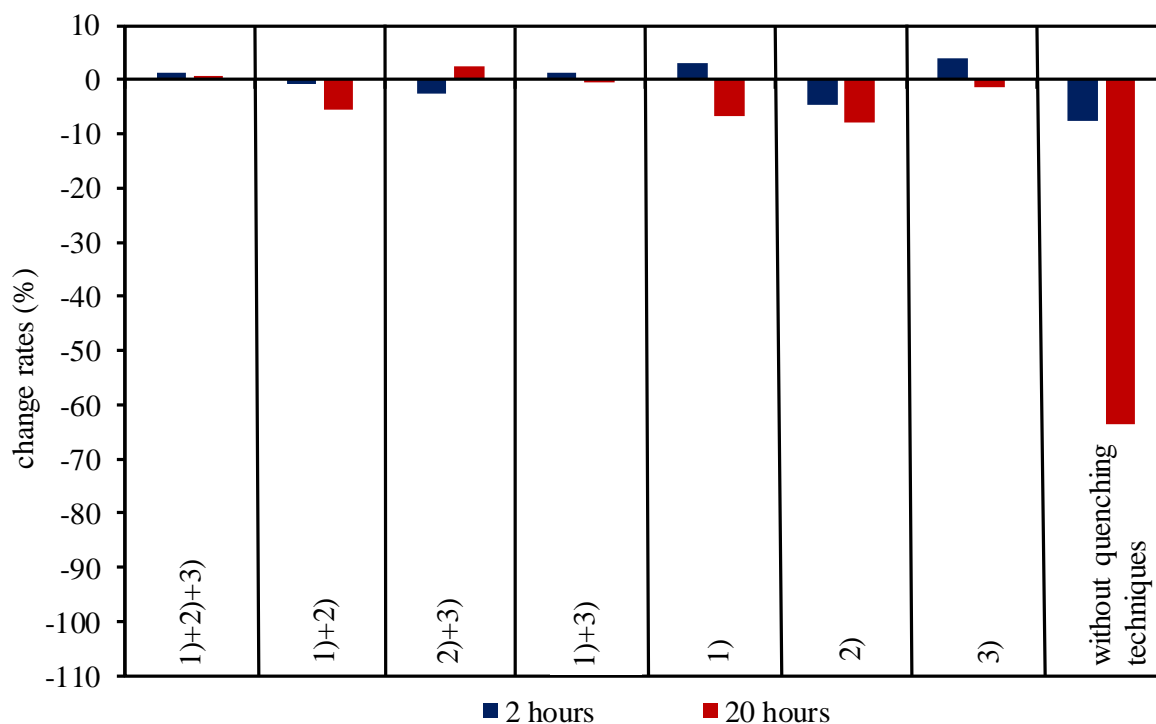

Figure 1: Quantitative Evaluation of Quenching Techniques for Degradation of Diclofenac by Photo-Fenton Reaction (1) Phosphate Buffer, 2) Manganese Dioxide, 3) Methanol).

Degradation of DCF by photo-Fenton reaction

The degradation reaction of DCF by the photo-Fenton reaction was carried out by the reaction of DCF with hydroxyl radicals. Therefore, the degradation of DCF is theoretically expressed by the following equation.

$$\frac{dC}{dt} = -k_{OH}C_{OH}C \tag{4}$$

where C is the concentration of DCF (mg L^{-1}), C_{OH} is the hydroxyl radical concentration (mg L^{-1}), k_{OH} is the reaction rate constant (L mg^{-1} min^{-1}), and t is the time (min). Because k_{OH} is extremely high (10^5–10^{10} L mol^{-1} s^{-1}), C_{OH} can be immediately achieved at the pseudo-steady-state. Therefore, C_{OH} can be regarded as a constant, and thus the degradation of DCF by the photo-Fenton reaction can be treated as the pseudo-first-order reaction as shown in the following equation.

$$\frac{dC}{dt} = -k_{OH}C_{OH}C = -k_{OH}C_{OH,SS}C = -kC \tag{5}$$

$$k = k_{OH}C_{OH,SS} \tag{6}$$

where $C_{OH,SS}$ is the hydroxyl radical concentration at steady-state (mg L^{-1}), k is the pseudo-first-order kinetic constant (min^{-1}). Integrating Eq. 5 yields the following equation.

