COD Removal from Mixed Dye Wastewater Using Natural Pyrite Ore by Heterogeneous Fenton Process

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Abstract – In this study, it was aimed to remove COD from wastewater prepared from a mixture of rhodamine 6G, methyl orange, and crystal violet dyes using natural pyrite ore as a heterogeneous fenton catalyst. The parameters of pH (2-9), H_2O_2 concentration (0.5-5 g/L), and catalyst dosage (0.5-5 g/L), which are thought to have major effects on the heterogeneous fenton process in COD removal, were investigated in a batch system. Characterization studies of natural pyrite ore were performed by X-Ray Diffractometer (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDX), and Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy analyses. According to the data obtained, optimum values were determined as pH of 2, H_2O_2 concentration of 2 g/L, and 1.5 g/L of catalyst dosage. The COD removal efficiency was calculated as 94.7% under optimum conditions. According to the characterization results, it was determined that the pyrite ore contains (wt. %) Fe (44.87%) and S (51.02%) in a major proportion. The pyrite ore had a well crystalline and irregular structure. The fingerprint bands such as Fe-O, Fe-S are determined by FTIR spectrum. Pyrite was found as an effective catalyst for COD removal in this study and can be used as a promising catalyst in future heterogeneous fenton studies by expanding its catalyst property.

Keywords: FeS_2, dye, wastewater, heterogeneous fenton, oxidation

1. Introduction

Industrial wastewaters pose a threat in receiving environments due to their multiple pollutant composition. Industries produce paints with various properties to meet the coloration needs of spaces, furniture, appliances, and even foods that are part of daily life. When such wastewater is discharged to receiving environments, it exchanges the water quality and threatens living life. For this reason, it has great importance to treat wastewater with organic and inorganic content before discharging it to the receiving environment. In the literature, many increment methods have been reported successfully applied for dye-containing wastewaters such as; Electrochemical treatment[1], Sonophotocatalytic treatment[2], membrane systems[3], adsorption[4], etc. The effectiveness of treatment methods for removing pollutants is one of the selection criteria of processes. Advanced oxidation processes have been reported as successful in removing organic pollutants[5], [6]. There are studies in the literature that fenton processes are investigated as both pre-treatment[7] and post-treatment[8]. The Fenton process can successfully apply to non-biodegradable pollutants[9]. Its easy application, being applicable at atmospheric pressure and room temperature can be listed among its advantages[10]. However, the use of additional chemicals such as Fe^{2+} and H_2O_2, the occurrence of iron sludge [10] and the need to adjust pH in a narrow range[11] are among its disadvantages. As an alternative to homogeneous Fenton processes, different forms of iron and nanoparticles synthesized in the laboratory environment or nanoparticles synthesized in different compositions of other metal catalysts can be used in heterogeneous fenton processes, which allows the use of a wide range of catalysts in heterogeneous Fenton processes. In addition, the use of natural catalysts, as well as catalysts synthesized only in the laboratory environment, is also very popular[12]–[14]. Minerals and ores such as hematite, pyrite, magnetite are among possible alternatives. The issue of benefiting from nature may indicate that it is an environmentally sensitive process. Natural minerals, rocks, and ores can preferable due to their abundance in nature, being economical and acting as a successful catalyst in oxidation. Pyrite is one of the most abundant ores that contain iron sulfide on the Earth[15]. He et al., [15] stated that pyrite ore is cheaper and easier to obtain compared to zerovalent iron (ZVI). Also, they stated that pyrite releases iron into the environment more slowly than ZVI, and it has a regulatory effect on the iron cycle. Although the efficiency of pyrite as a catalyst in Fenton processes for dye-containing wastewaters has been investigated[16], [17], as far as the author is aware, the effectiveness of Peru origin pyrite ore on COD

removal for the dye mixture wastewaters (Rhodamine 6G, methyl orange, and crystal violet dyes) has not been previously investigated with heterogeneous fenton processes.

In this study, the decomposition of dye mixtures using natural pyrite ore (Cerro de Pasco /Peru) as a catalyst by heterogeneous Fenton process is discussed in terms of COD removal. Characterization of pyrite ore such as XRD, FTIR, and SEM/EDX made to better understand the contribution of the catalyst to the heterogeneous fenton oxidation.

