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Heterogeneous Fenton process with Fe(III) based catalyst for treatment of textile industry wastewater

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In this study, colour and chemical oxygen demand (COD) removal from the textile wastewater by heterogeneous Fenton process have been investigated. Primarily, the Fe(III)/SnO_2 catalyst is prepared by co-precipitation method and characterized by BET analyses. The BET analysis results show that the pore size of the Fe(III)/SnO_2 catalyst is 2.013 nm and it is classified as a mesoporous catalyst. Then the prepared catalyst is used in the heterogeneous Fenton tests. The effects of the amount of the catalyst, *p*H of the solution, hydrogen peroxide (H_2O_2) concentration, temperature and reaction time on the color and COD removals have been studied and the optimum conditions are determined. In the optimum experimental conditions (2.0 g/L of 8 wt.% Fe/SnO_2, *p*H 2, hydrogen peroxide concentration 300 mg/L, temperature 35°C and reaction time 90 min), 91% colour and 86% COD removal efficiencies are obtained. The COD removal kinetics of textile wastewater is also investigated. It is determined that the removal of COD obeyed the second-order kinetics. Finally, stability and reuse of the catalyst are tested. This catalyst can be successfully used repeatedly and suitable for textile wastewater treatment.

Keywords: Colour removal ,COD removal, Fe(III)/SnO_2 catalyst, Heterogeneous Fenton, Industrial wastewater

The use of large amounts of water in the textile industry and the discharge of this water into the environment is one of the serious environmental problems. This wastewater discharged into the environment has a high colored and chemical oxygen demand (COD) value. Toxic substances formed by the hydrolysis of dyes, due to the mutagenic and the carcinogenic effect, is a significant threat to the living organism and human health[1,2]. Many textile dyes are resistant to light oxidation conditions. For this reason, strong oxidation agents (such as Fenton's reagent) are needed to disrupt these organic structures[3].

Advanced oxidation processes (AOPs) receive a great deal of attention in the treatment of wastewater containing biologically insoluble organic pollutants. Because hydroxyl radicals (·OH) produced in advanced oxidation processes have high oxidation potential (2.8 eV), they can disrupt organic pollutants through dehydrogenation, redox reaction and electrophilic addition reactions[4]. When the Fenton reagents are added to the wastewater in a strongly acidic environment, complex redox reactions are indicated in the following Eq. (1)-Eq. (4)[5,6].

$$H_2O_2 + Fe(II) \rightarrow Fe(III) + \cdot OH + HO^- \quad \ldots (1)$$

$$\cdot OH + RH \rightarrow H_2O + \cdot R \quad \ldots (2)$$

$$R + Fe(III) \rightarrow R^+ + Fe(II) \quad \ldots (3)$$

$$R^+ + H_2O \rightarrow ROH + H^+ \quad \ldots (4)$$

Fenton reactions constitute a large amount of iron sludge. This method has many disadvantages, such as deactivation and neutralization of the iron ion. These disadvantages can be overcome with a catalyst in heterogeneous Fenton processes[7]. Numerous catalysts have been used in heterogeneous Fenton processes. The most commonly used catalysts are iron minerals (such as magnetite, hematite, martit, goethite, pyrite, zeolite) that can be magnetically separated from the reaction medium and abundant in the earth[8]. In recent years, semiconductor metal oxides have been used as catalysts in oxidation processes. Semiconductors have two different energy bands, one of which is an electron and the other is an empty energy level. Unlike conductors, there is a gap band between the conductivity band and the valence band. Semiconductor metal oxides can oxidize all types organic compound due to their high oxidation potential[9]. As a result of the addition of metal ion to the surface at the semiconductor metal oxides, the appropriate change of potential is created and the areas under which the reduction reactions occur at the surface of the catalyst. In addition, the addition of metal or ions allows the reduction of the defective areas in the crystal mesh structure of the semiconductor particle[10]. Table 1 was represented the catalysts used in heterogeneous Fenton processes in recent years.

Table 1 — Catalysts used in recent studies.

