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Fenton Oxidation Process Control Using Oxidation-reduction Potential Measurement for Pigment Wastewater Treatment

Young-O Kim, Hai-Uk Nam, Yu-Ri Park*, Jong-Hyun Lee, Tae-Joo Park* and Tae-Ho Lee†**

Institutes for Environmental Technology and Industry, *Dept. of Environmental Engineering,
Pusan National University, Busan 609-735, Korea
**Korea Institute of Environmental Science and Technology, Bulgwang-Dong, Seoul 122-706, Korea
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Abstract−The Fenton oxidation process was applied as a pretreatment process to degrade non-biodegradable organic matters in pigment wastewater. It was necessary to continuously measure the fluctuating concentration of organics in the pigment wastewater and to determine the amount of Fenton's reagent required to oxidize the organics. Batch and continuous flow tests were used to evaluate the relationship between the concentration of organics (COD_{Cr}) and the amount of Fenton's reagent required to achieve a sufficient oxidation of the organics. On-line measurements of the oxidation-reduction potential (ORP) value in the batch and continuous flow tests showed that the maximum ORP values were highly related to the organic concentrations (expressed as COD_{Cr}) and the Fenton's reagent dosage (expressed as H_2O_2 concentration). The empirical equation was $[COD_{Cr}]=8808+0.494[H_2O_2]-14.6ORP$. A control program of Fenton's reagent dosage based on the empirical equation was applied to control of a pilot scale Fenton oxidation process using ORP measurement. The concentration of organics predicted with the control program well agreed with the observed concentration of organics in the pigment wastewater. The variation of the effluent organics concentration of the controlled Fenton oxidation process was significantly reduced compared to that of a process without the control system. These results suggested that the control system of Fenton's reagent dosage using ORP measurement would be applicable to the Fenton oxidation process for efficient pretreatment of pigment wastewater.

Key words: Fenton Oxidation, Oxidation-reduction Potential, Pigment Wastewater, Pretreatment, Auto-control System

INTRODUCTION

Wastewater from the pigment industry has various organic characteristics and is one of the most difficult types of wastewater to treat. Pigment wastewater is almost non-soluble in any solvent and contains high levels of COD, BOD_5, color and suspended solids [Kuo, 1992; Lin et al., 1993; Solozhenko et al., 1995]. Especially, it is hardly treated by conventional activated sludge treatment facilities, and the quality of effluent from the biological treatment process has often exceeded discharge regulations, because the pigment molecules are highly structured polymers and toxic to microorganisms [Halliday et al., 1986; Lin et al., 1993].

In recent years, advanced oxidation processes using ozone, titanium dioxide (TiO_2), ultra violet (UV), and Fenton's reagent (H_2O_2 and ferrous ion) have received considerable attention as effective pretreatment processes of less biodegradable wastewater [Lee et al., 2003]. Among them, Fenton's reagent has been widely used because it is cost effective, easy to treat, reacts well with organic compounds and does not produce toxic compounds during oxidation. In fact, Fenton's reagent, a mixture of H_2O_2 and $FeSO_4$, has been utilized to treat textile wastewater [Kuo, 1992; Lin and Peng, 1995]. The investigators found that Fenton oxidation is effective in decolorizing and degrading organic compounds of the wastewater that contains various types of reactive, acidic and disperse dyes. Fenton oxidation has also been applied to treat other various types of industrial wastewater [Porter and Roth, 1993; Venkatadri and Peters, 1993].

Although a combined use of Fenton oxidation as a pretreatment process with activated sludge process to treat pigment wastewater has produced acceptable process performance even with a short hydraulic retention time (HRT), the fluctuation of effluent quality of Fenton oxidation process has been often caused on decrease of the overall process performance. Because the highly fluctuated effluent quality of Fenton oxidation process depends on the fluctuation of organics concentration in the influent, the amount of Fenton's reagent added should be adjusted according to the influent organic concentrations. For this, it is necessary to measure the variation of organics concentration in the pigment wastewater and to determine the amount of Fenton's reagent required to oxidize the organics.

In this study, 1) on-line measurement of oxidation-reduction potential (ORP) was used to monitor and calculate the organics concentration in the pigment wastewater, and 2) the optimal Fenton's reagent dosage was determined on the base of the relationship between the concentration of organics and the amount of Fenton's reagent required to achieve a sufficient oxidation of the organics. This control system of Fenton's reagent dosage using ORP measurement was applied to a pilot scale process for Fenton oxidation of pigment wastewater.