2. Material and Method
2.1. Procurement and preparation of the catalyst
Natural pyrite (FeS_2) ore (Fig.1(a)) originating in Cerro de Pasco /Peru, was purchased commercially and was grounded first in a jaw crusher and then in a ceramic mortar and sieved with a size of 200 mesh (Fig.1 (b)). FeS_2 was subjected to ultrasonication for 5 min in 50 mL of a solution containing 95% ethanol to remove impurities in the ore. Then, the samples were washed with acid containing 1 M HNO_3 solution and rinsed several times with distilled water and dried in an oven at 30 °C for 24 hours, then sieved again and stored in a desiccator for use throughout the trials.
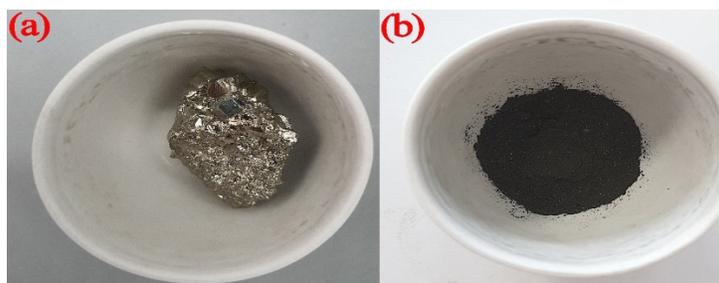

Fig.1: (a) Raw and **(b)** crushed natural pyrite ore

2.2. Chemicals and preparation of dye mixture
$HNO3$, $H2O2$, $NaOH$, $Na2SO3$ were purchased commercially from Sigma. While $HNO3$ and $NaOH$ were used to adjust the wastewater pH value, $Na2SO3$ was used as the quenching agent. Rhodamine 6G (CAS number: 989-38-8, Dye content, 99%), methyl orange (CAS number: 547-58-0, Dye content 85%) and crystal violet (CAS number: 548-62-9, 90.0% anhydrous basis), were used for dye mixture preparation. The dye solution was prepared as a mixture containing 50 mg/L concentrations of all three dye types and was used as wastewater throughout the trials.

2.3. Characterization of the catalyst
For $FeS2$ characterization, X-Ray Diffractometer (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDX), and Fourier Transform Infrared Spectroscopy (FTIR) were made. XRD, SEM / EDX, and FTIR analyses were performed using PANalytical Empyrean (CuKα radiation/2θ ranging from 15° to 90°), Zeiss Sigma 300, Micrometrics 3Flex, and Thermo Scientific-Nicoleti S10 FTIR Spectrometer, respectively.

2.4. Analysis and Calculations
Chemical oxygen demand (COD) analysis was made according to the closed reflux colorimetric method, and the color readings were made according to the Pt-Co standard method [18]. pH value of the solution was measured with a multimeter (wtw multi 340i). The efficiency of the process is evaluated on the pollutant removal (%) with the help of Eq. 1.

$$Removal\ efficiency\ (\%) = \frac{(C_0 - C_t)}{C_0} x100 \tag{1}$$

While C0 refers to the initial COD and Color concentration (mg/L) of the wastewater, Ct refers to the COD and Color concentration in the wastewater sample taken at time t.

2.4. Experimental Procedure

The COD and color removal from the dye mixture solution with the heterogeneous fenton process was conducted in a batch system. The experiments were carried out with a multi-magnetic stirrer (Daihan SMHS-3) in 250 mL flasks containing 150 mL of wastewater at a constant 200 rpm mixing speed. Operating parameters were selected as pH, H_2O_2 concentration (g/L), and catalyst dosage (g/L). In the experiments, the total reaction time was kept at 90 min and samples were taken at different time intervals. In the experiments that investigating the COD removal efficiency, to reach an equilibrium of adsorption before dye degradation reaction, the suspension containing dye mixture and catalyst was stirred for 60 min(Fig.5). Then, the desired concentration of H_2O_2 was added to the flasks. After this procedure, the reaction time of the heterogeneous Fenton process was initiated. For all experiments, 5 mL samples were taken at different times and filtered with 0.45 μm syringe filters. Filtered samples were transferred to tubes containing 10 μL of 2M Na_2SO_3 solution. Na_2SO_3 solution was used to quench possible hydroxyl radical reaction [19] before UV-vis analyses. To calculate the residual H_2O_2 concentration, readings were made according to the methods proposed by Talinli and Anderson [20] and Benatti et al.[21] . Color removal was investigated to determine catalyst performance. Samples taken at certain time intervals for color readings were passed through 0.45 syringe-type filters and read with UV-vis spectrophotometer according to the Pt-Co method[18]. All the experiments were repeated twice for duplicity purposes. For possible adsorption to the syringe filter and sampling container, the syringe and tube were washed several times with ultrapure water, and COD and color readings were made according to the closed reflux colorimetric method and the Pt-Co standard method, respectively, and found below the detection limit.

