Treatment of the Basic Yellow 2 Dyestuff with Fenton Advanced Oxidation Process

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Abstract
In this study, the removal of Basic Yellow 2 (BY2) dyestuff used in textile dyeing industry by Fenton process which is one of the Advanced Oxidation Processes (IOP) was investigated. Effect of pH, Fe^{2+}, hydrogen peroxide (H_2O_2) and temperature was evaluated on oxidation process. Removal of the colorant (BY2) was monitored by considering color and Chemical Oxygen Demand (COD). A COD removal efficiency of 62.05% and color of 90.71% were obtained under optimum experimental conditions where baseline solution pH is 3, the concentration of (BY2) colorant is 200 mgL^{-1}, rates of Fe^{2+} and H_2O_2 are 150 mgL^{-1} and 400 mgL^{-1}, reaction temperature is 20^0C and experiment time is 30min.

Keywords: Fenton, Basic Yellow 2, H_2O_2, pH

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Özet
Bu çalışmada tekstil boyama endüstrisinde kullanılan Basic Yellow 2 (BY2) boyar maddesinin İleri Oksidasyon Proseslerinden (İOP) biri olan Fenton prosesi ile giderimi araştırılmıştır. Proseste pH, Fe^{+2}, hidrojen peroksit (H_2O_2) ve sıcaklığın etkisi incelenmiştir. (BY2) boyar maddesinin giderimi renk ve Kimyasal Oksijen İhtiyacı (KOİ) üzerinden izlenmiştir. Optimizasyon çalışmaları sonucunda başlangıç çözelti pH=3, (BY2) boyar maddesi konsantrasyonu =200 mgL^{-1}, Fe^{+2} konsantrasyonu = 150 mgL^{-1}, H_2O_2= 400 mgL^{-1}, çözelti sıcaklığı 20^0C ve reaksiyon süresi 30 dakika olarak belirlenmiştir. Bu şartlar altında renk ve KOİ giderim verimi sırasıyla %90,71 ve 62,05 olarak bulunmuştur

Anahtar Kelimeler: Fenton, Basic Yellow 2, H_2O_2, pH

1. Introduction

With the increase in industrialization, environmental pollution has started to increase considerably. Waste from air, soil and water from different industrial establishments disrupts the natural balance and adversely affects the living organisms and ecosystem. The population growth throughout the world has contributed to the growth of the textile industry, and has made it a sector serving in many branches ranging from clothing to home textiles with different product and color options. One of these industry organizations is the textile industry and has a significant share in the economy of both developed and developing countries. Dyestuffs are contaminants that are resistant to biological degradation. Dyestuffs are mainly used in many industries such as cosmetics, plastics, paints, leather, paper, especially in textile industry. Colorful wastewaters released from the different processes of these industries, when given to natural water environments, disrupt the ecological balance by preventing photosynthesis because they reduce light transmission beyond aesthetic pollution. At the same time the textile industry wastewater contains high color and chemical oxygen demand (COD).

