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Photo-Fenton process for simultaneous colored wastewater treatment and electricity and hydrogen production

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HIGHLIGHTS

- The process consists of the photo-Fenton process and corrosion of an iron electrode.
- The process achieves wastewater treatment and energy production simultaneously.
- The model satisfactorily predicts the experimental results in the continuous process.

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ABSTRACT

The decolorization of Orange II (azo-dye) using a combination of the photo-Fenton process and electrochemical corrosion of iron, which can be used for wastewater treatment and electricity and hydrogen gas production simultaneously, was investigated. In order to quantitatively estimate experimental parameters such as ultraviolet (UV-A) light intensity, total iron ion concentration, hydrogen peroxide concentration, and Orange II concentration, a dynamics simulation of the proposed combined process for continuous decolorization was developed. As the total iron ion concentration and UV-A light intensity increased, the decolorization rate constant increased. The decolorization improved as the hydrogen peroxide concentration increased until a critical hydrogen peroxide concentration was achieved. An increase in the initial Orange II concentration depressed the photo-Fenton decolorization. The proposed model satisfactorily simulated the present experimental results for both batch and continuous systems. It can provide valuable information for reaction kinetics, start-up and shut-down operations, and operability studies, as well as steady-state performance. The electric current and amount of hydrogen gas obtained using the combined process were 3.8 mA and 1.88×10^{-3} mmol/min, respectively.

1. Introduction

Large amounts of synthetic dyes are produced and used in many different industries (e.g., textile, paper, and printing industries). During the manufacture and processing of dyes, significant losses are discharged into effluents [1,2]. Many of them are very toxic to the surrounding environment if they are not treated properly. They are resistant to biological degradation and color removal. Biological treatment is therefore difficult and incomplete [3].

The decolorization of azo-dyes using the photo-Fenton process has been investigated as a promising treatment technique [4–7]. The photo-Fenton process has been effectively used for wastewater treatment in recent years [8–13]. The overall mechanism of the photo-Fenton process is well known [14,15]. The Fenton reaction produces a hydroxyl radical in an acidic solution by the iron-catalyzed decomposition of hydrogen peroxide, as expressed in:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (1)$$

The photo-Fenton reaction, which is the photoreduction of the complex $Fe(OH)^{2+}$ under ultraviolet (UV-A) or adequate visible light, also produces a hydroxyl radical and reduces Fe(III) to Fe(II) [16].

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \cdot OH \quad (2)$$

This reaction is followed by Eq. (1), and an iron cycle between Fe(II) and Fe(III) occurs under light irradiation. The hydroxyl radicals generated by Eqs. (1) and (2) can react with target organic substances. Ultimately, the target organic substances are mineralized to carbon dioxide and water [17].

In a previous study [11], a combination of the photo-Fenton process and electrochemical corrosion of iron was investigated. This process is able to treat wastewater and simultaneously produce energy, which has the benefit of helping to reduce running costs. The combined process involves installing electrodes (an iron anode and a cathode) in a classic photo-Fenton process to produce

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energy. The mechanism of the process is as follows. In acidic solution, an iron anode is corroded, which leads to elution of ferrous ions and produces electrons. This yields hydrogen gas at the cathode via reduction of protons by the electrons and generates electric energy via electron transfer between the electrodes. The eluted ferrous ions can be used as an iron source for the photo-Fenton process. As a result, by using the combined process, the degradation of pollutants and energy production are simultaneously achieved. Although the combined process has many advantages, as mentioned above, there are still many problems to be solved. In particular, little effort has been made to understand the effects of the operating parameters on the degradation of pollutants and energy production.

In this study, the effects of experimental parameters such as initial concentrations of total iron ions, hydrogen peroxide, and pollutants, and UV-A light intensity on the photo-Fenton process and on the combined process were investigated. Additionally, in order to quantitatively evaluate the effects of the experimental parameters, a simple kinetic model of the photo-Fenton process and the combined process was developed. The model was developed based on experimental data for a photo-Fenton batch process, and it was then evaluated using the experimental data for the combined process in continuous mode. Although models of the continuous process can provide valuable information for the determination of the optimum operational parameters at process start-up and shut-down, there have only been a few studies of continuous process models. A better understanding of these processes will enable rational design and scale-up of photoreactors. In this study, Orange II was used as a model dyestuff; it is a typical non-biodegradable azo-dye.

2. Experimental

2.1. Chemicals

Reagent grade hydrogen peroxide (30 wt% solution), iron(II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), sulfuric acid, sodium hydroxide, and Orange II were all purchased from Kanto Chemical (Japan). They were used without any further purification. The iron and carbon plates used as electrodes were obtained from Narika (Japan).