Catalyst	Removed component	Reference
Iron slag (Fe-S)	Paracetamol	11
Iron phthalocyanine ($NiCo_2O_4$@FePc)	Dye in wastewater	12
Fe^0/CeO_2	Tetracycline	13
TiO_2	Toxic dye and 5-Sulfosalicylic acid	14
Goethite-montmorillonite	Naproxen	15
Fe_2GeS_4	Organic dye	16
Goethite, magnetite, hydrated iron(III) oxide , hematite.	2,4,4′-trichlobiphenyl hexachloroethane	17
Fe/AC and Fe/γ-Al_2O_3	Persulfate	18
Magnetite (Fe_3O_4)	Ciprofloxacin	19
Fe-Zn-oxide /hydrocarbon catalyst	Rhodamine B, methylene blue, antipyrine and phenol	20
Fe_3O_4/C/Cu	Methylene blue	21
$FeCl_3$	Olive oil industry wastewater	22
Zeolite	Melas wastewater	23
Magnetite (Fe_3O_4)	Basic violet 10	24
Fe_2O_3, TiO_2 and Fe_2O_3-TiO_2	Ciprofloxacin, sulfamoxazole and trimethoprim	25
Fe/CuO	Textile industry wastewater	26
Fe_3O_4/Pd	Pentachlorophenol	27
Pyrite (FeS_2)	C.I. Reactive Orange 29	28
Magnetite (Fe_3O_4)	Tetracycline antibiotics	29
Fe-impregnated nanoporous clinoptilolite (Fe-NP-Clin)	Acid Red 17	30

Since SnO_2 has very good mechanical, optical, magnetic and physical properties, they have attracted a lot of attention recently. SnO_2 particles with a wide bandwidth range are widely used in industries such as automotive, aircraft, paint, glass, chemical, electronics and electricity. Also it is suitable for use as a catalyst due to its strong oxidizing and easy availability[31].

In this study, it is aimed to synthesize Fe(III)/SnO_2 catalyst and treat industrial textile wastewater by using heterogeneous Fenton process with Fe(III)/SnO_2 catalyst. For this purpose; the parameters which effected on color and COD removal such as the catalyst amount, *p*H, H_2O_2 concentration, temperature and reaction time were examined and the optimum experimental conditions were determined.

Experimental Section

Materials

Experimental studies were carried out with industrial wastewater obtained from a textile factory in Bursa. The wastewater used is the reactive dyeing process exit water of an enterprise that produces printed curtain and tulle (synthetic textile). Fe(III)/SnO_2 containing 8 wt% iron ion was used as catalyst. Iron(III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$) and hydrogen peroxide (30 wt%) were supplied from Sigma Aldrich and tin (IV) oxide (SnO_2) was supplied from Merck. Sodium hydroxide (NaOH) (Sigma Aldrich) and sulfuric acid (H_2SO_4) (Merck) were used to adjust the *p*H of the samples.

Preparation of catalyst

Fe(III)/SnO_2 catalyst containing 4, 8 and 12 wt% of iron ions was synthesized using the precipitation method for use in experimental studies. Firstly when synthesizing the catalyst, $Fe(NO_3)_3.9H_2O$ and SnO_2 were dissolved in distilled water (100 mL). It was then stirred in a heated magnetic stirrer until the temperature reached 65°C. Then NH_4OH (26%) was added dropwise to the stirred solution and the *p*H value was adjusted to 9. The solution was stirred at 300 rpm for 2 h at a constant temperature of 65°C. At the end of mixing, the solution was filtered and dried at 105°C in an oven for 24 h. The dried sample was then stored in an ash oven at 600^{o}C for 2 h[32,33].

Heterogeneous Fenton experimental procedure

In the experimental study of the heterogeneous Fenton process, the *p*H value of a certain volume of wastewater sample was brought to the desired working range using 2.0 M H_2SO_4. Subsequently, the amount of the determined catalyst and H_2O_2 solution were added to the sample. The samples were shaken during the reaction time in the shaking water bath. At the end of the determined reaction time, the precipitation was enforced by adding 2.0 M NaOH. The catalyst was separated from solution by centrifuged and the analyses were performed.

Colour and COD Analysis

Colour analysis was performed by using the Hach Lange DR 3900 brand spectrophotometer. The maximum wavelength of the industrial wastewater sample was defined by scanning at the spectrophotometer. The maximum wavelength for the industrial wastewater sample was measured as 356.3 nm (λ_{max}). The absorbance values measured at this wavelength in spectrophotometer were indicated the change in the colour of the wastewater before and after the treatment. The measured absorbance values of wastewater were used in colour removal efficiency.