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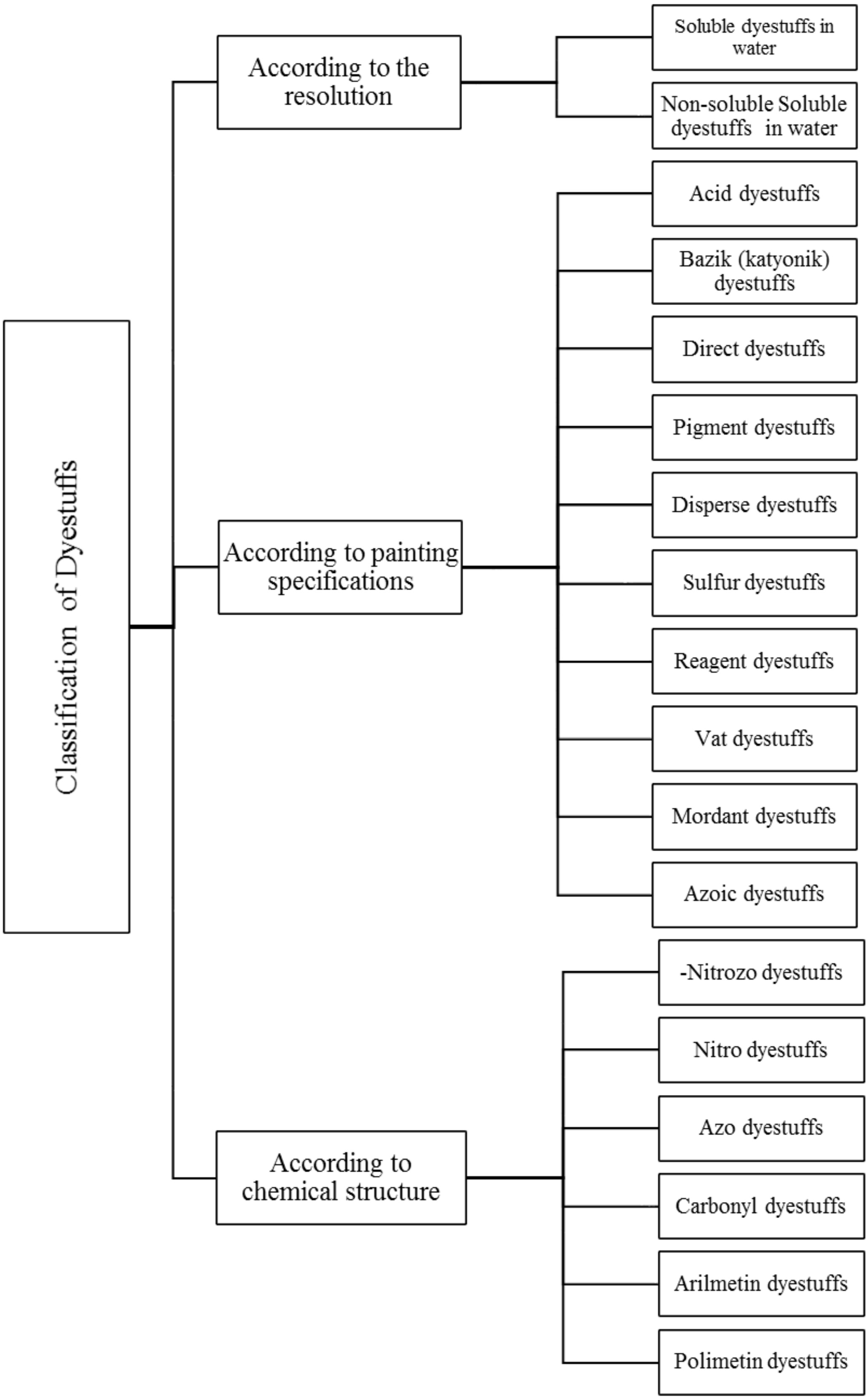

Figure 1. Classification of Dyestuffs (Ertugay, 2012)

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The pollutants in these wastewaters are very difficult and resistant compounds in natural environment and also have carcinogenic and toxic effects. For this reason, it is extremely dangerous to give these wastewater to any natural environment without treatment. Figure 1 below gives the classification of dyestuffs.

Recently, Advanced oxidation processes known as environmentally friendly, have been used in the treatment of biologically difficult to degrade waste water. Advanced oxidation processes are based on the formation of hydroxyl radicals with high electrochemical oxidation potential. Hydroxyl radicals are not selective and react with all organic substances and form the end product CO_2 and H_2O. The Fenton process is based on the reaction of Fe $^{+2}$ ion with hydrogen peroxide under acidic conditions. Hydroxyl radicals are formed by this reaction. The iron ion initiates the decomposition of H_2O_2, catalysis and hydroxyl radicals occur. The formation of hydroxyl radicals is in the form of a complex reaction chain in aqueous solutions. Fenton oxidation process steps are as follows (Bayhan and Değermenci 2017);

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\bullet} + OH^{-}$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + HO_2^{\bullet} + H^{+}$$

All in all, the Fenton process consists of four steps. These are pH adjusting, oxidation reactions, neutralization process and finally, the process of precipitation with coagulation.

