Innovative water treatment system coupled with energy production using photo-Fenton reaction

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ABSTRACT

The treatment of colored effluent coupled with energy production using a modified photo-Fenton process has been examined. Fe and carbon plates were employed as an anode and cathode, respectively. In acidic solution, Fe plates would corrode, which leads to elute ferrous ion from Fe plates into the solution and to yield hydrogen gas at the cathode and to generate an electric energy. The eluted ferrous ion could be used for the photo-Fenton reaction. As a result, decolorization of colored effluent and production of electricity and hydrogen could be carried out simultaneously and effectively. It was found that the Orange II concentration in the colored effluent flow decreased up to 84.2% of inlet concentration at 0.8 of relative position in the liquid flow path of continuous photo-reactor. In our proposed system, the energy production, such as an electric power and a hydrogen gas, can be generated at the same time as the decolorization of colored effluent. The produced electric power was 16.5 Wh kg\(^{-1}\)-Fe\(_{\text{reacted}}\). The produced hydrogen gas was estimated as 13 g-H\(_2\) kg\(^{-1}\)-Fe\(_{\text{reacted}}\).

Key words | colored effluent, decolorization, energy production, hydrogen gas, photo-Fenton reaction

INTRODUCTION

Over 100,000 different types of synthetic dyes are commercially available and 700,000 tons are produced yearly all over the world. They have been extensively used in textile, paper and printing industries and significant losses during manufacture and processing of dyes have been discharged in the effluent (Nishio et al. 2006). Many of them are very toxic to the surrounding environment if not treated properly. They are resistant to biological degradation and color removal by bioprocessing is difficult and not complete. Therefore, the colored effluent including dye stuff required the decolorization and degradation before discharge to the aquatic environment.

Advanced oxidation processes (AOPs) are based on the generation of very reactive species such as hydroxyl radicals that rapidly and nonselectively oxidize a broad range of organic pollutants. The photo-Fenton process, which consists of reactions (1) and (2), has been known as one of the AOPs. Because OH radicals produced by the photo-Fenton reaction have a powerful oxidation, dye stuffs being persistent substances in a colored effluent can be degraded and mineralized to CO\(_2\) and H\(_2\)O by the reaction with OH radicals (Rodriguez et al. 2002). This process may present a potential alternative ability to decolorize recalcitrant colored effluent (Lopez & Kiwi 2001; Sum et al. 2004; Tokumura et al. 2006b).

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow & \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \quad \text{(Reaction 1)} \\
\text{Fe}^{3+} + \text{H}_2\text{O} + \hbar \nu \rightarrow & \text{Fe}^{2+} + \cdot \text{OH} + \text{H}^+ \quad \text{(Reaction 2)}
\end{align*}
\]

A corrosion of iron in an acidic solution has been known well. As byproducts of the corrosion of iron,
electricity and hydrogen could be produced (Rau 2004). On the other hand, the photo-Fenton reaction requires an iron source and acidic condition to avoid the precipitation of Fe\(^{3+}\) ion. From the corrosion of iron, Fe ion can be gained with electric energy and hydrogen energy. Then Fe ion can be utilized for an iron source of the photo-Fenton reaction. Therefore, by the combination of the photo-Fenton reaction and corrosion of iron, the wastewater treatment system coupled with energy production would be developed. A combination of energy production and the photo-Fenton reaction has not been reported in open literature as far as we know. In order to save running cost of the wastewater treatment, the process coupled with energy production is very attractive. In this study, the combination of the photo-Fenton process and the corrosion of iron has been examined, and effects of experimental parameters, such as inlet effluent concentration, Fe and H\(_2\)O\(_2\) concentration, effluent flow rate and surface area of electrodes, on the performance of proposed system have been studied. Fe and carbon plates were employed as an anode and cathode, respectively. In an acidic solution, Fe plates would corrode and it leads to elute ferrous ion from Fe plates into the solution and yield hydrogen gas by the reduction of proton and generate an electric energy by the electron transfer from the anode to the cathode. The eluted ferrous ion could be used for the photo-Fenton reaction. As a result, the decolorization of colored effluent and productions of an electricity and hydrogen gas could be carried out simultaneously and effectively.

