Investigation of Color Removal of Sunflower Oil Industrial Wastewater with Fenton Process

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Abstract: Recently, advanced oxidation processes (AOPs) based on the generation of a free hydroxyl radical (OH) which degrades most organic pollutants quickly and non-selectively, are reported as a potential alternative for the treatment of industrial wastewater containing non-biodegradable organic pollutants. Fenton process, one of the AOP's, employs ferrous ions and hydrogen peroxide under acidic pH conditions. Strong oxidative hydroxyl radical is produced and the ferrous ions are oxidized to ferric ions. Since both ferrous and ferric ions are coagulants, the Fenton process can therefore have the dual functions of oxidation and coagulation in the treatment process. This study was performed to investigate the removal of color from sunflower oil industry wastewater using the Fenton process. The effect of parameters such as the concentration of $FeSO_4.7H_2O$ (150-400 ppm), pH (1.5-5), the concentration of H_2O_2 (100-400 ppm), the temperature (20- 50° C), reaction time and stirring speed were evaluated to determine the optimum conditions for the removal of color in the industrial wastewater. Under optimum conditions removal of color were achieved 97%. Keywords: Color removal, Industrial wastewater, Treatment, Fenton Process, Oxidation

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INTRODUCTION T

Treatment of industrial wastewater which is harm for the environment, recover and reuse have become the main topic of the researches in recent years. It is extremely important that the organic matter, suspended solids, nutrients and toxic substances in the wastewater should be reduced to the desired level by various treatment methods. For this reason, the traditional treatment methods have been insufficient to bring the wastewater pollution to discharge standards, and the increasing costs of removing the wastewater from the industrial wastewater have led the industry to search for more effective water management approaches [1].

The sunflower oil industry discharges waste water in large quantities and the discharged waste water is quite polluted. In the production of sunflower oil, the waste water from the refining section contains considerable amounts of chemicals such as oil, soap, sodium hydroxide, sodium carbonate, phosphoric acid and sulfuric acid. The release of these wastewater into the environment is causing great problems. Particularly in aqueous environments, water cuts in contact with air, reducing the amount of oxygen in the water and posing a great danger to live life [2].

Advanced oxidation processes (AOPs) have come to forefront among the methods used for the treatment of industrial wastewater in recent years [3]. One of the advanced oxidation methods, fenton process is successfully applied treatment of wastewater containing toxic and non-biodegradable substances. The Fenton process is based on the reaction of Fe (II) ion with hydrogen peroxide under acidic conditions. At the end of this reaction hydroxyl radicals (OH), which is a strong and non-selective chemical oxidant, are formed. Oxidation of the organic compounds by hydroxyl radicals is rapid and results in the oxidation of contaminants to primarily carbon dioxide and water [4]. The fenton process generally takes place in four stages: pH adjustment, oxidation reaction, neutralization-coagulation and precipitation. In this way, the organic substances are removed in two stages by oxidation and coagulation [5].

This study was performed to investigate the removal of color from sunflower oil industry wastewater using the Fenton process. Optimal values of some parameters such as the pH, concentration of Fe(II) and H_2O_2 , temperature, reaction time and mixing speed were investigated.

Π MATERIALS AND METHODS

In this study, the removal of color in sunflower oil wastewater by Fenton process was examined. The wastewater was provided from at a factory located in Eskisehir. The characteristics of the wastewater are shown Table 1. Iron sulphate hepta hydrate (FeSO₄,7H₂O) and sulfuric acid (H₂SO₄) were supplied by Merck. Hydrogen peroxide (30% w/w) and sodium hydroxide (NaOH) were supplied by Sigma Aldrich.

Table 1. The characteristics of the wastewater.		
The characteristic	Value	
рН	9.5	
COD (mg/l)	7100	
Colour (Abs)	3.00	
$\lambda_{\max}(nm)$	359.2	
Oil and grease (mg/l)	600	

All experiments were performed in erlenmeyer flasks with a total volume of 50 ml in batch mode. First the pH of wastewater was adjusted to desired value using 2.0 M H_2SO_4 solutions. FeSO₄.7H₂O was added to obtain the desired Fe (II) concentration than H_2O_2 (30%) was carefully added to start the Fenton reaction. The samples were shaken in constant temperature shaking water bath. After Fenton oxidation process, pH of treated wastewater was adjusted to pH 8 by the addition of 2.0 M NaOH. The Fenton oxidized samples were scanned using UV–Visible spectrophotometer.