In this study, color and COD removal from synthetic textile wastewaters prepared with Basic Yellow 2 (BY2) dye were investigated with Fenton process. In experimental studies, the effects of pH, Fe $^{2+}$ concentration, H_2O_2 concentration, initial dye concentration and temperature parameters were investigated.

2. Materials and Methods

The dyestuff used in this study (BY2) was obtained from Duraner Boya A.Ş. Molecular formula ($C_{17}H_{22}ClN_3$) and molecular weight of BY2 dystuff are 303.83 g.mol^{-1}. The maximum absorbance wavelength (λ_{max}) of BY2 dyestuff was 430 nm. The molecular structure of the dyestuff (BY2) is given in Figure 2. Firstly, pH was adjusted by adding dilute H_2SO_4 and NaOH in Fenton process experiments. Following this stage, FeSO4.7H2O or FeCl3.6H2O and H2O2 were added and stirred fast for 3 min at 150 rpm and then slowly for 27 min at 50 rpm and the resultant mixture was filtered through 0.45 µm membrane filter. Color measurements for (BY2) dyestuff were performed spectrophotometrically at a wavelength of 430 nm. COD analyzes were performed spectrophotometrically at 148 ^{0}C according to the Standard Methods in Merck Spectroquant TR320 at 600 nm (APHA, 1985).

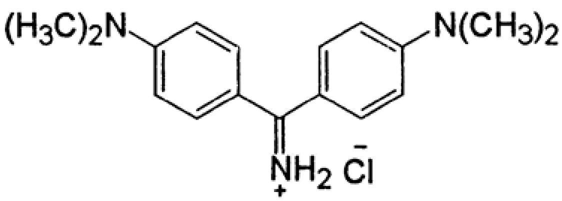

Figure 2. Molecular structure of (BY2).

3. Results and discussion

3.1. Effect of Fe^{2+} dosage

The concentration of the Fenton reagent plays an important role in the degradation of organic substances in the Fenton process. Generally, as the dosage of Fe^{2+} increases, the rate of degradation of organic substances increases. However, the very large increase in Fe^{+2} ion leads to an increase in the amount of total dissolved iron ions resulting in sludge formation in the solution. Therefore, it is necessary to avoid excessive sludge formation. Firstly, the effect of Fe^{2+} dosage was examined in Fenton process. The effect of Fe^{2+} dosage on color and COD removal efficiency was investigated in 100, 150, 200, 250 and 300 mg L^{-1} concentrations and the results are shown graphically in Figure 3. Experiments were performed at pH: 3, temperature at 20^{0}C and at H_2O_2=500 mgL^{-1}.As can be seen from Figure 3, the highest color and COD removal efficiencies were obtained as 88.75% color and 61.42% COD removal efficiency at 150 mgL^{-1} Fe $^{2+}$ concentration.

Since there is no basic factor to produce hydroxyl radical in the medium in the absence of Fe^{2+}, an effective oxidation does not occur based on the fenton reaction. As the Fe^{2+} concentration increases, theoretically more $OH^{\bullet}$ radicals will be produced. Therefore, when Fe^{+2} concentration increased from 100 mgL^{-1} to 150 mgL^{-1}, the color removal efficiency increased from 80.80% to 88.75%, while COD removal efficiency increased from 48.6% to 58.66%. In the experiments above 150 mgL^{-1} Fe^{2+} concentration, decreasing of both COD and color removal efficiencies were seen. This situation is thought that excess Fe^{2+} concentration effected negatively of the oxidation capacity. High concentrations of Fe^{2+} are known to cause consumption of $OH^{\bullet}$ radicals in the medium (radical scavenging effect) and consequently decrease in removal efficiency (Xu et al. 2004; Chacon et al. 2006; Kaykıoğlu and Debik 2006; Primo and 2008).