### METHODS

Hydrogen peroxide (H\(_2\)O\(_2\), 30 wt\%) and iron(II) sulfate heptahydrate (FeSO\(_4\)·7H\(_2\)O) were used as Fenton reagents. In this study, Orange II (C\(_{16}\)H\(_{11}\)N\(_2\)NaO\(_4\)S) being one of azo-dyes was employed for a model azo-dye. Sulfuric acid was used to adjust the initial solution pH. All chemicals were reagent grade and purchased from Kanto Chemical Co., Inc. (Japan). A schematic diagram of the experimental setup is shown in Figure 1. All Experiments were conducted in a continuous mode. The continuous photo-reactor was made of acrylic material and five UV light lamps (20 W, \(\lambda_{\text{max}} = 352\) nm, photon flux = \(5.89 \times 10^{-5}\) einstein s\(^{-1}\)) as a light source of the photo-Fenton reaction were located over the photo-reactor. Top of the photo-reactor was covered by TEMPAX plate which is a material with high transmission over the whole spectrum of irradiated light. The working volume was 10.5 L. Fe plates as an anode and carbon plates as a cathode were set in the photo-reactor as shown in Figure 1. The number of Fe and carbon plates were three, respectively and the total surface area of each plates was 190 cm\(^2\). The inlet flow rate of the colored effluent and H\(_2\)O\(_2\) solution were 250 ml min\(^{-1}\) and 8 ml min\(^{-1}\), respectively. The colored effluent is adjusted the Orange II inlet concentration to 60 mg L\(^{-1}\) and pH to 3 which is optimum pH for the photo-Fenton reaction (Tokumura et al. 2006a). During the experiment, concentrations of Orange II, Fe and H\(_2\)O\(_2\), pH and temperature of effluent were measured. Samples from the liquid phase were withdrawn at predetermined time intervals using a syringe.
from sampling points 2 and 4 (see Figure 1). A produced electric current between electrodes were monitored by a multimeter. Concentration changes of Orange II, Fe and H2O2 was analyzed by an absorptiometry (measured at 486 nm), 1, 10-phenanthroline method (Tokumura et al. 2007) and the glucose C2 reagent method, respectively (Tokumura et al. 2008). The reaction temperature was kept constant at the room temperature ($18 \pm 1^\circ C$). The pH of the model colored effluent was not controlled but did not changed significantly during experiments. In order to estimate a produced hydrogen gas during the reaction, another small experimental set-up (0.4 L) was used because to measure a produced hydrogen gas due to a minimum detectable hydrogen gas concentration of the detector.

**RESULTS AND DISCUSSION**

The optimum pH for the photo-Fenton reaction is around 3 which is an acidic condition. As mentioned before, an iron corrodes in an acidic solution. Therefore, Fe plates used as an anode in the colored effluent adjusted pH to 3 would corrode. This led to dissolve Fe$^{2+}$ ions into the effluent and generate electrons (Reaction 3). Electrons generated by the corrosion of Fe plates transferred from the Fe anode to the C cathode through the lead. At the cathode, electrons transferred from the anode reduce an oxygen or proton, which produce a hydroxide ion or hydrogen gas (Reaction 4 or 5). As a result, a chemical cell was constructed, which can generate an electric power. Incidentally, the standard electromotive force of the chemical cell assumed that the reduction of proton occurs at the cathode was 0.44 V.

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad E^\circ = -0.44 \text{ V vs. SHE} \quad \text{(Reaction 3)}
\]

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad E^\circ = 1.23 \text{ V vs. SHE} \quad \text{(Reaction 4)}
\]

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad E^\circ = 0 \text{ V vs. SHE} \quad \text{(Reaction 5)}
\]

Although two electrodes were applied, a local cell was also consisted on the anode. Therefore, Reaction (4) or (5) might also occur on the anode. As a result, a hydroxide ion was produced on the anode, which increases the pH around the surface of the anode and produces a ferrous hydroxide (Reaction 6).

\[
2\text{OH}^- + \text{Fe}^{2+} \rightarrow \text{Fe}(	ext{OH})_2 \quad \text{(Reaction 6)}
\]

Ferrous hydroxide quickly dissolves in an acidic solution (Reaction 7).

\[
\text{Fe}(	ext{OH})_2 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O} \quad \text{(Reaction 7)}
\]

However, when a potent oxidant (e.g. hydrogen peroxide) existed in the solution, Reaction (8) would occur instantaneously and produce a ferric hydroxide which is a brownish-red insoluble complex.

\[
\text{Fe}(	ext{OH})_2 + 1/2\text{H}_2\text{O} + 1/4\text{O}_2 \rightarrow \text{Fe(OH)}_3 \text{ or } 1/2\text{Fe}_2\text{O}_3 + 3/2\text{H}_2\text{O} \quad \text{(Reaction 8)}
\]