Then, the colour removal efficiency was calculated by Eq (5).

$$\text{Color Removal (\%)} = \frac{A_0 - A_t}{A_0} \times 100 \qquad \ldots(5)$$

A_0: Absorbance value measured at maximum wavelength before the treatment of wastewater.

A_t: Absorbance value measured at maximum wavelength after the treatment of wastewater.

In COD analysis, COD test kits brand of Hach Lange LCK 514 were used and measurements were accomplished by Hach Lange DR 3900 spectrophotometer. Initial COD value of wastewater was assigned as 2535 mg/L. The COD removal was determined by Eq (6).

$$\text{COD Removal(\%)} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_o} \times 100 \qquad \ldots(6)$$

COD_0: The initial COD value of wastewater, mg/L.
COD_t: The COD value of wastewater at any time t, mg/L.

Results and Discussion

Effect of the iron amount loaded on the catalyst

To determine the effect of the iron amount loaded on the catalyst, *p*H=2, 2.0 g/L catalyst amount, 300 mg/L H_2O_2 concentration, temperature 30°C and reaction time 120 min were kept constant. The results were given in Fig. 1. As seen in Fig. 1, the best colour and COD removal from textile wastewater was achieved in the catalyst containing 8 wt% iron ions. Therefore experiments were performed with this catalyst.

Characterization of catalyst

BET analysis was performed to appoint the surface area and pore size of the synthesized Fe(III)/SnO_2 catalyst. The surface area was determined at Afyon Kocatepe University Technology Application and Research Center using 7-point nitrogen gas adsorption isotherms. According to the results of the analysis, it is found that the surface area of the catalyst was 9.30 m^2/g and the pore size was 2.013 nm[32].

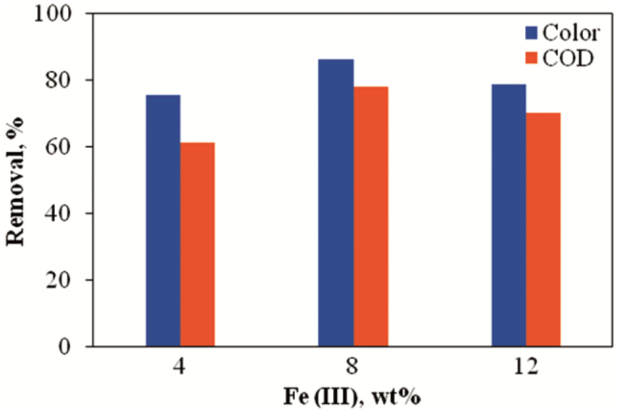

Fig. 1 — Colour and COD removal at different iron percentages.

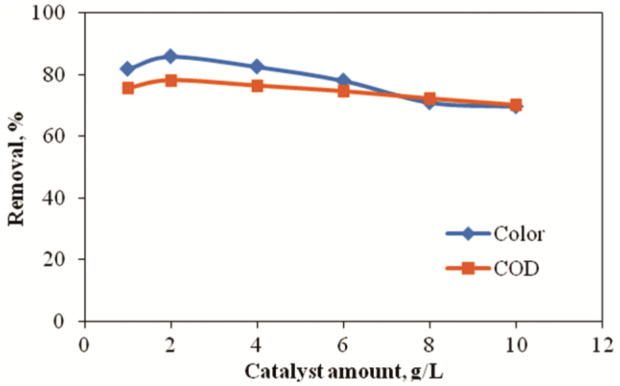

Fig. 2 — Change in colour and COD removal efficiency with catalyst amount (*p*H=2, H_2O_2=200 mg/L, reaction time 120 min, T=30°C).

According to the BET analysis results, the pore size of the Fe(III)/SnO_2 catalyst was between 2nm-50nm and it was classified as a mesoporous catalyst. Microporous solids are limited in their use in liquid systems due to their mass transfer limitations. In mesoporous solids, it is easier for larger molecules to enter the pore system, process them and leave the pore system again. Mesoporous solids are widely used with attempts to increase the diffusion of reagents into catalytic regions[34,35].