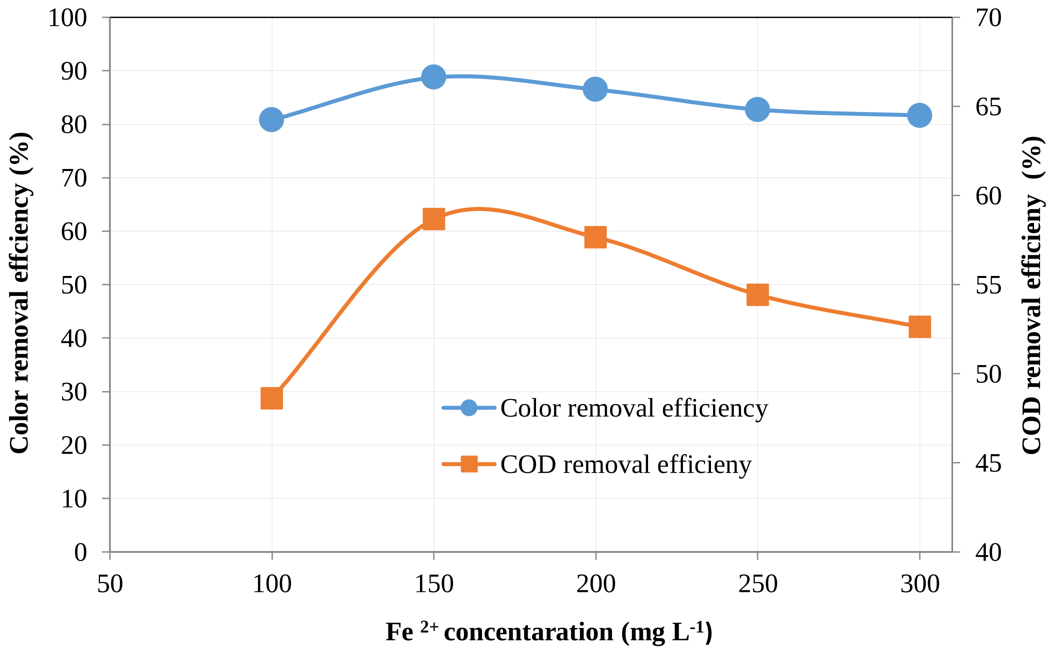

Figure 3. Effect of Fe^{2+} concentration on color and COD removal efficiency in fenton oxidation (C_0=200 mgL^{-1}, H_2O_2=400 mg L^{-1}, pH=3,T=20^{0}C, t=30 min.)

3.2. Effect of H_2O_2 dosage

One of the important parameters in the Fenton process is the H_2O_2 concentration. The determination of the optimum H_2O_2 concentration in Fenton processes is important both for the treatment efficiency of the process and for the applicability of the process due to the cost of H_2O_2. The effect of H_2O_2 concentration was investigated in 6 different values ranging from 100 mg L^{-1}to 600 mg L^{-1}. In the experiment; C_0= 200 mg L^{-1}, Fe^{2+} = 150 mgL^{-1}, pH= 3 and T = 20^{0}C were kept constant. The results obtained from the experiments are shown in Figure 4.

When Figure 4 was examined, at the end of the 30 min. experiment period with the increasing H_2O_2 concentrations from 100 mgL^{-1} to 400 mgL^{-1} resulted in an increase in both color and COD removal efficiencies. Color and COD removal efficiencies were 90.71% and 62.04% at 400 mgL^{-1} H_2O_2 concentration, respectively. When H_2O_2 concentration increased from 400 mgL^{-1} to 500 mgL^{-1}, color and COD removal efficiencies decreased to 83.67% and 38.50%, respectively.