3. Results and discussion

3.1. Characterization of the catalyst

SEM analysis provides information about the surface morphology of the catalyst. The image of the SEM analysis is shown in Fig.2. As seen, FeS_2 has an irregular structure, and particles are distributed in various sizes. In addition, rough and porous structures attract attention. Thiam et al. [22] reported that irregular structures are useful for the heterogeneous fenton process. Rough surfaces provide an advantage for more iron to participate in the reaction compared to smooth surfaces. According to the EDX analysis results, major components (wt. %) such as Fe (44.87%) and S (51.02%) are present in the ore. As well as these components, impurities such as Ca (0.28%), Si (0.23%), Cu (0.19%), Al (0.11%), O (2.14%), C (1.02%) and others (0.14%) are present. These impurities can be attributed to the natural availability of the ore. So, it can be said that used FeS_2 ore is not completely pure. Sun et al. [23] reported that laboratory synthesized FeS_2 had 25% iron in FeS_2 according to EDX results. This difference can be attributed to the fact that pyrite ore differs depending on the local characteristics.
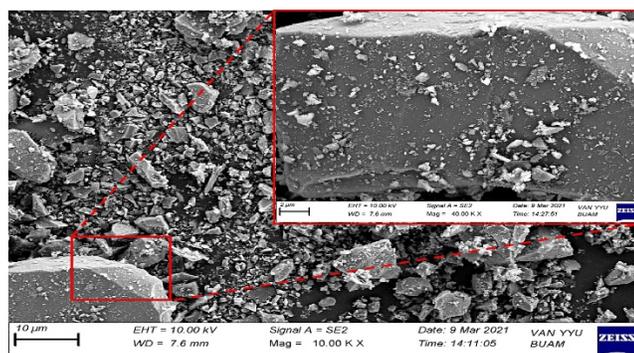

Fig.2. SEM analysis of natural pyrite ore

XRD analysis provides important information about the crystallographic structures of materials. The result of the XRD analysis of the FeS_2 ore is shown in Fig.3. From the XRD pattern, characteristic diffraction peaks of FeS_2 are observed at 33.09°, 37.14°, 40.84°, 47.49°, 56.34°, 61.75°, and 64.35° (JCPDS: 42-1340). Observed peaks at 28.58° and 58.84° correspond to cubic FeS_2 (111) and (222) plane reflections (JCPDS: 42-1340), respectively [24]. The peak with the highest density observed at 33.09° can be attributed to the crystal face (200)[25]. The non-broad sharp peaks of the XRD pattern can indicate that FeS_2 is well crystallized.
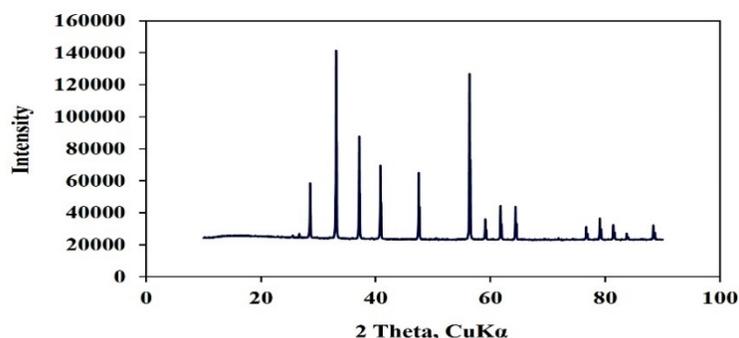
Fig.3: XRD Pattern of natural pyrite ore