MATERIALS AND METHODS

1. Pigment Wastewater

Throughout this research, a mixed pigment wastewater from two

†To whom correspondence should be addressed.
E-mail: leeth55@pusan.ac.kr

Table 1. Characteristics of the mixed pigment wastewater used in this study

Item	Concentration range (mg/L)	Average (mg/L)
COD_{Cr}	1,480-1,820	1,640
COD_{Mn}	280-390	330
BOD_5	136-840	480
TSS	62-530	305
VSS	16-120	74
pH	7.2-7.8	7.5

main units of manufacturing process in Songwon color Co. in Ulsan, Korea was used. The process was for manufacturing 1,425 kg/batch of Azo pigment containing yellow and red type polymer pigments. The mean concentration of organics in the mixed pigment wastewater was 1,640 mg/L as COD_{Cr} (chemical oxygen demand measured by using Cr) and 480 mg/L as BOD_5 (biochemical oxygen demand for 5 days). Characteristics of the pigment wastewater used in this study are shown in Table 1. Concentrations of organics (COD and BOD_5) were analyzed according to Standard Methods [APHA, 1995] and the pH value was measured with a digital pH meter (Model HM-14P, TOA, Japan).

2. Batch Fenton Oxidation Test

Evaluation of the relationship among organics concentration (COD_{Cr}), Fenton's reagent dosage, and ORP value was conducted with a batch test. 1-L of the mixed pigment wastewater in a 2-L volume of beaker was added with H_2SO_4 to adjust the pH to 3.0 and received a certain amount of Fenton's reagent dosage consisting of H_2O_2 (35% (v/v)) and $FeCl_2$ (containing 13.5% (w/v) of Fe^{2+}). And then, the change of ORP value depending on the concentration of organics in the pigment wastewater and dosage of Fenton's reagent was measured for 120 min. During that period, the ORP value reached the maximum value and decreased again. The maximum ORP value was used to make the empirical equation between concentration of organics and Fenton's reagent dosage. Experimental conditions of the batch Fenton oxidation test are shown in Table 2.

3. Continuous Flow Fenton Oxidation Test

Table 2. Experimental conditions for the batch Fenton oxidation test

Organics concentration (mg COD_{Cr}/L)	H_2O_2 dosage (mg/L)	Oxidation time (min)	Fe^{2+}/H_2O_2 molar ratio	pH
560	1,000-2,000			
660	2,000-3,000			
860	2,000-3,000	40-120	0.1	3.0
1,000	2,000-4,000			
1,500	2,500-4,500			
1,750	3,000-5,500			

Table 3. Experimental conditions for the continuous flow Fenton oxidation test

Organics concentration (mg COD_{Cr}/L)	H_2O_2 dosage (mg/L)	Oxidation time (min)	Fe^{2+}/H_2O_2 molar ratio	pH
500	400-600			
900	2,000-3,000			
1,260	2,500-3,500	100	0.1	3.0
1,320	2,500-3,500			
1,880	3,000-4,000			

To test the effect of continuous flow on ORP value, a continuous flow Fenton oxidation test was conducted. 50-L of the mixed pigment wastewater with various organics concentration was continuously pumped to a 4.5-L oxidation tank with the flow rate of 44 ml/min. Fenton reagent having different concentrations was also continuously added to the oxidation tank and the change of ORP value was measured until the ORP value reached steady state. Table 3 shows the experimental conditions for the continuous flow test. To establish the relationship among the ORP value, concentration of organics and Fenton reagent dosage, multiple regressions method with Minitap software was used. The derived equation was ap-