Generally, an increase in the concentration of H_2O_2 causes an increase in the rate of degratation of pollutants. (Kang ve Hwang 2000; Sun vd. 2009; Fan vd. 2013; Zhang vd. 2014). In Fenton process, is important to determine the appropriate H_2O_2 dosage. Because the excess amount of H_2O_2 in the fenton processes will be a positive interference for COD, excessive amount of H_2O_2 is not recommended (Mofrad vd. 2015). Another negative effect of excessive amount H_2O_2 concentration is the radical scavenging effect on the OH• radicals produced as in the Fe^{+2} concentration.(Bouasla et al. 2010; Latif et al. 2015; Ertugay and Acar 2017; Bayhan and Değermenci 2017). At the end of the experiments, the optimum H_2O_2 concentration was determined as 400 mgL^{-1} considering both the removal efficiencies and the cost of H_2O_2.

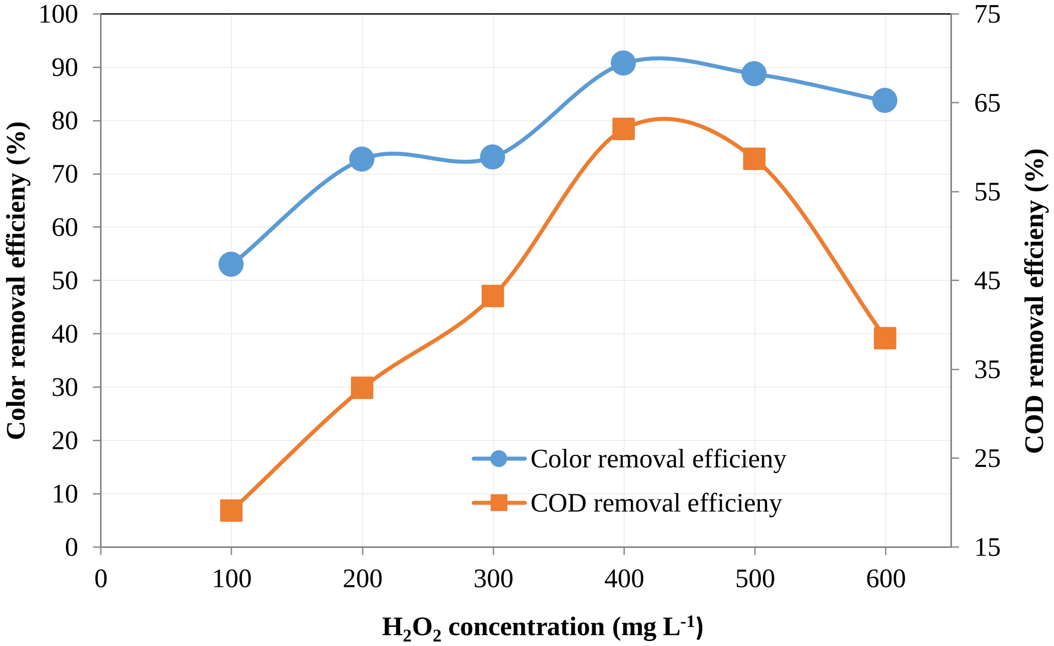

Figure 4. Effect of H_2O_2 concentration on color and COD removal efficiency in fenton oxidation (C_0=200 mgL^{-1}, Fe^{2+}=150 mgL^{-1}, pH=3, T=20^{0}C, t=30 min.)