A ferric hydroxide was dewatered, and it produces iron oxyhydroxides (Reaction 9), subsequently iron oxyhydroxides would be reduced and form a triiron tetroxide (Reaction 10).

\[
\text{Fe(OH)}_3 \rightarrow \text{FeOOH} + \text{H}_2\text{O} \quad \text{(Reaction 9)}
\]

\[
6\text{FeOOH} + 2e^- \rightarrow 2\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + 2\text{OH}^- \quad \text{(Reaction 10)}
\]

The formation of a triiron tetroxide on the Fe plate leads to passivate the Fe plate. The passivated Fe plate which was covered with a triiron tetroxide film inhibits the dissolution of iron. In order to avoid the passivation of Fe plate, the H2O2 inlet located after the place where Fe plates were set. On the other hand, Fe$^{2+}$ ions dissolved from the anode were used to decolorize the colored effluent by the photo-Fenton reaction (Reactions 1 and 2). The photo-Fenton reaction produces OH radicals, which attack to dye stuffs in the colored effluent. Ultimately, dye stuffs would be mineralized to CO2 and H2O (Reactions 11 and 12).

\[
\cdot\text{OH} + \text{pollutants or dyestuffs} \rightarrow \text{intermediates} \quad \text{(Reaction 11)}
\]

\[
\cdot\text{OH} + \text{intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \text{(Reaction 12)}
\]

The schematic of mechanism for the innovative water treatment system was shown in Figure 2.
Typical experimental results

The time changes of concentrations of Orange II, Fe and H$_2$O$_2$ at 0.8 of the relative position in the liquid flow path of the continuous photo-reactor and the electric current between electrodes were depicted in Figure 3A). It can be seen from this figure that the H$_2$O$_2$ concentration increased earlier than concentrations of Fe and Orange II at about 25 min of elapsed time. The reason for this was that the inlet position of H$_2$O$_2$ solution is 0.2 of the relative position in the liquid flow path which is later than inlet positions of Orange II and Fe. The Fe concentration in the effluent flow increased about 33 min of elapsed time due to the dissolution of Fe plates (Reaction 3). When Fe and H$_2$O$_2$ exist in the effluent flow, the photo-Fenton reaction (Reactions 1 and 2) could occur, the Orange II concentration in the effluent flow decreased gradually due to the photo-Fenton reactions (Reactions 1–2 & 11–12) while going through the continuous photo-reactor. At about 50 min of elapsed time, the Fe concentration in the effluent flow reaches the maximum value of 3.67 mg L$^{-1}$, and the Orange II concentration in the effluent flow decreased up to 10.4 mg L$^{-1}$ being the minimum value. In other word, 84.2% of inlet Orange II concentration could be treated until 0.8 of the relative position in the liquid flow path (see Figure 3B).

After reaching the maximum values of the Fe concentration in the effluent flow, it decreases gradually. The decrease in the Fe concentration inhibited the consumption of H$_2$O$_2$ by the photo-Fenton reaction, and the H$_2$O$_2$ concentration in the effluent flow was increased. These might be attributed to the formation of the oxide layer (a triiron tetroxide film) on the surface of the anode by Reactions (6–10). The oxide layer prevents to elute Fe ions from the anode. The decreasing of the Fe concentration inhibits the photo-Fenton reaction, which leads to decrease the consumption of H$_2$O$_2$ and increase the concentration of H$_2$O$_2$ in the effluent flow. As a result, the decolorization rate dropped, and the Orange II concentration increases slightly. Finally, the Fe concentration in the effluent flow achieved at a pseudo-steady state, which concentration was about 3 mg L$^{-1}$.
On the other hand, the electric current between electrodes decreased sharply at the beginning of the experiment, and then increased gradually. After 70 min of elapsed time, it reached about 1.96 mA which is 0.10 A m\(^{-2}\) of the current density. The formation of an oxide layer on the surface of the anode decreased the redox potential of the anode due to the inhibition of provision reductants (e.g. oxygen and proton) to the surface of the anode, which led to increase the current. The theoretical produced electric power, \(P\) [Wh kg\(^{-1}\)Fe\(_{\text{reacted}}\)] was calculated following Equation (Equation 1).