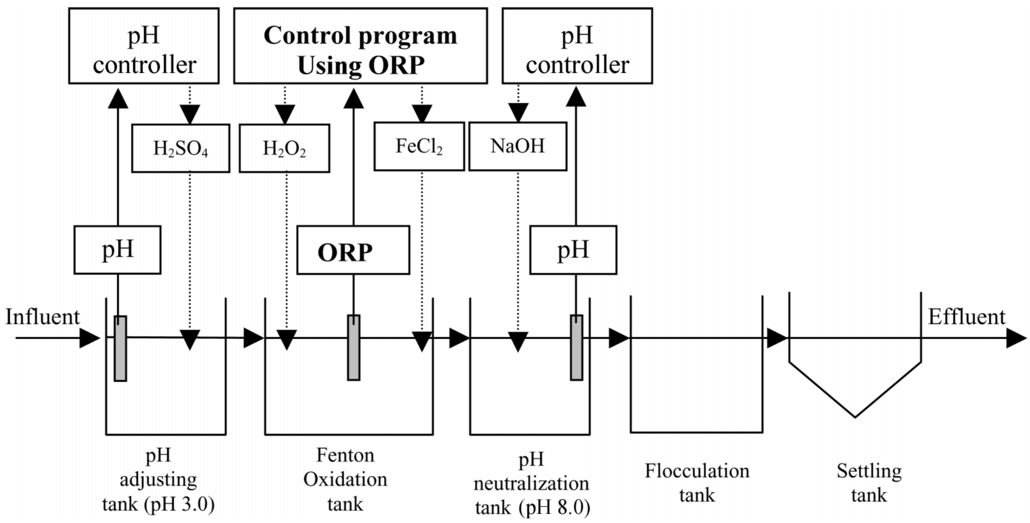

Fig. 1. Schematic diagram of a pilot scale Fenton oxidation process with the control system using ORP measurement.

plied to develop a control program for a pilot scale Fenton oxidation process.

4. Pilot plant Fenton Oxidation Test

A pilot plant with the control system for Fenton oxidation of pigment wastewater consisted of five serial tanks: a pH adjusting tank, a Fenton oxidation tank, a pH neutralization tank, a flocculation tank, and a settling tank. The volume and hydraulic retention time (HRT) of each tank was 0.096 m^3 (HRT: 1.08 hr), 0.144 m^3 (HRT: 1.62 hr), 0.12 m^3 (HRT: 1.35 hr), 0.10 m^3 (HRT: 1.13 hr), and 0.618 m^3 (HRT: 6.90 hr), respectively. The schematic diagram of the pilot plant is shown in Fig. 1. The influent of pigment wastewater entered into the pH-adjusting tank and its pH was adjusted to 3.0±0.1 by adding H_2SO_4. The pH-adjusted wastewater flowed into the oxidation tank and received the Fenton's reagent. The amount of Fenton's reagent was calculated from the empirical equation (see continuous flow test section) by the control program. After Fenton oxidation, the pH of the wastewater was neutralized to pH 8.3±0.1 with NaOH (50% (v/v)) in the pH neutralization tank followed by the flocculation tank. Finally, liquid and solids in the wastewater were separated in the settling tank and the effluent was sent to a following biological treatment system.

RESULTS AND DISCUSSION

1. Evaluation of Relation Among Organic Concentration, Fenton's Reagent Dosage, and ORP Value

To evaluate the relationship among organics concentration, Fenton's reagent dosage and ORP value, the change of ORP value was measured at various concentration matrix of organics (expressed as COD_{Cr}) and Fenton's reagent dosage (expressed as H_2O_2 concentration) for 120 min. Fig. 2 represents a typical pattern of ORP and COD_{Cr} concentration change after addition of Fenton's reagent (H_2O_2, 3,000 mg/L; the Fe^{2+}/H_2O_2 molar ratio, 0.1) to pigment wastewater with 1,500 mg/L of COD_{Cr} concentration. When Fenton's reagent was added, ORP value increased from 560 mV to the maximum

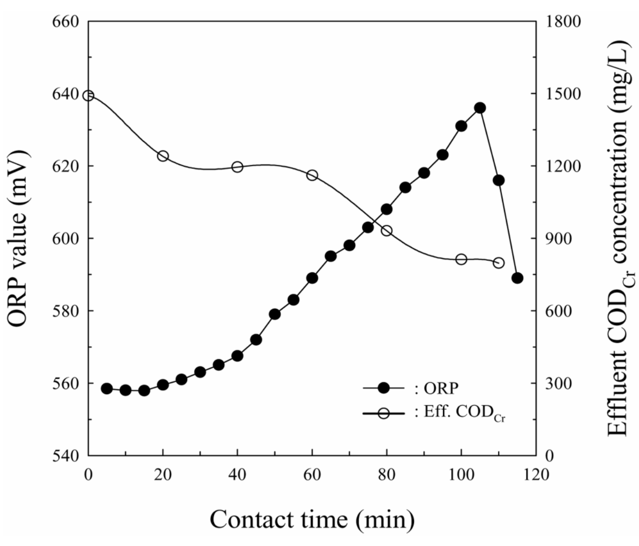

Fig. 2. Change of ORP value and COD_{Cr} concentration by addition of Fenton's reagent into the batch reactor (Initial COD_{Cr} concentration, 1,500 mg/L; H_2O_2 dosage, 3,000 mg/L; Fe^{2+}/H_2O_2 molar ratio, 0.1; pH, 3.0).

