Decolorization and COD reduction of wastewater from ethanol production by Fenton oxidation

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Abstract

The decolorization and COD reduction in wastewater of ethanol production from molasses by Fenton oxidation was investigated. The operating conditions (types of catalyst, initial pH, reaction time, specific catalyst concentration and H_2O_2 concentrations) have been optimized. Results showed that the most suitable catalyst for Fenton oxidation was $FeSO_4$ with the optimal condition at reaction time 30 minutes, initial pH 3.5, $FeSO_4$ concentrations 0.01 mol/L and H_2O_2 concentrations 0.10 mol/L. Form this condition, the color and COD removal efficiencies were 93.50% and 59.28%, respectively.

Keywords: molasses, wastewater, melanoidin, Fenton oxidation

Introduction

The wastewater of ethanol production from molasses has a dark brown color. It cannot be allowed to discharge into the river because it to affects to the environment. It is required treatment to reduce the intensity of the color. The molasses wastewater is characterized as extremely high chemical oxygen demand (COD) (80,000–100,000 mg/l), dark brown color, low pH and strong odor (Satyawali and Balakrishanan, 2008). Compound responsible for dark color in that wastewater is known as "Melanoidin" formed by Maillard reaction (Jiranuntipon, 2009)

Melanoidin is formed by the condensation of amino acids and reducing sugar (Peña et al., 2003). The treatment method for the color of melanoidin is mainly based on physical or chemical procedures such as oxidation, adsorption, coagulation, and precipitation, while biological treatment is barely affected on color removal (Chine and Korake, 2012), because melanoidin holds antioxidant, antimicrobial and cytotoxic properties (Rufián-Henares and Morales, 2007).

Fenton oxidation is one of the advanced oxidation processes using hydrogen peroxide (H_2O_2) reacting with ferrous ions (Fe^{2+}) to generate hydroxyl radicals ($OH^{\bullet}$), which has high oxidation potential (Bautista et al., 2007) leading to decolorization of the wastewater (Pala and Erden, 2005).

Although Fenton oxidation is one of the most suitable treatment processes for wastewater in term of easiness and fast response which can reach up to 98% color removal, Fenton oxidation is sensitive to condition of operation as well as pollutants inside the wastewater.

To realize Fenton oxidation to the treatment of this kind of water, in this proposed work, the effect of operating conditions such as types of catalyst, initial pH, reaction time, specific catalyst concentration and H_2O_2 concentrations was investigated.

Methodology

The molasses wastewater used in this study was obtained from Thai Alcohol PCL (Nakhon Pathom, Thailand). The wastewater was characterized as given in Table 1. The experiments were carried out in batch operation in 250 mL flask containing 100 mL of wastewater. All procedures was carried out at room temperature and atmospheric pressure. The initial pH of the sample was adjusted to the desired pH value using 1M H_2SO_4 and 1M NaOH, then the specific type and amount of catalyst and H_2O_2 solution (50% v/v) were added to the flask (Figure 1). All experiments was done in duplicate.

Table 1 Characteristic of the molasses wastewater

Parameter	Unit	Value
pH	-	4.5 – 4.7
Color (ADMI)	-	75,000-80,000
COD	mg/l	53,000-59,000

The pH value was measured with a pH meter (pH700, Eutech Instrument, China). Color of samples was measured according to American Dye Manufacturers Institute (ADMI) (DR6000, HACH, USA). COD was measured by a closed reflux colorimetric method (DR6000, HACH, USA). H_2O_2 solution (50% v/v) was commercial grade. The reagents including NaOH, H_2SO_4, $MnSO_4$, $FeSO_4$, $CoSO_4$, $NiSO_4$, $CuSO_4$ and $ZnSO_4$ used in the experiments were analytical grade.