Effect of catalyst amount

The amount of catalyst is an important parameter as it catalyzes hydrogen peroxide to form the hydroxyl radical. While the effect of the catalyst amount on the colour and COD removal were examined (Fig. 2), *p*H=2, H_2O_2 concentration of 200 mg/L, temperature 30°C and reaction time were kept constant for 120 minutes, the amount of catalyst was changed in the range of 1.0-10.0 g/L.

As shown in Fig. 2, when the amount of Fe(III)/SnO_2 catalyst increased from 1.0 g/L to 2.0 g/L, the colour and COD removal efficiency increased. Maximum efficiencies were achieved with 86.0% colour and 78.2% COD at a 2.0 g/L catalyst amount. In higher catalyst amounts, the yield decreased due to the radical scavenging effect of excess iron. The optimum amount of catalyst was determined as 2.0 g/L. The amount of catalyst is an important parameter for oxidation processes. Generally, it is expected that organic compounds will decompose more rapidly at higher catalyst amounts. This can be explained by an increase in catalyst amount and an increase in H_2O_2 decomposition rate and a high concentration of ·OH radicals in the medium[36]. However, in the presence of more than the optimum amount of catalyst in the environment, the ferric ions react with hydrogen peroxide and form $HO_2\cdot$ with the less oxidizing ability and it causes the formation of iron hydroxyl sludge. In this case, the degradation efficiency is reduced. In case the amount of catalyst is less than the optimum amount in the environment, the decomposition of H_2O_2 stops because of the rapid consumption of the iron ion, and the degradation efficiency is reduced[37,38].

Effect of *p*H

The other important parameter, which must be determined since the affects the oxidation potential, is *p*H. The effect of *p*H on colour and COD removal were examined in the *p*H range of 1.5-5 at the constant amount of catalyst (2.0 g/L) and H_2O_2 concentration (200 mg/L). The results were presented in Fig. 3.

According to Fig. 3, the highest removal efficiency was attained at *p*H 2. The colour and COD removal efficiency decreased at increasing *p*H values. Khatee *et al.* (2016)[28] studied the heterogeneous Fenton process with natural pyrite particles and determined the optimum pH value as 2. In a similar study, Youssef *et al*. (2016)[39] carried out his experimental studies at the same *p*H value. The most important parameter in the Fenton oxidation process is *p*H. The *p*H value ranges from 2 to 4 in a narrow range. At the *p*H values outside of this range, oxidation decreases because less ·OH is produced. Moreover, H_2O_2 easily decomposed water and oxygen under the basic conditions (Zhao *et al.*, 2018)[17]. Formation of the formed iron hydroxide complexes and the sweeping of ·OH radicals reduce the oxidation ability[40].

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \qquad \ldots(7)$$

$$OH + H^+ + e^- \rightarrow H_2O \qquad \ldots(8)$$

When the *p*H is too low, as stated Eq.(7) and Eq. (8), the iron ions are inactive and their rate of generation of hydroxyl radicals is reduced[41]. In addition, strong acidic conditions can have a detrimental effect on both H_2O_2 and ·OH radicals[24]. Iron ions are not stable at high *p*H values and these ions are converted to the colloidal ferric species. They produce hydroxo complexes without generating hydroxyl radicals. In addition, hydrogen peroxide is unstable in the basic *p*H environment and in the presence of oxygen; decomposes and loses its oxidation ability[32].

Effect of hydrogen peroxide concentration

Hydrogen peroxide is the main source of ·OH radicals that are produced as a result of the oxidation reaction and which carry out the oxidation. While studying the effect of hydrogen peroxide concentration, experimental studies were performed at the optimum *p*H 2 and optimized catalyst amount. The concentration of hydrogen peroxide was changed between 50 and 500 mg/L and the experimental results were given in Fig. 4.