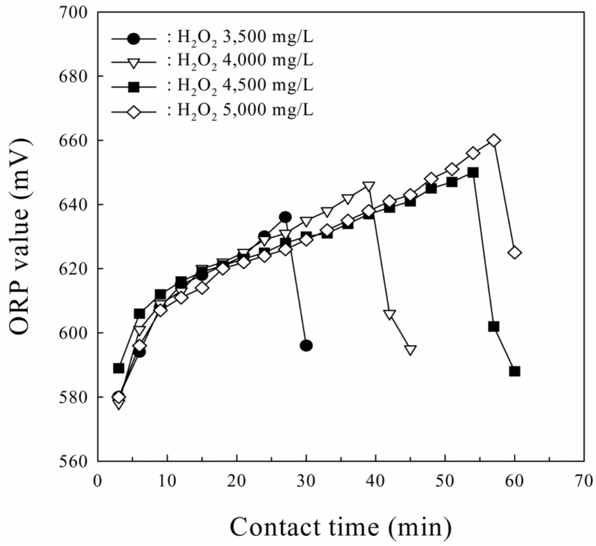

Fig. 3. ORP value vs. H_2O_2 dosage for Fenton oxidation in batch reactor (influent COD_{Cr} concentration: 1,750 mg/L, Fe^{2+}/H_2O_2 molar ratio: 0.1, pH: 3.0).

value of 640 mV within 100 min and then decreased again. According to increase of ORP value, COD_{Cr} concentration was decreased to 720 mg COD_{Cr}/L, suggesting that organic compounds in the pigment wastewater were oxidized by OH radical that was produced directly by Fenton's reagent and generated by subsequent reactions. After 100 min, ORP value rapidly dropped due to depletion of Fenton's reagent to produce OH radicals.

Fig. 3 shows the variation of ORP values according to the Fenton's reagent dosage (expressed as H_2O_2 concentration) to the pigment wastewater with 1,750 mg/L of COD_{Cr} concentration. As the added amount of Fenton's reagent was increased, the maximum ORP value increased and the time required to reach the maximum ORP value was also extended. The maximum ORP value was used to make the empirical equation to calculate the organics concentration of pigment wastewater at a certain concentration of Fenton's reagent.

2. Continuous Flow Fenton Oxidation

The effect of continuous flow on ORP value was evaluated with continuous flow Fenton oxidation test. The amount of Fe^{2+} in the continuous flow test was increased from the Fe^{2+}/H_2O_2 molar ratio of 0.1 to 0.3, because COD_{Cr} removal efficiency was increased according to increase of the Fe^{2+}/H_2O_2 molar ratio 0.1 to 0.3. No more increase of the COD_{Cr} removal efficiency was observed at the ratio above 0.3 (data not shown).

Fig. 4 shows a typical pattern of the variation of the ORP value at a steady state when 3,500 mg/L of H_2O_2 was continuously added into the oxidation reactors receiving continuous flow of pigment wastewater with two different influent concentrations of organics, 1,320 and 1,880 mg/L, respectively. The steady state ORP values were decreased from 625±4.0 to 595±5.0 at the same amount of Fenton's reagent addition (as 3,500 mg/L of H_2O_2), as the influent organics concentration was increased from 1,320 to 1,880 mg/L. The mean value of ORP measurements was used to create the empirical equation to calculate influent organics concentration (COD_{Cr}) at a certain H_2O_2 concentration. Multiple regression of results from the batch and continuous flow Fenton oxidation test produced an