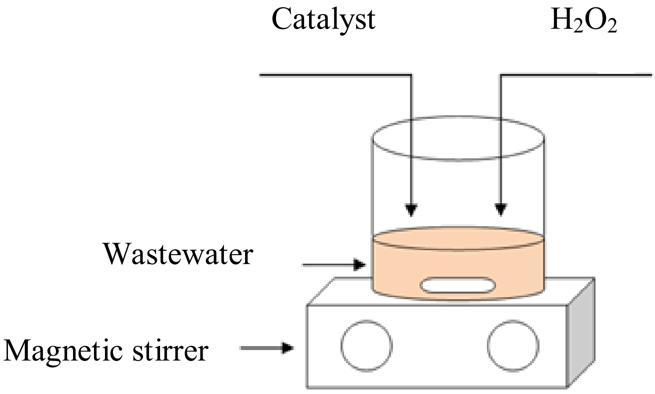

Figure 1 Batch treatment with Fenton oxidation

Results and Discussion

1. Effect of catalyst types

The catalysts including $MnSO_4$, $FeSO_4$, $CoSO_4$, $NiSO_4$, $CuSO_4$ and $ZnSO_4$ were investigated to be the suitable catalyst for Fenton oxidation under the same condition, namely, initial pH 3.5, reaction time at 30 min, 0.017 mol/L catalyst concentration and 0.17 mol/L H_2O_2 concentration. The color of wastewater was measured in term of ADMI unit before and after treatment process. The color removal efficiency was calculated from Equation (1).

$$\%\text{ removal efficiency} = \frac{\text{ADMI}_{\text{before}} - \text{ADMI}_{\text{after}}}{\text{ADMI}_{\text{before}}} \tag{1}$$

The result was shown in Figure 2. The most suitable catalyst for Fenton oxidation in this case was $FeSO_4$ with the highest color removal efficiency at 82.38%. $FeSO_4$ and $CuSO_4$ were almost equally effective, the just different 4.66%, however $FeSO_4$ is cheaper than $CuSO_4$, thus $FeSO_4$ was used for further experiments. While the other catalysts could not catalyze the reaction because at pH 3.5 these catalysts precipitate or oxidize.

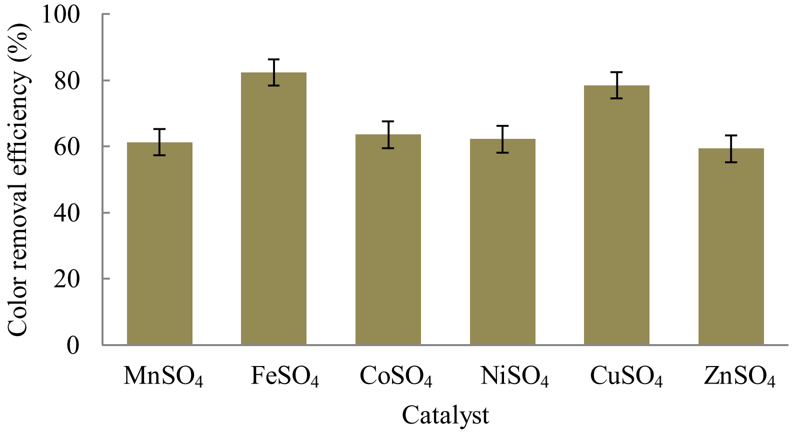

Figure 2 Effect of types of catalyst on color removal efficiency.

2. Effect of reaction time

The reaction time was varied between 30 and 90 minutes. The initial pH, $FeSO_4$ concentration and H_2O_2 concentrations were fixed at 3.5, 0.01 mol/L and 0.10 mol/L, respectively. The effects of reaction time on the removal efficiency of color and COD was shown in Figure 3. The maximum removal efficiencies of color and COD were 93.70% and 73.02%, respectively, at 30 min. After 30 min, the change of residual color and COD became insignificant. This means that the reaction between Fe^{2+} and H_2O_2 to generate the production of $OH^\bullet$ was almost completed in 30 min. Thus, the optimum of reaction time for the Fenton oxidation treatment was 30 min.

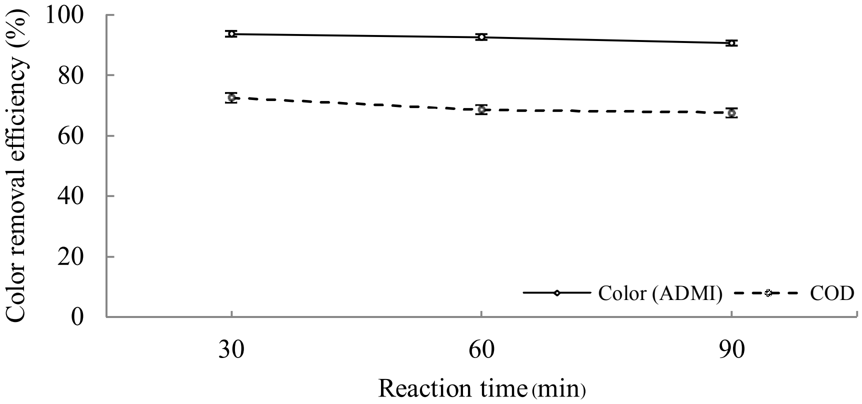

Figure 3 Effect of reaction time on color and COD removal efficiency.

