Treatment of Wastewaters from Offset Printing Industry by Fenton's Reaction

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Abstract

Offset printing is currently one of the most widely used techniques in the printing industry. This technique can be applied for the production of reading materials including newspapers, brochures, leaflets, magazines, and books. The offset printing business expansion in Thailand has been reported as high as 5-7.5% per year, posing adverse effects on the environment as larger volumes of wastewaters have been produced. Analysis of offset printing wastewater revealed that the chemical compounds in the form of COD were typically in the range of 600-2,100 mg/L, whereas its high color content was also difficult to be treated. Therefore, in this study, advanced oxidation processes (AOPs), using the Fenton's reaction were employed to remove COD and color from the actual wastewater collected from an offset printing company. Batch experiments were conducted to study the effects of Fe^{2+} and H_2O_2 on COD and color removal. The wastewater used in this experiment was previously kept in a container for 3 hours to allow settling of suspended matters. During the Fenton's reaction, the pH of the wastewater was controlled at 3.0 and under ambient conditions. The results demonstrated that the COD removal efficiency was greatly influenced by Fe^{2+} and H_2O_2. At an Fe^{2+}: H_2O_2 ratio of 0.04: 0.20 (w/w), the maximum COD removal efficiency achieved was 89.4%, while the color removal efficiency was 74.8%. Increasing of the H_2O_2 dosages obviously showed an improvement of the color removal efficiency.

Keywords: *Offset printing industry, Fenton's reaction, COD removal, Color removal.*

1. Introduction

Rapid growth of the offset printing industry has been widely recognized in the last decade as can be seen by expansion of publishing and advertising businesses. At present, the production of reading materials including newspapers, brochures, leaflets, magazines, and books generally apply offset printing techniques. In Thailand, 398 printing companies recently registered at the Publishers and Booksellers Association of Thailand in 2011, which is equivalent to a 5-7.5% annual growth rate. This growing scale of the offset printing industry poses detrimental effects to the environment as larger volumes of wastewater have been produced. It has been reported that wastewater discharged from the offset printing industry usually consists of various chemicals used during the manufacturing process, such as lubricating oils, solvents for cleaning, film developing chemicals, waste paint, and metals [1]. These contaminants are originated during pre-printing, printing, and post printing. The major pollutants found in offset printing waste are mainly characterized as volatile organic carbon (VOC), which is extremely toxic to the environment and difficult to be treated by the conventional process [2]. Investigation on chemical characteristics of printing ink wastewater revealed that the BOD_5/COD ratio was relatively low, indicating less biodegradability [3].

Analysis of wastewaters from the offset printing industry showed that various contaminants usually exhibited high COD, suspended solid (SS), and color [3,4 and this study].

The AOPs, based on the formation and reaction of hydroxyl radical ($OH^{\cdot}$), are recommended for degrading non-biodegradable organic substances due to their powerful oxidizing potential [5]. In situ generation of the reactive $OH^{\cdot}$ radicals can be achieved by several approaches such as the Fenton's reaction, photo Fenton's reaction (Fe^{3+}, H_2O_2, hv), UV/H_2O_2, peroxone reaction (O_3/H_2O_2), O_3/activated carbon, O_3/dissolved organic carbon of water matrix, ionizing radiation, vacuum UV, and ultrasound [6]. Among these strategies, generation of $OH^{\cdot}$ by Fenton's reaction seems to be the most cost effective, simple in terms of operation, and the most applicable method for non-biodegraded wastewater treatment [5].

The Fenton's reaction was initiated in 1894 by Fenton [7]. This reaction employs ferrous iron and hydrogen peroxide under the acidic conditions as described in Eq. (1) – (5) [adapted from 8].

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

$$R\text{-}H + HO^{\cdot} \rightarrow R^{\cdot} + H_2O \qquad (2)$$

$$R^{\cdot} + H_2O_2 \rightarrow ROH + HO^{\cdot} \qquad (3)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^{-} \qquad (4)$$

$$R^{\cdot} + HO^{\cdot} \rightarrow ROH \qquad (5)$$

$$2R^{\cdot} \rightarrow \text{Product (dimer)} \qquad (6)$$

During the reactions, the formation of $OH^{\cdot}$ radicals are greatly pH dependent. Thus, organic contaminant degradation can be effectively accomplished under acidic condition (pH < 4.0). Under these conditions, generation of $OH^{\cdot}$ radicals are favorable and Fe^{3+} formed does not precipitated [9].