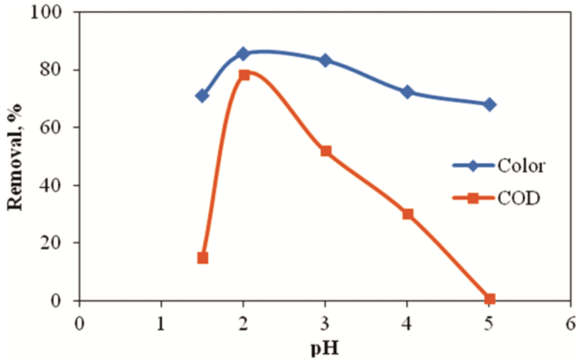

Fig. 3 — Change of colour and COD removal efficiency with *p*H (catalyst amount 2.0 g/L, H_2O_2=200 mg/L, reaction time 120 min, T=30°C).

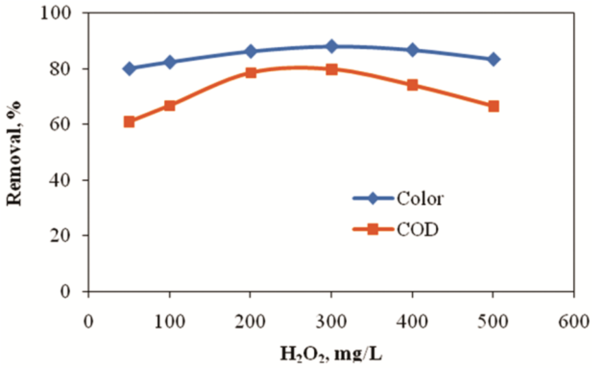

Fig. 4 — Change of colour and COD removal efficiency with hydrogen peroxide concentration (catalyst amount 2.0 g/L, *p*H=2, reaction time 120 min, T=30°C).

When Fig. 4 is examined, the colour and COD removal efficiency also increased rapidly with the H_2O_2 concentration increased from 50 mg/L to 300 mg/L. The increase in colour and COD removal efficiency with increasing concentration of hydrogen peroxide can be explained by the formation of ·OH radicals[30]. However, at high concentrations of H_2O_2, the colour and COD removal efficiency were reduced. This can be explained by the sweeping effect of excess hydrogen peroxide on the hydroxyl radicals in the medium[42]. Excess hydrogen peroxide reacts with hydroxyl radicals to cause a reduction of the hydroxyl radicals in the environment and the resulting hydroperoxyl radicals react with hydroxyl radicals to form H_2O and O_2[43]. In this study, the optimum hydrogen peroxide concentration for Fe(III)/SnO_2 catalyst was determined as 300 mg/L.

Effect of temperature

To determine the effect of temperature, *p*H=2, 2.0 g/L catalyst amount and 300 mg/L H_2O_2 concentration were kept constant, colour and COD removal at different temperatures (20-50°C) were investigated. The results were given in Fig. 5.

Considering the Fig. 5, when the temperature increased from 20 to 35°C, colour and COD removal efficiency increased. This can be explained by the increase the reaction rate between the hydrogen peroxide and catalyst in the increased temperature. This accelerates the decomposition of hydrogen peroxide to the hydroxyl radical and leads to an increase in colour and COD removal efficiency[2,44]. When the reaction temperature was higher than 35°C, color and COD removal efficiencies have decreased. It can be possible that hydrogen peroxide may undergo self-decomposition at high temperature. Ayodele *et al*. reported that H_2O_2 has become thermally decomposed into H_2O and O_2, and is subjected to a scavenging effect at high temperature[45-47]. Yip *et al*. also reported that H_2O_2 is thermally unstable at elevated temperature[48]. In addition, high temperature causes both investment and operating costs to be high. Therefore, the tests were conducted at an optimum temperature of 35°C.

Effect of reaction time

The effect of the reaction time on colour and COD removal was investigated for different times in the range of 5-240 min and the results are given in Fig. 6. Other parameters were kept constant at optimum values.

At the first 30 min of the experimental study, the oxidation reaction was very fast, the colour removal efficiency was 80.6% and the COD removal was 65.1%. This can be explained by the fact that the reaction components, iron ion and hydrogen peroxide, are abundant in the environment[49]. After the 90th minute of the reaction, it was found that the reaction was decelerated due to the reduction of hydrogen peroxide concentration resulting in the reduction of ·OH radicals produced in the medium. For this reason, optimum reaction time was chosen as 90 min in which maximum color (90.8%) and COD (86.2%) removal efficiency were obtained.