3.3. Effect of pH

Due to the relationship between the oxidation potential and the pH, the pH value has a decisive effect on the oxidation potential of OH• radical. In Fenton reactions, organic compounds with OH• radicals can react rapidly in acidic medium. Therefore, pH value is important for the formation of OH• radicals which affect the treatment efficiency. In the Fenton oxidation process, the most effective pH values are generally in the narrow range of 2.5 and 4, the highest treatment efficiency are generally obtained at pH 3 in the literatüre (Swamkar et al. 2015). The effect of pH was investigated in the range of pH (2.5-5.0). In the experiments, the temperature was kept constant at T= 25 ^{0}C, C_0= 200 mgL^{-1}, Fe^{2+}=150 mgL^{-1} and H_2O_2= 400 mgL^{-1}.

The results are shown graphically in Figure 5. In Figure 5, the highest removal efficiencies are 90.77% and 62.02% for color and COD, respectively at the end of 30 – minute experiment time with a pH initial value of 3. Color and COD removal efficiencies decreased in experiments performed above and below pH 3.

When pH is below 3, since complex iron types reacting with H_2O_2 slower are formed, down and in that case oxidation removals also decrease. Production of OH• radical decreases since precipitating $Fe(OH)_3$ is formed when pH is above 3 and as a result, the removal efficiency decreases (Bouasla et al. 2010).

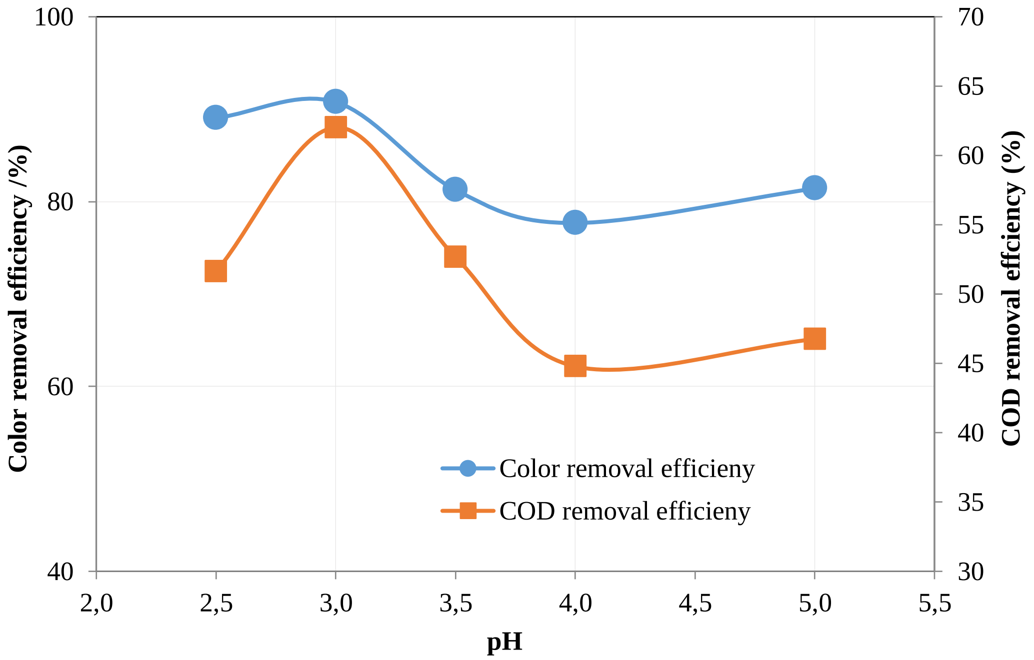

Figure 5. Effect of pH concentration on color and COD removal efficiency in fenton oxidation (C_0=200 mgL^{-1}, H_2O_2= 400 mgL^{-1}, Fe^{2+}=150 mgL^{-1}, T=20^{0}C, t=30 min)

3.4. Effect of temperature

The effect of temperature in the experiments was examined in the range of 20-60 ^{0}C. Experiments were conducted under the conditions, where pH is 3, H_2O_2 is 400 mgL^{-1}, T is 30 min and Fe^{2+} is 150 mg L^{-1}. The data obtained are shown graphically in Figure 6. As seen in Figure 6, no significant change in color and COD removal was observed in all temperature experiment. The color removal efficiencies were between 87,53% and 89,94% and the COD removal efficiencies were between 61,62% and 63,76%.