3. Effect of initial pH

The effect of initial pH between 2 and 6 was investigated. For this part, the reaction time, $FeSO_4$ concentration and H_2O_2 concentrations were fixed at 30 min, 0.01 and 0.10 mol/L respectively. From Figure 4, the maximum of color and COD removal efficiencies (93.70% and 73.02%) were obtained at initial pH values of 3.5 and decreased with initial pH increased. The Fenton oxidation is highly sensitive to pH. Hydroxyl radicals ($OH^•$) is highly generated at acidic pH (Gulkaya et al., 2006), while at pH > 4, the generation of $OH^•$ is low because Fe^{2+} is transformed to Fe^{3+} and the precipitation of Fe^{3+} as ferric hydroxo ($Fe(OH)_3$) occurs. From this phenomenon, $Fe(OH)_3$ stimulates the decomposition of H_2O_2 to oxygen and water, thus the production of $OH^•$ decreased (Bautista et al., 2007). Therefore, $OH^•$ decreased with oxidize organic compounds decreased and the lower color and COD removal efficiency.

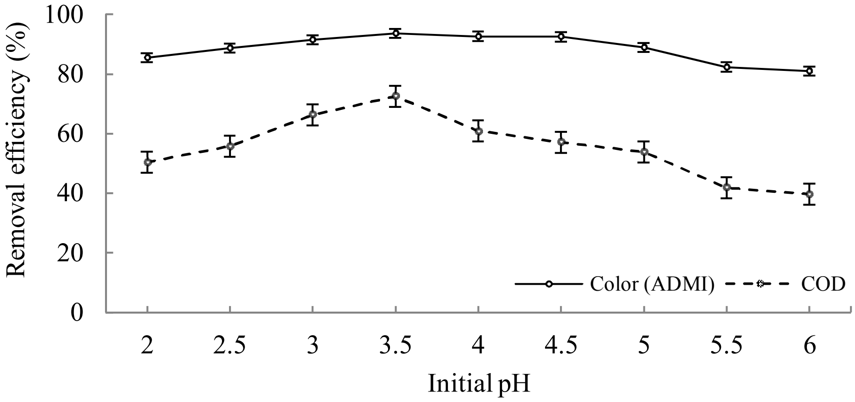

Figure 4 Effect of different initial pHs on color and COD removal efficiency.

4. Effect of $FeSO_4$ concentration

The effect of $FeSO_4$ concentration on color and COD removal efficiencies was examined in the range of 0.005 to 0.03 mol/L $FeSO_4$. The concentration of H_2O_2, initial pH and reaction time were kept at 0.10 mol/L, 3.5 and 30 min, respectively. According to Figure 5, the maximum of color and COD removal efficiencies (94.17% and 63.97%) was obtained by using 0.01 mol/L and 0.02 mol/L $FeSO_4$, respectively. However, when concentration of Fe^{2+} increased further, the removal efficiency of color and COD decreased. This behavior came from that fact that higher Fe^{2+} dosage leaded to the generation of more $OH^•$ (Benitez et al., 2001), however, this high amount of Fe^{2+} caused coagulation resulting in removal of the residual iron in the wastewater (Meric et al., 2004).

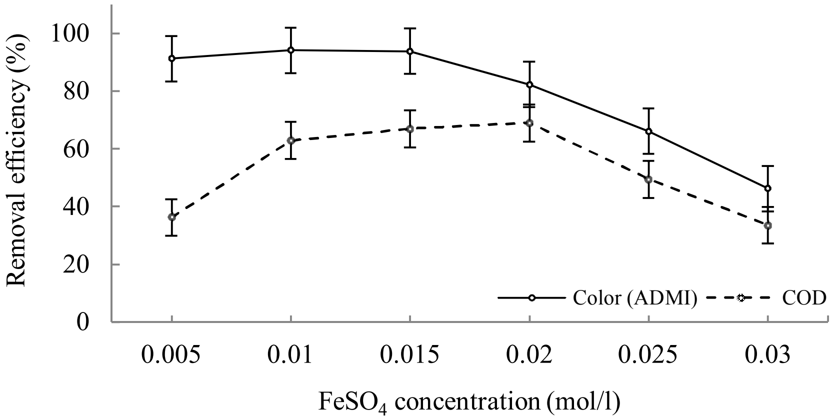

Figure 5 Effect of $FeSO_4$ concentration on color and COD removal efficiency.