Accordingly, the Fenton's reaction is employed to treat wastewaters from the offset printing industry. The objectives of this research are to examine the use of the Fenton's reaction to remove COD and color from the actual wastewater collected from an offset printing company and to determine the optimum Fe^{2}: H_2O_2 ratio for the COD and color removal.

2. Methodology

2.1 Wastewater

The actual wastewaters used in the experiments was collected from an offset printing company. Before being used the wastewater was kept for 3 hrs in a 20 L polyethylene container to allow the suspended solids to partially settle and to separate of lubricating oil from the top layer. After settling, the characteristics of the homogeneous wastewaters were analyzed as described in Table 1.

2.2 Experimental design and operation

The experiments were designed to study the effect of Fe^{2+} and H_2O_2 dosages and obtain the optimum $Fe^{2+}$and H_2O_2 at satisfactory COD and color removal efficiency. Batch experiments of the Fenton's oxidation process were conducted by using jar test apparatus (PHIPP & BIRD, U.S.A.) comprised of six paddle rotors and equipped with six 1-L beakers. Each beaker was filled with 500 L of actual wastewater, The pH of wastewater was adjusted to 3.0 by 1 N H_2SO_4 solution. $FeSO_4.7H_2O$ and H_2O_2 were added according to the experimental setup as described in Table 2. The mixtures were processed with constant rotational speeds of 120 rpm for 10 minutes and 95 rpm for 10 minutes. The reaction was allowed to continued for 30 minutes to complete the oxidation process [9,10]. NaOH was then added to raise the pH to the neutral range to enhance the oxidized products precipitated [11]. The supernatants were withdrawn for COD and color analysis. Furthermore, all the experiments were carried out under ambient conditions (28±5ºC).

2.3 Chemical and statistical analysis

In this study, water samples were analyzed according to the Standard Methods for Examination of Water and Wastewater [12]. COD, SS, and color were measured by using close reflux and tritrimetric, gravimetric, and colorimetric methods, respectively. The colorimeter model Hach DR890, U.S.A. was used to determine color in terms of unit, while Hach Senion 156, U.S.A. was used for pH adjustment and measurement.

The process performance data are presented in terms of arithmetic average of value ± standard deviation. All statistical analyses were performed using Microsoft Excel 2007.

3. Results and Discussion

Investigations of offset printing wastewater treatment by using the Fenton's reaction were completed within three replicates. Therefore, the results described in this sections are presented in terms of the average values. The actual wastewaters used in batch experiments after suspended solids partly being removed contained an average COD and color of 1,010 mg/L and 1,616 unit, respectively.

Table 1. Actual wastewater characteristics collected from the offset printing industry.

Parameter	Unit	Range
pH	-	7.5-8.0
Temperature	ºC	25-30
BOD_5	mg/L	70-90
COD	mg/L	600 - 2,100
Color	unit	790 - 2,700
Fat, Oil and Grease	mg/L	5-10
Suspended solids	mg/L	14-50
Total Dissolved Solids	mg/L	1100-1500
Total Kjeldahl Nitrogen	mg/L	10-20

3.1 Effects of H_2O_2 dosage on the COD and color removal

The key factor to achieve an efficient oxidation of organic substances is the $OH^{\cdot}$ radicals. The amount of complex substances contained in the actual wastewater typically corresponds with the $OH^{\cdot}$ radical requirements, which can be supplied by H_2O_2 during the oxidation reaction [9,13]. The effects of H_2O_2 dosage on the COD and color removal at various Fe dosages are illustrated in Figure 1. The maximum COD removal efficiency was achieved at 94.7% when the H_2O_2 and Fe dosages were kept at 0.15 g and 0.04 g, respectively. This corresponds to an Fe: H_2O_2 of 1: 3.73, indicating most of organic substances present in the offset printing company can be oxidized by $OH^{\cdot}$ radicals . The overall results also revealed that at various Fe dosages, H_2O_2 of 0.15 g always yielded the maximum COD removal efficiency. However, the COD removal efficiency increased as H_2O_2 dosage ranged from 0.05 to 0.15 g. The COD removal efficiency obviously decreased when applying a higher dosage of H_2O_2 . At this stage, the oxidizing power of $OH^{\cdot}$ radical is decreased due to the regeneration of Fe^{2+} in the solution and consequent scavenging effect of H_2O_2 on $OH^{\cdot}$ radicals [14,11] as described as follows:

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HOO^{\cdot} + H^+ \quad (7)$$

$$HOO^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+ \quad (8)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow OH^- + Fe^{3+} \quad (9)$$

$$H_2O_2 + HO^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \quad (10)$$

The H_2O_2 has the potential to react with Fe^{3+} formed and $OH^{\cdot}$ radicals and generate Fe^{2+} ,resulting in a decrease in the COD removal. Moreover, the results showed high variation of color removal efficiency at various Fe^{2+} and H_2O_2 dosages. However, high color removal efficiency was attained when the Fe and H_2O_2 were kept constant at 0.4 g. The results indicated that maximum color removal efficiency was at 86.4%. It was also noticed that an increase of H_2O_2 dosage resulted an improvement of color removal efficiency. At an Fe^{2+} dosage of 0.04 g, the COD remaining after being treated by the Fenton's reaction was in the range of 53-107 mg/L. This indicates the efficient reduction of complex molecules such as lubricating oils, solvents for cleaning, film developing chemicals, and waste paint to lower molecular weight aromatic compounds [15,16].

3.2 Effects of Fe^{2+} dosage on the COD and color removal

Other experimental operations were conducted to study the effects of ferrous on the COD and color removal. As shown in equation 1, Fe^{2+} plays an important role in the Fenton's reactions. Sufficient amounts of Fe^{2+} are required during the reaction with H_2O_2 to generate $OH^{\cdot}$ radical. From Figure (2), the COD removal efficiency increased with respect to an increase of Fe^{2+} dosage at H_2O_2 of 0.01 and 0.02 g. However, further increase of H_2O_2 dosage to 0.03 g yielded less COD removal efficiency. The reaction (9) may take place and the oxidation of organic compounds can then be hindered at high Fe^{2+} dosage [17,18]. On the other hand, higher Fe^{2+} dosage also decreases the color removal efficiency as extra Fe^{2+} leads to the formation of Fe^{3+} brownish flocs, which can be easily re-suspended.

3.3 Optimum Fe^{2+} and H_2O_2 dosage on the COD and color removal

Accordingly, the overall results showed that at 0.04 g of Fe^{2+} and 0.02 g of H_2O_2, satisfactory COD and color removal efficiency were achieved at 89.4% and 74.8%, respectively, during the treatment of the wastewater discharged from an offset printing company. This corresponds to an Fe^{2+}: H_2O_2 ratio of 1: 4.98. The Fe^{2+} and H_2O_2 dosage required depends on types of organic compounds, although the $OH^{\cdot}$ radicals can oxidize organics non-selectively [19]. Removal of organic compounds which can be easily biodegradable

such as livestock wastewater may need a less amount of H_2O_2 [20]. Complex organic substances such as phenolic compounds may require higher H_2O_2 dosage as the Fe^{2+}: H_2O_2 ratio increase up to 1: 10 [21]. However, the Fenton's reaction with the Fe^{2+}: H_2O_2 ratio of 1: 15 can also be recommended to treat actual olive mill wastewater containing high COD [22].

Table 2. Operation conditions of the Fenton's oxidation of offset printing wastewater.

Experiment	**Fe^{2+} *(g)***	**H_2O_2*(g)***	**Fe^{2+}: H_2O_2 *(w/w)***	**Experiment**	**Fe^{2+} *(g)***	**H_2O_2 *(g)***	**Fe^{2+}: H_2O_2 *(w/w)***
1	0.01	0.05	1: 4.98	6	0.01	0.01	1:9.96
		0.10	1: 9.96		0.02		1:4.98
		0.15	1: 14.9		0.03		1:3.32
		0.20	1: 19.9		0.04		1:2.49
		0.25	1: 24.9		0.05		1:1.99
2	0.02	0.05	1: 2.49	7	0.01	0.02	1:19.91
		0.10	1: 4.98		0.02		1:9.96
		0.15	1: 7.47		0.03		1:6.64
		0.20	1: 9.96		0.04		1:4.98
		0.25	1: 12.44		0.05		1:3.98
3	0.04	0.05	1: 1.24	8	0.01	0.03	1:29.87
		0.10	1: 2.49		0.02		1:14.93
		0.15	1: 3.73		0.03		1:9.96
		0.20	1: 4.98		0.04		1:7.47
		0.25	1: 6.22		0.05		1:5.97
4	0.06	0.05	1: 0.83				
		0.10	1: 1.66				
		0.15	1: 2.49				
		0.20	1: 3.32				
		0.25	1: 4.15				