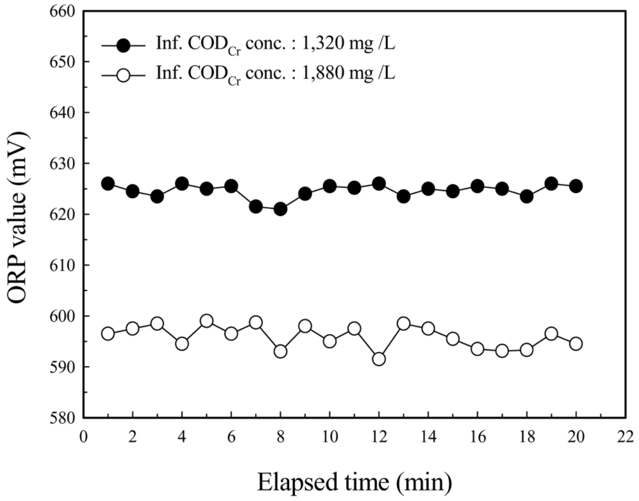

Fig. 4. ORP value at different COD_{Cr} concentrations of influent wastewater that received the same dosage of Fenton's reagent in the continuous flow test (Influent COD_{Cr} concentration, 1,320 mg/L and 1,880 mg/L; H_2O_2 concentration, 3,500 mg/L; Fe^{2+}/H_2O_2 molar ratio, 0.3; pH, 3.0).

equation expressed the relationship among ORP value, Fenton's reagent concentration, and organics concentration as follows:

$$[COD_{Cr}]=8808+0.494\,[H_2O_2]-14.6\,ORP \quad (1)$$

Where, $[COD_{Cr}]$ means organics concentration of the pigment wastewater, $[H_2O_2]$ means the concentration of H_2O_2 added, and ORP is the averaged ORP value measured 5 times for 1 min. The relation coefficient of the equation (R^2) was 0.958.

Fig. 5 shows removal of organics compounds in the continuous flow pigment wastewater with 1,320 mg/L of influent COD_{Cr} depending on the amount of Fenton's reagent added. Increase of Fenton's reagent dosage (i.e., increase of H_2O_2 concentration) shows increase of COD_{Cr} removal. However, the extended H_2O_2 concentration above 2,500 mg/L could not extend COD_{Cr} removal efficiency. This result suggests the optimal dosage of Fenton's reagent to degrade a certain concentration of organics in the pigment wastewater. Based on the results from repeated tests to find out optimal dosage of Fenton's reagent at various concentrations of organics in pigment wastewater, the following equation was established:

$$[H_2O_2]_{opt}=1781+1.27\,[COD_{Cr}] \quad (2)$$

Where, $[H_2O_2]_{opt}$ means optimal dosage of Fenton's reagent expressed as H_2O_2 concentration and $[COD_{Cr}]$ means the concentration of organics in the pigment wastewater.

3. Control of Pilot Scale Fenton Oxidation Process

A control program of Fenton's reagent dosage using ORP measurement was applied to control of a pilot scale Fenton oxidation process. The ORP measurement was used to calculate the concentration of organics in the oxidation reactor by Eq. (1) modified considered scale-up effect and then the amount of Fenton's reagent required to oxidize the organics was determined by using Eq. (2). The concentration of organics ($COD_{predicted}$) in the oxidation reactor predicted by using the control program was well matched with the real organics concentration ($COD_{observed}$) measured by COD_{Cr} method as shown in Fig. 6.

The effect of a pilot scale Fenton oxidation process control using ORP measurement is shown in Fig. 7. The COD_{Cr} concentration of the wastewater in the oxidation reactor was 1,480-1,820 mg/L and the effective addition of the Fenton's reagent obtained a constant COD_{Cr} removal efficiency of 46.9-47.8%. Therefore, the results suggest that the control system with ORP measurement would be effective for Fenton oxidation due to maintaining the relatively stable effluent quality. Consequently, the control system made it possible to reduce the organic loading to the flowing biological treatment process.