2.2. Methods

2.2.1. Decolorization of Orange II in batch process using photo-Fenton process

Batch process experiments were carried out in a Pyrex glass photoreactor of diameter 7.5 cm and height 9 cm. The working volume was 0.4 L. The model colored effluent (the Orange II solution) containing iron(II) sulfate heptahydrate was adjusted to pH 2.5 using sulfuric acid. In general, the optimum pH for the photo-Fenton process is 3.0 [18]. However, in order to effectively produce hydrogen gas from the reduction of protons, a lower pH is adequate. A solution pH of 2.5 was therefore used in this study. This will be discussed in detail in section 3.3. The UV-A light irradiation sources were three 6-W near-UV-A (black light) fluorescent lamps (Sankyo Electronics, Japan) with a radiation peak at 352 nm. The lamps were located around the photoreactor, and they externally irradiated the reactor. The distance between the reactor wall and each lamp was 2.5 cm. The UV-A light intensity at the surface of the reactor was measured using a UV-A radiometer (Topcon, Japan).

All experiments were initiated by addition of a known amount of hydrogen peroxide to the reactor. The solution in the reactor was thoroughly stirred with a magnetic stirrer to ensure complete mixing. Samples from the liquid phase were withdrawn at predetermined time intervals using a syringe. A UV–visible spectrophotometer (Hitachi, Japan) was used to determine the Orange II concentration by absorption photometry (486 nm). The hydrogen peroxide concentration was measured using the glucose oxidase method [19]. The concentrations of ferrous ions and total iron ions (the sum of ferrous ions and ferric ions) were analyzed using the 1,10-phenanthroline method.

2.2.2. Determination of effects of cathode surface area on elution rate

A Pyrex glass reactor of diameter 7.5 cm and height 9 cm was used as a reactor. The working volume was 0.4 L. The solution pH was adjusted to pH 2.5 using sulfuric acid. An iron anode and a carbon cathode in the reactor were connected by a leading wire and fixed using a polyurethane foam support. The ratio of the cathode and anode surface areas was changed by varying the cathode surface area from 0 to 88 cm^2, with a constant anode surface area of 31.5 cm^2. The solution was thoroughly stirred with a shaker (Yamato Scientific, Japan) to ensure complete mixing. The experiments were started when the iron anode was immersed in the solution. Samples from the liquid phase were withdrawn at predetermined time intervals using a syringe. The concentrations of total iron ions and ferrous ions were measured during the process using the same analytical methods as in the batch process.

2.2.3. Decolorization of Orange II using continuous combined process

A schematic diagram of the experimental setup in the continuous process is shown in Fig. 1. The experimental setup consisted of three reactors. The first reactor (Reactor 1) generates energy and supplies ferrous ions for the photo-Fenton process. The second and third reactors (Reactors 2 and 3) decolorize the model colored effluent (the Orange II solution). The reactors were made of Pyrex glass. Three UV-A light lamps (6 W, λ_{max} = 352 nm) as light sources for the photo-Fenton process were located around the reactor. The working volume of each reactor was 0.4 L. Iron anodes and carbon cathodes were set in Reactor 1, as shown in Fig. 1. The model colored effluent was adjusted to an Orange II concentration of 60 ppm and the solution pH was adjusted to 2.5. The inlet flow rates of the model colored effluent and the hydrogen peroxide solution (9.0 g/L) were 18 mL/min and 1.0 mL/min, respectively. The electric current produced was monitored using a multimeter (Mastech, China). Concentration changes with time of Orange II, total iron ions, ferrous ions, and hydrogen peroxide were analyzed

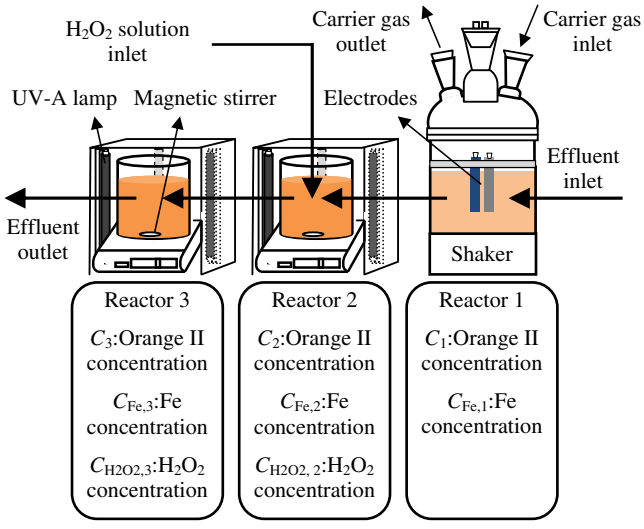

Fig. 1. Experimental setup for continuous process.