\[
P = \frac{IE}{5.6V_{\text{elute}}M_{\text{Fe}}} \quad \text{(1)}
\]

where \(I\) [A m\(^{-2}\)] is a current density, \(E\) [V] is the standard electromotive force of the chemical cell which is 0.44 V assumed in this study, \(M_{\text{Fe}}\) is the molecular weight of Fe and \(V_{\text{elute}}\) [mol m\(^{-2}\)s\(^{-1}\)] is the elution rate of Fe ion from the anode, which was calculated by:

\[
V_{\text{elute}} = \frac{C_{\text{Fe,eq}}Q}{6.0 \times 10^5AM_{\text{Fe}}} \quad \text{(2)}
\]

where \(C_{\text{Fe,eq}}\) [mg L\(^{-1}\)] is the Fe concentration in the effluent flow at the pseudo-steady state, \(Q\) [mL min\(^{-1}\)] is the liquid flow rate of the colored effluent and \(A\) [m\(^2\)] is the superficial area of liquid flow path. The elution rate of Fe ion, \(V_{\text{elute}}\) of 1.36 \times 10\(^{-3}\) mol m\(^{-2}\)s\(^{-1}\) was obtained. This value is very similar to the Rau’s result (2004) which is 10\(^{-5}\) mol m\(^{-2}\)s\(^{-1}\). Consequently, the theoretical produced electric power was calculated with 16.5 Wh kg\(^{-1}\)Fe\(_{\text{reacted}}\).

From Reaction (3), 1 mole of Fe can produces 2 moles of electron. An electron charge of an electron is 1.602 \times 10^{-19} C. Assuming that all electrons produced by the corrosion of Fe plates transfer to the cathode, the theoretical current density would be 0.26 A m\(^{-2}\). However, 0.10 A m\(^{-2}\) of the current density was observed in this study. Therefore, 3.9% of electrons produced by the corrosion of Fe might be reacted at the cathode as the chemical cell mechanism and other electrons might be reacted at the anode as the local cell mechanism. In other words, 3.9% of produced electrons could be recovered as an electric power. This electric power generation efficiency depended on the distance between electrodes. Therefore it could increase by the decrease in the distance between electrodes.

In generally, the decolorization reaction by the photo-Fenton reaction was obeyed a first-order kinetics corresponding to the time with respect to the concentration of dye stuffs. In this study, therefore, we assumed that the decolorization of Orange II by the modified photo-Fenton reaction coupled with energy production was obeyed following equation.

\[
\frac{dC}{dx} = \frac{dC}{dt} \times \frac{dt}{dx} = -kL C
\]

where \(C\) [mg L\(^{-1}\)] is the Orange II concentration in the effluent flow, \(x\) [-] is a relative position in the liquid flow path of continuous photo-reactor, \(k\) [min\(^{-1}\)] is a pseudo first order kinetic constant, \(L\) [m] is the total liquid flow path length of continuous photo-reactor and \(u\) [m s\(^{-1}\)] is the superficial liquid velocity of the effluent. The plots of ln\((C/C_{\text{in}})\) vs. the relative position in the liquid flow path for the experimental data results in a straight line (see Figure 3B), and the slope presents \(-kL/u\). From the slope of Figure 3B), a pseudo first order kinetic constant could be calculated, and it was determined as 0.055 min\(^{-1}\).

**Effects of experimental parameters**

In order to investigate effects of the inlet Orange II concentration on the decolorization rate, the inlet Orange II concentration was varied from 40 to 80 mg L\(^{-1}\), and all the other parameters were kept on constant. Experimental results were shown in Figure 4A). As you can see from Figure 4A), the pseudo first order kinetic constant decreases with the inlet Orange II concentration and the Fe concentration in the effluent flow also decreases with the inlet Orange II concentration.

The oxidation–reduction potential of Orange II was 0.15 V vs. Ag/AgCl. Therefore, it could act as a weak oxidant, which improves Reaction (8) and the formation of an oxide layer on the surface of the anode. Moreover, higher Orange II concentration reduces the transmission of light, which leads to decrease the light intensity in the effluent. Therefore, Reaction (2), which is the rate-controlling step of the photo-Fenton reaction, would be inhibited. As a result, the increase in the inlet Orange II concentration causes the depression of the decolorization rate.
It can be seen from Figure 4A that the produced electric power increases slightly with increasing the inlet Orange II concentration. This is why that the electric current increases by the formation of an oxide layer which was enhanced by the increase in the inlet Orange II concentration.