5. Effect of H_2O_2 concentration

The concentration of H_2O_2 between 0.05 and 0.25 mol/L was investigated at initial pH 3.5, reaction time at 30 min and 0.01 mol/L $FeSO_4$. From Figure 6, when H_2O_2 concentration increased the removal efficiency of color and COD increased due to the increased formation of $OH^{\bullet}$ (Gulkaya et al., 2006). However, when H_2O_2 was added higher than 0.05 mol/L (in case of color) or 0.15 mol/L (in case of COD), the color and COD removal efficiencies changed slightly. It was implied that Fe^{2+} dosage was already sufficient for the reaction with H_2O_2. The color of the wastewater after finish the Fenton oxidation was shown in Figure 7.

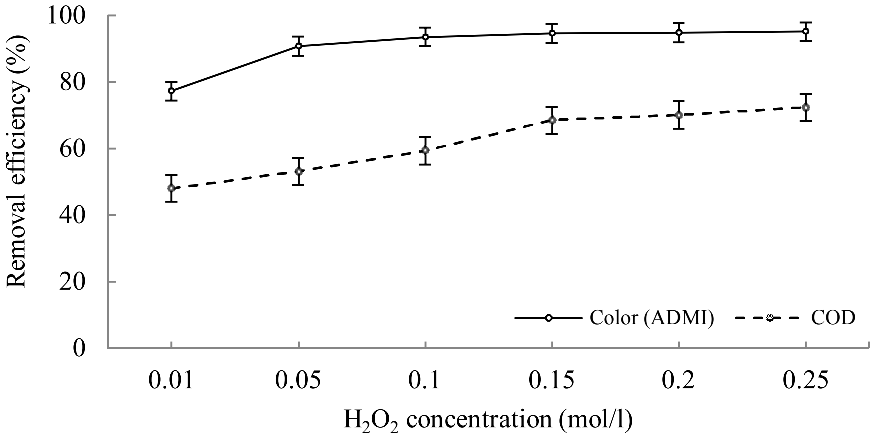

Figure 6 Effect of H_2O_2 concentration on color and COD removal efficiency.

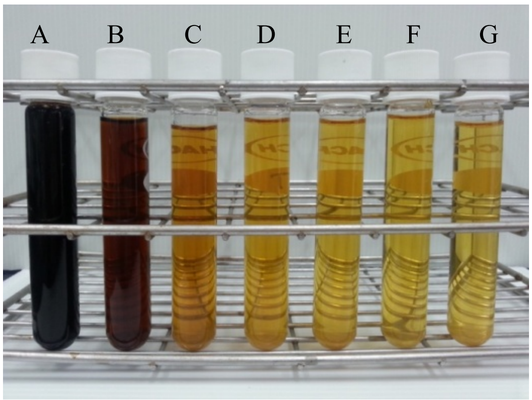

Figure 7 The color of the wastewater after Fenton oxidation at different H_2O_2 concentrations;
A = raw wastewater, B = 0.01 mol/L H_2O_2 , C = 0.05 mol/L H_2O_2 , D = 0.10 mol/L
H_2O_2 , E = 0.15 mol/L H_2O_2 , F = 0.20 mol/L H_2O_2 and G = 0.25 mol/L H_2O_2

Conclusion

Fenton oxidation was an effective treatment for wastewater allowing a significant removal color and COD to be achieved. The result showed that, the most suitable catalyst for Fenton oxidation of the real wastewater obtained from ethanol production from molasses was $FeSO_4$. The maximum of color and COD removal efficiencies (93.50% and 59.28%) were obtained from the conditions with initial pH 3.5, reaction time at 30 minutes, $FeSO_4$ and H_2O_2 concentrations at 0.01 and 0.10 mol/L, respectively.

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