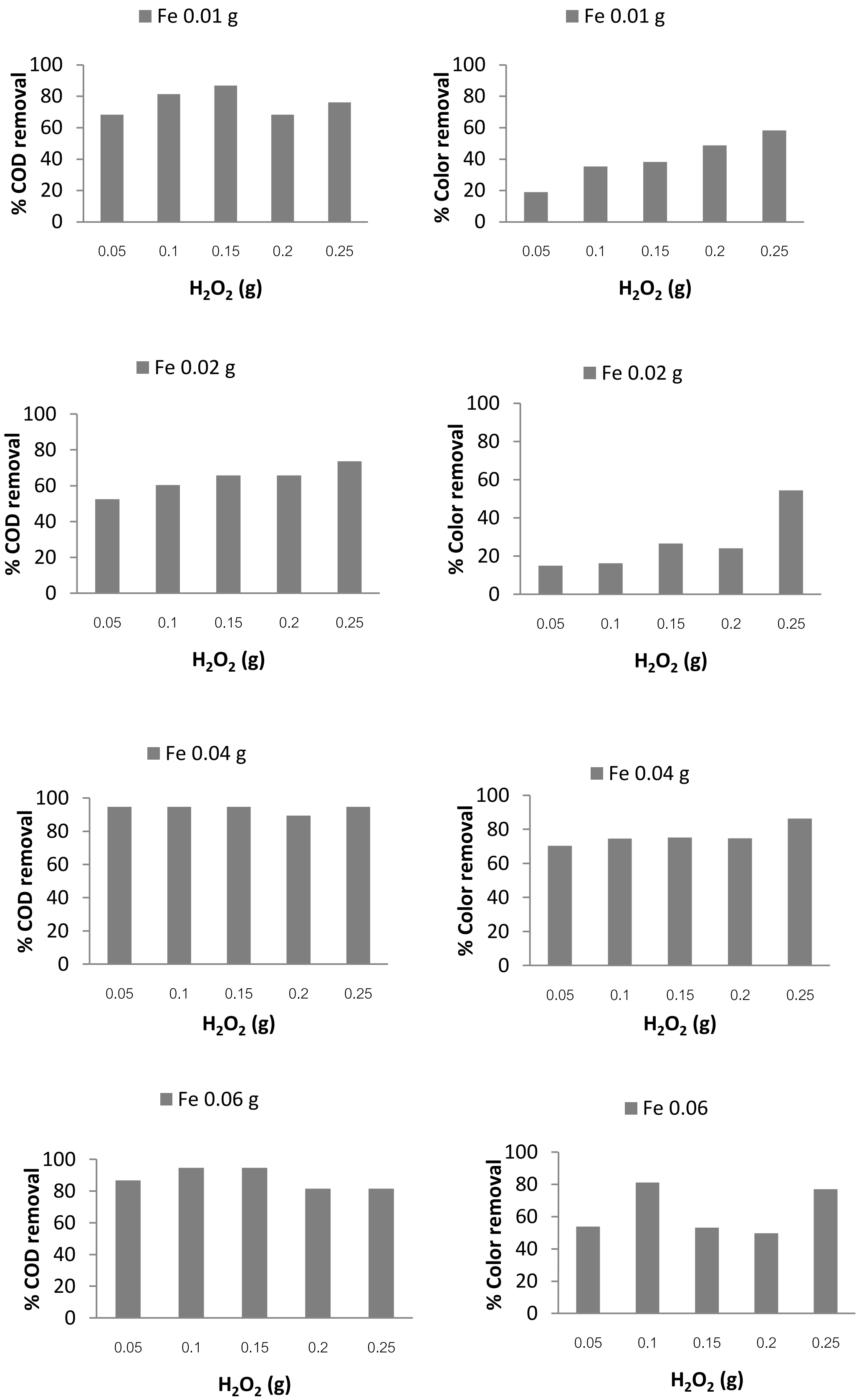

Fig. 1. (a) COD removal efficiency; (b) Color removal efficiency at various H_2O_2 .