The Fe concentration is very essential parameter in the decolorization by the photo-Fenton reaction. In this study, the Fe concentration in the effluent flow was varied by means of the changing number of Fe plates setting at 0.1 of the relative position in the liquid flow path of continuous photo-reactor, and 1, 3, and 5 Fe plates having 63.3, 190 and 316.7 cm² of surface area, respectively, were studied. It should be noted that the effect of surface area of electrodes includes the effect of distance between electrodes due to the limitation of the experimental setup configuration. All the other parameters were kept on constant. Experimental results were shown in Figure 4B. It was found that higher surface area causes higher Fe concentration in the effluent flow as expected, and the increase in the Fe concentration enhances the decolorization rate of the colored effluent.

Moreover, the increase in the surface area of the anode leads to not only enhance the decolorization, but also improve the electric current and the generation of hydrogen gas. The dissolution of Fe and the generation of hydrogen are very in correlation because hydrogen gas was generated by the reduction of proton at the cathode, and the reduction reaction occurred by electrons generated by the dissolution of Fe at the anode. Therefore, more dissolution of Fe into the solution enhances the generation of electrons, and they would reduce more protons in the effluent to generate hydrogen gas.

On the other hand, the produced electric power decreases with increases in the surface area of Fe plates.

Figure 4  |  Effects of experimental parameters on the process. (—pseudo first order kinetic constant, —Fe concentration in the effluent flow, —produced electric energy, —amount of eluted Fe ion).
Since Fe plates were placed along the liquid flow pass in this study, added Fe plates were far from cathode, which leads to increase the electric resistance between electrodes. Therefore, electrons produced at added Fe plates would become the tendency to be consumed at the anode by the local cell mechanism, and electric current decreased with increases in the number of Fe plate.

Effects of effluent flow rate were shown in Figure 4C). The effluent flow rate was varied from 150 mL min$^{-1}$ to 400 mL min$^{-1}$, which was from 0.754 × 10$^{-3}$ to 1.94 × 10$^{-3}$ m s$^{-1}$ in the superficial liquid velocity. All the other parameters were kept on constant. It can be seen from Figure 4C) that the increase in effluent flow rate from 150 mL min$^{-1}$ to 250 mL min$^{-1}$ enhanced the decolorization rate slightly. Conversely, over 250 mL min$^{-1}$ of the effluent flow rate, the decolorization rate decrease with increase in the effluent flow rate. The increase in the effluent flow enhances the transfer of a proton or oxygen, which could act as the electron acceptor, from the bulk solution to the surface of Fe plate due to the promotion of the convection flow. As mentioned before, the Fe dissolution rate was controlled by the supply rate of the electron acceptor to the cathode or the local cathode on the anode. Therefore, the corrosion of Fe plates was improved by the increase in the effluent flow rate, and the amount of eluted Fe increased. However, excessive augmenting of the effluent flow rate leads to the excessive supply of the electron acceptor. The excess electron acceptor improves the formation of an oxide layer, which inhibits to elute Fe ion from Fe plates. Furthermore, the Fe concentration in the effluent would be diluted with the increase in the effluent flow, and decrease. Consequently, the Fe concentration in the effluent flow would decrease. On the other hand, the augmenting of the effluent flow rate also decreases the residence time due to the increase in the superficial liquid velocity and it depresses the extent of decolorization at each relative position in the liquid flow path. From these reasons, the optimum effluent flow rate existed, and it was 250 mL min$^{-1}$.

Effects of the inlet H$_2$O$_2$ concentration on the decolorization rate were investigated in the range of 5–22 g L$^{-1}$ and results were shown in Figure 4D). All the other parameters were kept on constant. It may be seen from Figure 4D) that the increase in the inlet H$_2$O$_2$ concentration improves the decolorization rate of the colored effluent.

At the low inlet H$_2$O$_2$ concentration, more OH radicals formed as the inlet H$_2$O$_2$ concentration increased and OH radicals preferentially attacked the Orange II in the effluent. However, when the inlet H$_2$O$_2$ concentration increased over 11 g L$^{-1}$, decolorization rates were not changed significantly. While the excess hydrogen peroxide also enhanced the formation of OH radicals, excess OH radicals reacted with other excess OH radicals or excess hydrogen peroxide acted as a radical scavenger. Consequently, the decolorization rate decreased. From above reasons, the inlet hydrogen peroxide concentration had the optimum concentration, which was about 11 g L$^{-1}$.