III RESULTS AND DISCUSSION

3.1. Effect of the Fe (II) concentration

Fe (II) concentration was varied from 150 ppm to 400 ppm and the other conditions were fixed (initial pH value of 2, H_2O_2 concentration of 200 ppm, temperature of 30°C and reaction time of 120 min). It was obvious that the Fe (II) concentration significantly affected the color removal. The decolorization efficiency decreased when the Fe (II) concentration increased further. This may be explained as follows: the increase in amount of iron facilitates decomposition of H_2O_2 and allows formation of more OH⁻ radicals. But, high concentration of iron reduces the oxidation potential of the formed OH⁻ radicals and causes reduction of the decolorization efficiency [6].



Figure 1. Effects of concentration Fe(II) on color removal.

3.2. Effect of the pH

The pH also significantly affects the treatment efficiency of the Fenton process. Under the conditions of Fe (II) concentration of 200 ppm, H_2O_2 concentration of 200 ppm, temperature of 30°C and reaction time of 120 min, the effect of pH (1.5-5) was investigated. As shown in Figure 2, the maximum color removal was obtained at pH 2. It also decreased from 95% to 66% after pH 4. This is because the activity of the Fenton reagent is reduced at higher pH values due to the presence of passive iron oxohydroxides and the formation of ferric hydroxide precipitate. In this case, less hydroxyl radical is formed due to the presence of less free iron ions. In addition, the oxidation potential of hydroxyl radicals decreases as the pH increases [7].



Figure 2. Effects of pH on color removal.

3.3. Effect of the H₂O₂ concentration

In the Fenton process, H_2O_2 is the most important parameter because it is the source of hydroxyl radicals (OH) [8]. As shown in the following figure, color removal increased with increasing H_2O_2 concentration to 200 ppm by 100 ppm. Other values began to decline. For this reason, the optimal concentration of H_2O_2 was selected as 200 ppm. When working with high concentrations of hydrogen peroxide, hydrogen peroxide reacts with hydroxyl radicals, causing the hydroxyl radicals in the environment to decrease. The resulting hydroperoxyl radicals react with the hydroxyl radical to form H_2O and O_2 [9]. For this reason, it is very important to determine the optimum amount of hydrogen peroxide in experimental studies.

$$\begin{array}{ll} H_2O_2 + \cdot OH \rightarrow H_2O + HO_2 \cdot & (1) \\ \cdot OH + HO_2 \cdot \rightarrow H_2O + O_2 & (2) \end{array}$$



Figure 3. Effects of concentration H₂O₂ on color removal.

3.4. Effect of the temperature

The effect of the temperature (20-50°C) on the color removal efficiency was investigated at an initial pH value of 2, Fe (II) concentration of 200 ppm, H_2O_2 concentration of 200 ppm and reaction time of 120 min. When the temperature increased from 20 degrees to 30 degrees, the color purity increased, but then decreased slightly. For this reason, the optimum temperature was chosen to be 30 degrees. This result is consistent with the literature. Optimum temperature range in the literature is 20-40°C for the fenton process. The reason for the decrease in yield at high temperatures is the thermal decomposition of hydrogen peroxide [10].



Figure 4. Effects of temperature on color removal.

3.5. Effect of the reaction time

The effect of the reaction time on the color removal efficiency was investigated under the following conditions: pH value of 2, Fe (II) concentration of 200 ppm, H_2O_2 concentration of 200 ppm and temperature of 30°C. The great advantage of advanced oxidation processes is that they have effective removal efficiency at low reaction times. When Figure 5 is examined, it is concluded that high efficiency is obtained from the first minute for fenton processing and optimum reaction time is determined as 30 minutes.



Figure 5. Effects of reaction time on color removal.

3.6. Effect of the mixing speed

As you can see in the figure the removal of color increased with increasing mixing speed (initial pH value of 2, Fe (II) concentration of 200 ppm, H_2O_2 concentration of 200 ppm, temperature of 30°C and reaction time of 30 min). For this reason, a mixing speed of 160 rpm was used in the experiments. In advanced oxidation processes, increasing the mixing speed increases the color removal efficiency. In addition, the high mixing speed provides homogeneous distribution of iron ions and hydrogen peroxide [11].



Figure 6. Effects of stirring speed on color removal.

IV CONCLUSION

In this work, color removal of sunflower oil industrial wastewater was investigated in batch system by Fenton process and was effectively achieved. The Fenton oxidation process was evaluated by examining pH, H_2O_2 concentration, Fe(II) concentration, temperature, reaction time and stirring speed. The optimal operational parameters were found to be a pH of 2.0, a 200 ppm H_2O_2 concentration, a 200 ppm Fe (II) concentration, and a stirring speed of 160 rpm at a temperature of 30°C. Under these conditions, the color removal of oil industrial wastewater was found as 96.47% within 30 min. Overall, it can be concluded that it is feasible to treat contaminated wastewater by using Fenton oxidation process.

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