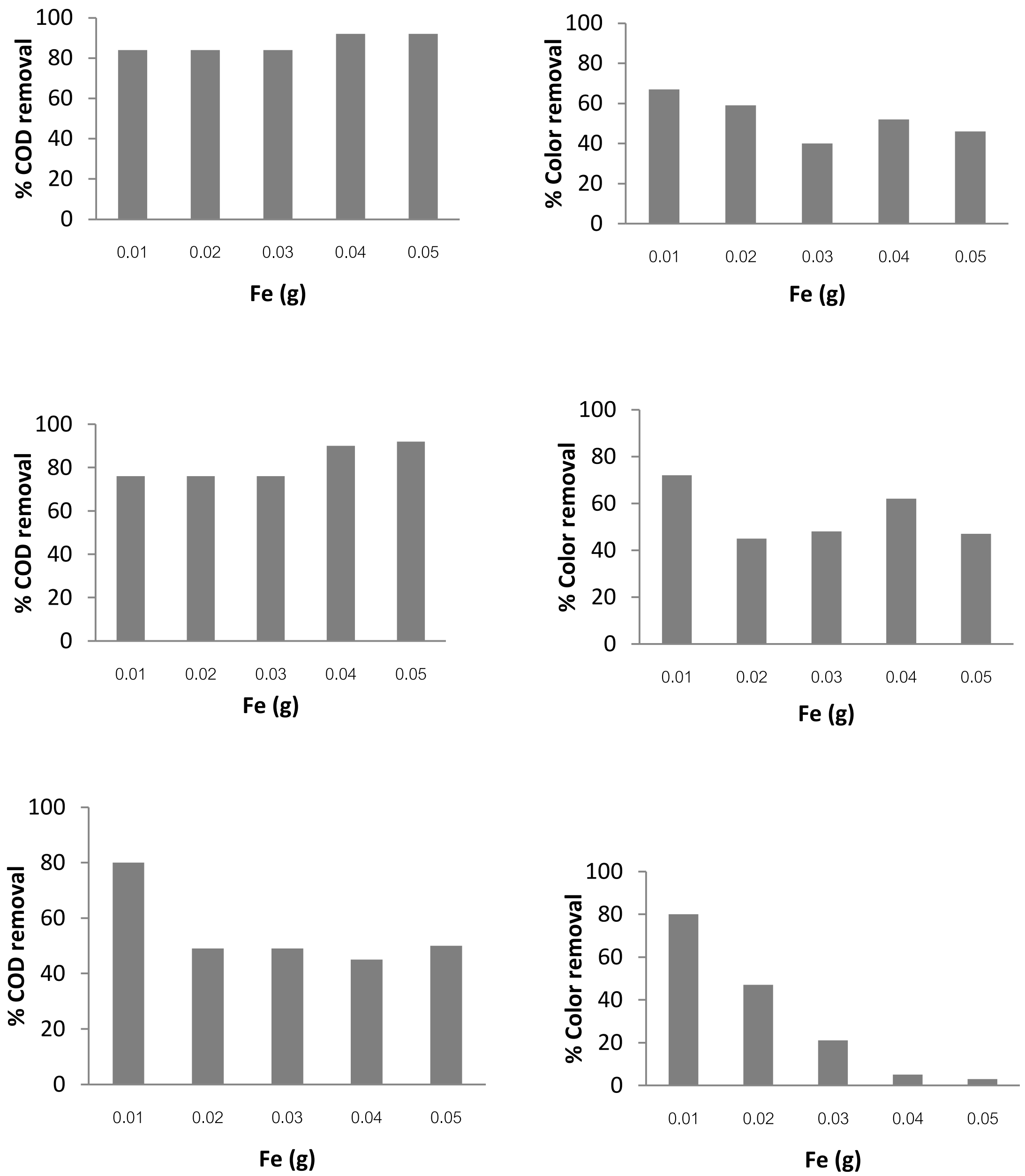

Fig .2. (a) COD removal efficiency; (b) Color removal efficiency at various Fe.

4. Conclusion

From this study, an advanced oxidation process using the Fenton's reaction has a great potential to oxidize the organic compounds present in offset printing wastewater, which can be observed through the COD and color removal efficiency. The Fe^{2+} dosage and H_2O_2 dosage were the major key factors to optimize the Fenton process. The results obtained from the experiment showed that the COD removal efficiency was greatly influenced by the Fe^{2+}: H_2O_2 ratio. At the Fe^{2+}: H_2O_2 ratio of 1: 4.98 (0.04: 0.2 (w/w)), satisfactory COD and color removal efficiency were achieved at 89.4% and 74.8%, respectively. However, increasing of the H_2O_2 dosages obviously showed an improvement of the color removal efficiency.

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