Kinetic studies

While the kinetics study of the treatment of the textile industry with the heterogeneous Fenton process was investigated, the COD values of the wastewater, a parameter representing the organic matter, were utilized[50] (Lucas and Peres, 2009). For this purpose, the reaction time was changed between 5 min and 240 min and the COD oxidation at 35°C was investigated and the time to balance was determined as 90 min.

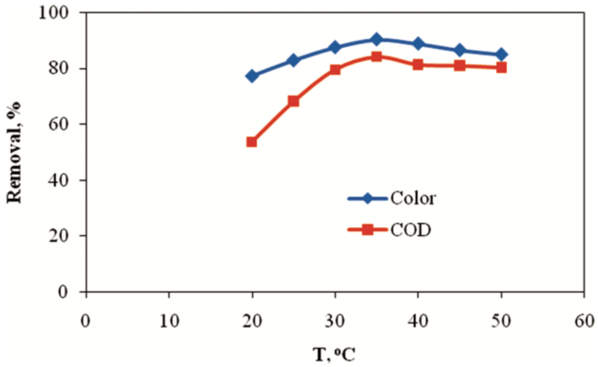

Fig. 5 — Change of colour and COD removal efficiency with temperature (catalyst amount 2.0 g/L, *p*H=2, H_2O_2=300 mg/L, reaction time 120 min).

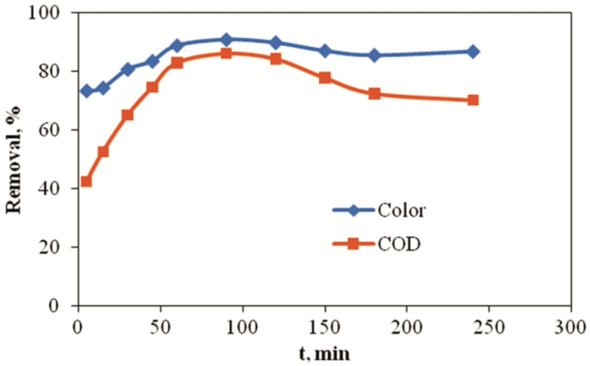

Fig. 6 — Change of colour and COD removal efficiency with reaction time (catalyst amount 2.0 g/L, *p*H=2, H_2O_2=300 mg/L, T=35°C).

The COD values acquired were applied to the zero-order Eq. (9), first-order Eq. (10), and second-order Eq. (11) reaction kinetics, and regression equations were deduced. The calculated kinetic parameters were reported in Table 2[51,52].

$$C_t = C_o - k_o t \qquad \ldots(9)$$

$$\ln C_t = \ln C_o - k_1 t \qquad \ldots(10)$$

$$\frac{1}{C_t} = \frac{1}{C_o} + k_2 t \qquad \ldots(11)$$

where C_0 is the initial COD value (mg/L)of wastewater, C_t is the COD value (mg/L) of wastewater at anytime t, the k_0(mg/L.min) zero-order, the k_1(1/min) first-order and the k_2(L/mg.min) second-order kinetic constants.

When the obtained regression data were compared, the highest regression coefficient (R^2) value was in the second-order kinetic (Table 2 and Fig. 7). Therefore, it can be said that the removal of the textile industry wastewater by the heterogeneous Fenton process is the second-order reaction kinetics.

The better fit of the reaction rate to second-order kinetics can be explained as follows: Equation 1 shows Fenton's oxidation rate is affected by two important factors such as hydrogen peroxide dose and iron concentration. Although the iron concentration is important in terms of reaction kinetics, the peroxide dose is also important in terms of providing better oxidation efficiency. Already in this study, we found that the amount of iron and peroxide concentration affect the reaction efficiency. In other words, parametric studies confirm that the reaction rate expression is second order. In this case, the rate of formation of the hydroxyl radical can be expressed as:

$$\text{Reaction rate} = k_2\,(\text{Fe(II)})\,(H_2O_2) \qquad \ldots(12)$$

However, the initial peroxide or iron amount being less or more affects the formation of $OH^{\cdot}$ radicals and the progress of the reaction. For example, if there is excess hydrogen peroxide or Fe(III) in the environment, more oxygen will result in the Fenton system[53]. Therefore, it is vital to determine the optimum dose of peroxide or iron.