On the other hands, the inlet H$_2$O$_2$ concentration should not affect the Fe concentration in the effluent flow and the produced electric power in this study. As mentioned before, the H$_2$O$_2$ solution was added to the liquid passed the electrodes. Therefore, the H$_2$O$_2$ was not contact with Fe plates. As a result, the Fe concentration in the effluent flow and the produced electric power are not related to the inlet H$_2$O$_2$ concentrations theoretically. However, the slight increase in Fe concentration with increasing inlet H$_2$O$_2$ concentrations was found. This might be possibility of local backflow of the liquid including H$_2$O$_2$ in the reactor with the low effluent flow rate. An increase in hydrogen peroxide around the electrodes might improve the elution of Fe ion from the anode.

**Estimation of the produced hydrogen gas**

As mentioned before, in order to estimate the produced hydrogen gas during the decolorization of the colored effluent, another small experimental set-up was used, and results were shown in Figure 5. It can be seen from this figure that the produced hydrogen gas was 13 g H$_2$ kg$^{-1}$ Fe$_{reacted}$ at the inlet Orange II concentration of 60 mg L$^{-1}$ and decreased with increases in the inlet Orange II concentration. An Orange II could act as the electron accepter and was reduced by the electrons generated by the corrosion of Fe plates. Therefore, the usage ratio of the produced electrons by the Fe corrosion to the reduction of protons for the generation of the hydrogen gas was reduced. Consequently, the produced hydrogen gas decreased with the increase in the inlet Orange II concentration.
Economic evaluation of this system

Fe being the catalyst of the photo-Fenton reaction is the 4th most abundant element in the earth, especially in Japan, has been extensively used in industries, and many waste irons were produced over the world. In the USA, scrap iron of $10^7$ tons were produced per year, while $3.5 \times 10^7$ tons in Japan. According to the research of Rau (2004), the scraped iron can be reused as the anode, and its cost is $100 per ton-Fe. In this experiment, the hydrogen energy of $13 \text{ g-H}_2 \text{ kg}^{-1}\text{-Fe}_{\text{reacted}}$ and the electric power of $16.5 \text{ Wh kg}^{-1}\text{-Fe}_{\text{reacted}}$ were generated with the decolorization of the colored effluent. Assuming a value of $3.6 \text{ kg}^{-1}\text{-H}_2$ and $0.05 \text{ kWh}^{-1}$, it was estimated that their benefits were $46.6$ and $0.82$ per ton-Fe reacted, respectively, and $47.4$ was recovered totally. However, the hydrogen energy of $36 \text{ g-H}_2 \text{ kg}^{-1}\text{-Fe}_{\text{reacted}}$ and the electric power of $421 \text{ Wh kg}^{-1}\text{-Fe}_{\text{reacted}}$ could be generated theoretically, and about $150$ per ton-Fe reacted would be recovered totally. As a result, $50$ per ton-Fe reacted could be recovered in our proposed system.

CONCLUSIONS

The treatment of colored effluent coupled with energy production using a modified photo-Fenton process has been examined. The increases in the inlet H$_2$O$_2$ concentration and the surface area of Fe plates and the decrease in the inlet Orange II concentration enhanced the decolorization rate of the colored effluent. Optimum effluent flow rate and inlet H$_2$O$_2$ concentration existed, which were 250 mL min$^{-1}$ and $11 \text{ g L}^{-1}$, respectively. In optimum experimental conditions, the Orange II concentration in the colored effluent flow decreased up to 84.2% of the inlet concentration at 0.8 of the relative position in the liquid flow path of the continuous photo-reactor. In our proposed system, the energy production, such as an electric power and hydrogen gas, can be generated at the same time as the decolorization of the colored effluent. The produced electric power was about $16.5 \text{ Wh kg}^{-1}\text{-Fe}_{\text{reacted}}$ and the hydrogen gas of $15 \text{ g-H}_2 \text{ kg}^{-1}\text{-Fe}_{\text{reacted}}$ could be produced. It is emphasis that the increase in the surface area of the anode or the decrease in the distance between electrodes can improve productions of the electric power and hydrogen gas.

Moreover, Fe ion in the treated effluent could precipitate with the dissolved carbon dioxide produced by the mineralization of pollutants as a final production of the photo-Fenton reaction, and it would produce an iron carbonate. Therefore, the carbon dioxide emission could be reduced, and immobilized as a metal carboxylate. The sequestration of carbon dioxide could be carried out simultaneously with the decolorization of the colored effluent coupled with the energy production using a modified photo-Fenton process.

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