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{7}$$

where C_0 is the initial concentration of DCF (mg L^{-1}). The plot of $\ln\left(\frac{C}{C_0}\right)$ versus t results in a linear relationship. The pseudo-first-order kinetic constant, $k,$ can be obtained from slope of the line.

The results of the degradation of DCF by the photo-Fenton reaction using the developed quenching technique is shown in Figure 2. The experimental conditions were as follows: the initial DCF concentration of 1 mg L^{-1}; the initial ferrous ion concentration of 0.2 mg L^{-1}; the initial hydrogen peroxide concentration of 100 mg L^{-1}. Using the developed quenching technique, the removal of DCF by the photo-Fenton reaction was successfully carried out, and 97% DCF was degraded in 70 min (the final concentration: 0.033 mg L^{-1}). The hydroxyl radicals, which

act as an electrophilic reagent, produced by the photo-Fenton reaction react with pi-conjugated system in DCF (e.g., aromatic ring), which results in shortening the carbon chain. DCF is eventually oxidized into carbon dioxide, water, and inorganic chemicals[9]. Therefore, DCF could be degraded by the hydroxyl radicals produced by the photo-Fenton reaction.

In this study, ferrous ions were used as an iron source for the photo-Fenton reaction. Therefore, the Fenton reaction was instantaneously occurred at first ($t < 1$), and most ferrous ions were oxidized into ferric ions. This resulted in the change in the rate-controlling step. Specifically, the rate-controlling step was changed from the Fenton reaction at the beginning of the experiment ($t < 1$) to the photo-reduction reaction ($t > 1$). As a results, the degradation of DCF by the photo-Fenton reaction can be divided into two phases and expressed by two pseudo-first-order reaction rate constants. The left figure in Figure 2 shows the first phase, in which the Fenton reaction is the rate-controlling step, and the right figure shows the second phase, in which the photo-reduction reaction is the rate-controlling step. The pseudo-first-order reaction rate constants for the first and second phases were 0.28 and 0.044 min^{-1}, respectively.
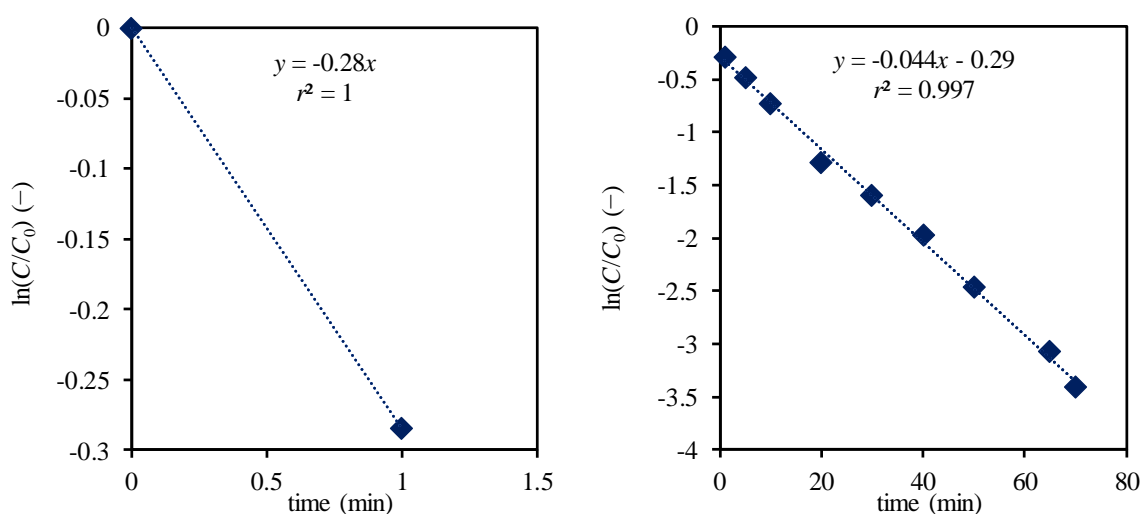

Figure 2: Degradation of Diclofenac by Photo-Fenton Reaction (Left: First Phase, Right: Second Phase).

Conclusions:
In this study, the quenching technique for the degradation of DCF by the photo-Fenton reaction was developed. Using the developed method, the degradation of DCF by the photo-Fenton reaction was carried out. The degradation of DCF was successfully measured, and DCF was degraded by the photo-Fenton reaction.

Acknowledgements:

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