CONCLUSIONS

In order to find out the relation among ORP value, organics con-

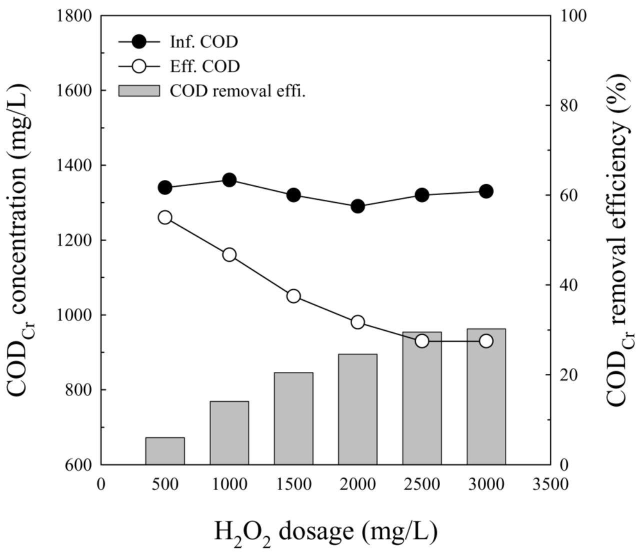

Fig. 5. COD_{Cr} removal according to the amount of Fenton's reagent added in the continuous flow test (Influent COD_{Cr} concentration, 1,320 mg/L; Fe^{2+}/H_2O_2 molar ratio, 0.3; pH, 3.0).

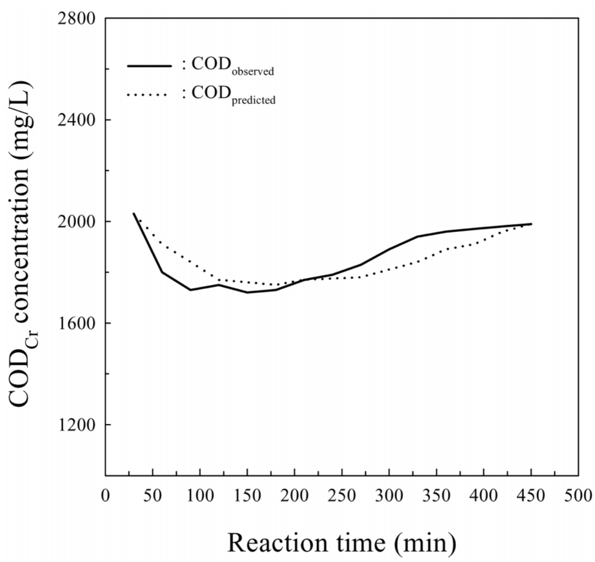

Fig. 6. The real COD_{Cr} measurements and the control program calculated COD_{Cr} in the oxidation reactor of the pilot plant (Fe^{2+}/H_2O_2 molar ratio, 0.3; pH, 3).

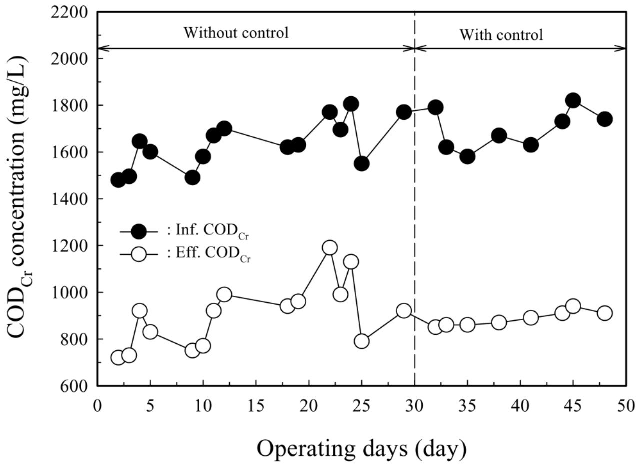

Fig. 7. Influent and effluent COD_{Cr} concentration in the oxidation reactor of the pilot scale Fenton oxidation process with and without the control system using ORP measurements (Fe^{2+}/H_2O_2 molar ratio, 0.3; pH, 3).

centration in the pigment wastewater, and Fenton's reagent dosage, batch and continuous flow tests were conducted. A multiple regression equation to determine the relationship between the maximum ORP value, COD_{Cr} concentration and Fenton reagent dosage was established as follows: $[COD_{Cr}]=8808+0.494\,[H_2O_2]-14.6$ ORP.

Based on the obtained empirical equation, a control system using ORP measurements for optimal Fenton's reagent dosage was applied to a pilot scale Fenton oxidation process to pretreat a mixed pigment wastewater. The concentration of organics in the oxidation reactor predicted by using the control program was well matched with the real organics concentration measured by COD_{Cr} method and the effluent COD_{Cr} fluctuation was apparently decreased compared to that of the not controlled system. These results suggest a control system with ORP measurement would be effective for Fenton oxidation due to saving Fenton's reagent dosage and to maintaining the relatively stable effluent COD_{Cr} concentration, and consequently, to reducing the organics loading to the flowing biological treatment process.

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