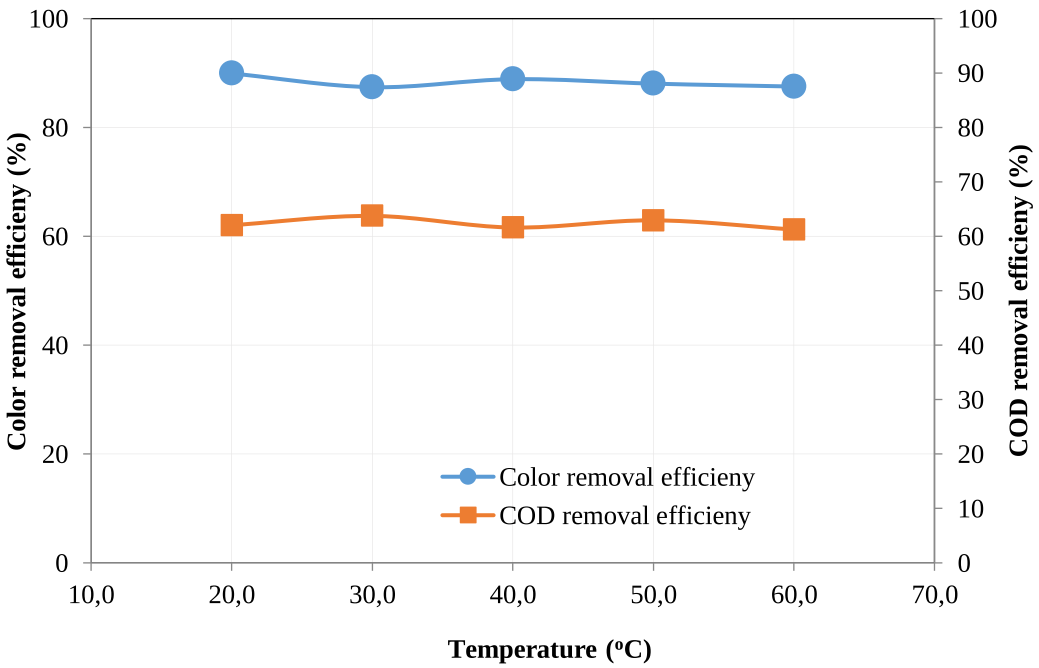

Figure 6. Effect of temperature on color and COD removal efficiency in fenton oxidation (C_0=200 mg L^{-1}, H_2O_2=400 mg L^{-1}, Fe^{+2}=150 mg L^{-1}, pH=3, t=30 min.)

4. Conclusion

In this study, the degradability of reactive BY2 dyestuffs by Fenton oxidation process which is one of the advanced oxidation processes (IOP) was investigated. The degradability of the dyestuff (BY2) was evaluated by color and COD parameters. Trials were performed within 30 minutes. The amount of Fe^{2+} (25, 50, 75, 100, 125, 150 and 200 mg L^{-1}), H_2O_2 amount (100, 200, 300, 400, 500 and 600), pH (2.5; 3; 3.5; 4 and 5), the concentration of dyestuffs (150, 200, 250, 300, 350 and 500 mgL^{-1}) and the temperature (20, 30, 40, 50 and 60 ^{0}C). Optimum conditions in the study were determined to be as follows: pH=3, C_0=200 mg L^{-1}, 150 mg L^{-1} Fe^{2+}, 400 mg L^{-1} H_2O_2, 20^{0}C temperature and 30 min of reaction time. Under these conditions, color and COD removal efficiencies were 90.71% and 62.04%, respectively. As the result of this study, it can be suggested that Fenton oxidation is an effective treatment alternative for BY2 dystuff.

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