Reuse of the catalyst

Experimental studies were performed to examine the reusability of the catalyst at optimum conditions (catalyst amount 0.2 g/L, pH 2, H_2O_2=300 mg/L, temperature 35°C and reaction time 90 min) were carried out in four cycles. In each experimental study, the catalyst was filtered and separated from the sample. It was then washed with deionized water and dried in a 105°C oven.

Figure 8 represent the results acquired in four steps of colour and COD removal efficiency. According to these results, the colour and COD removal efficiency of wastewater treatment gradually decreased. This situation can be explained by the fact that the amount of iron ion separated from the catalyst surface is low[32,54]. High colour and COD yield were obtained in four consecutive cycles. This is very important in practical terms because of the possibility that the catalyst will be used over a longer period of time.

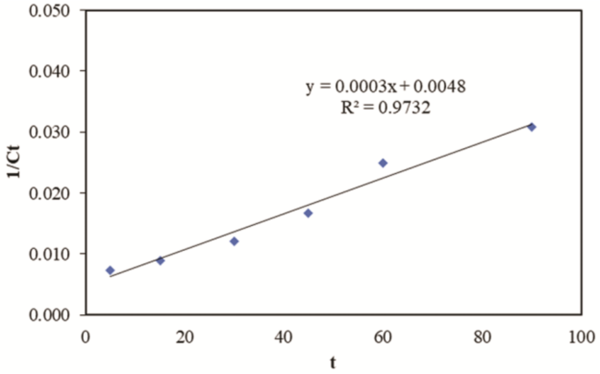

Fig. 7 — Second-order kinetic for COD removal by heterogeneous Fenton oxidation.

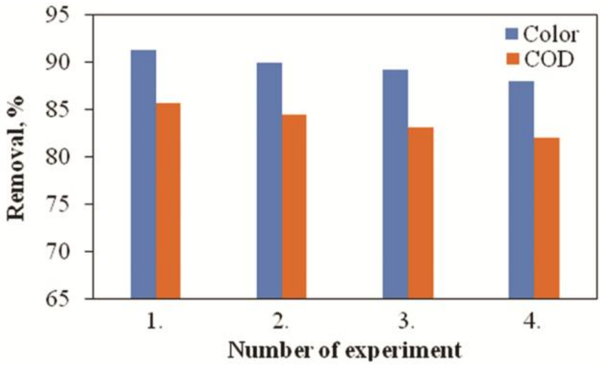

Fig. 8 — Reuse of catalyst at optimum experimental condition.

Table 2 — The kinetic constants for the COD removal of textile wastewater at 35°C.

Zero-order kinetic		First-order kinetic		Second-order kinetic	
k_0 (mg/L.min)	R^2	k_1 (1/min)	R^2	k_2 (L/mg.min)	R^2
1.2408	0.896	0.0178	0.962	0.0003	0.973

Conclusions

The color and COD removal by the heterogeneous Fenton process are investigated from textile wastewater and Fe(III)/SnO_2 containing 8% by weight of iron ion as catalyst is used. In experimental studies, the effects of *p*H, catalyst amount, hydrogen peroxide concentration, temperature and reaction time on the colour and COD removal have been investigated. Catalyst amount 2.0 g/L, *p*H 2, hydrogen peroxide concentration 300 mg/L, temperature 35°C and reaction time 90 min are determined the optimum conditions and under these conditions 91% color removal efficiency and 86% COD removal efficiency have been obtained. Kinetic study is performed and it is determined that it obeys the second-order kinetic model. The high colour and COD removal efficiency as a result of the study report that the heterogeneous Fenton process is an appropriate process for the treatment of textile industry wastewater. The metal oxides used as catalysts in the heterogeneous Fenton process provide large surface area. The large surface area provides more active site, thus more hydroxyl radicals are catalyzed than hydrogen peroxide. Therefore, the treatment of wastewater performs in a short time with high efficiency. In heterogeneous Fenton processes, iron ions are stabilized with metal oxides, preventing the formation of iron-containing sludge. In addition, the catalyst can be easily separated from solution and reused in oxidation processes. The heterogeneous Fenton process in wastewater treatment is the preferred process in recent years due to its advantageous features and effective removal.

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