It is possible to obtain information about the chemical structure of FeS2 ore by FTIR analysis. FTIR analysis results of the catalyst are shown in Fig.4. As can be seen from Fig.4, the material exhibited reflections at 545.59 cm-1and 609.76 cm-1. These can be attributed to possible Fe-S stretching bonds[26]. The band observed around 1020 cm-1 can be attributed to possible Fe-O vibration [27]. In addition, the band observed at 3676.34 cm-1 corresponds to the O-H stretch. Reflections observed at 2988.35 cm-1 and 2902.36 cm-1 can be attributed to -CH stretching vibrations. The presence of C (1.02%) in the natural pyrite ore was also proven by EDX analysis. The band observed at 2168.45 cm-1 and 2088.44 cm-1 can be associated with -Si-H stretching. [28], [29].
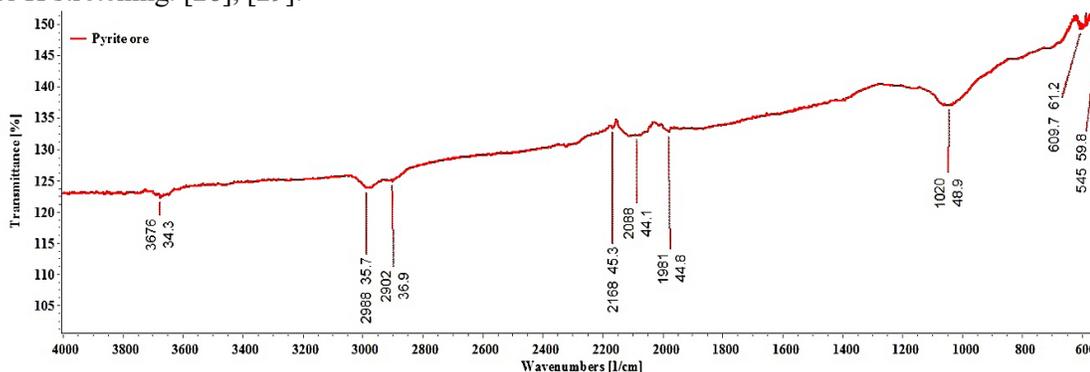

Fig. 4: FTIR analysis of natural pyrite ore

According to all the results obtained, it was confirmed that the FeS2 ore contains Fe and S densely, its morphology was found to be irregular and it was observed that it had a good crystal structure. Based on these findings, it can be concluded that natural pyrite ore can be a good source of iron for the heterogeneous fenton process.

3.2. Catalytic performance of the catalyst

Although the catalyst used is considered as a source of iron in the reaction, it is an ore due to its formation and can show an adsorbent property by nature. For this reason, a series of trials were conducted to determine the adsorption effect via a response of color removal (%). In the experiments, three wastewater samples containing the same concentration of contaminants (50 mg/L conc. of each dye) in 150 mL volume were treated at a constant 200 rpm stirring speed, initial wastewater pH of 3. Samples were taken at different time intervals (15-90 min). Only H2O2 (2 g/L) was added to the first trial, only FeS2 (1 g/L) was added to the second trial. The third trial contained FeS2 (1 g/L) and H2O2 (2 g/L) (heterogeneous fenton process). The results are shown in Fig.5. As can be understood from Fig 5, while the color removal efficiency for 1st trial and the 2nd trial remained below 60%, for the 3rd experiment the efficiency increased over 80%. The removal efficiency (55.23%) observed in FeS2 can be attributed to the adsorptive property of FeS2. The color removal efficiency for 1st trial

(H2O2 only) was observed as 32.71%. In this case, it may be evidence of how much the iron source affects the oxidation process. It is clear that the adsorption (FeS2 only) process is effective in color removal, but it is not possible to say that the main process is adsorption. When Fig.5 is examined, it is seen that the dominant process is heterogeneous fenton in varying time intervals (15, 30, 60, and 90 min). In addition, it is seen that the heterogeneous fenton process conducts faster while the adsorption process is taking place. Therefore, in this study, it can be said that the dominant process in removing pollutants from wastewater is the heterogeneous fenton process.
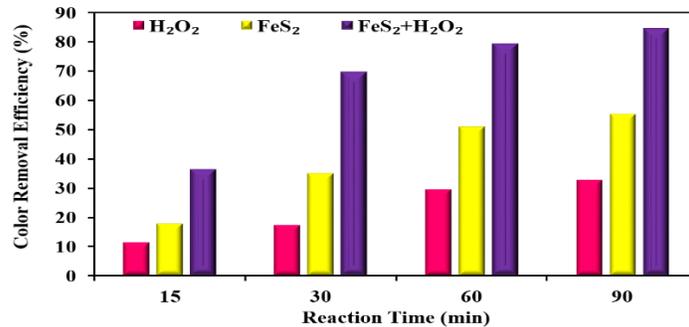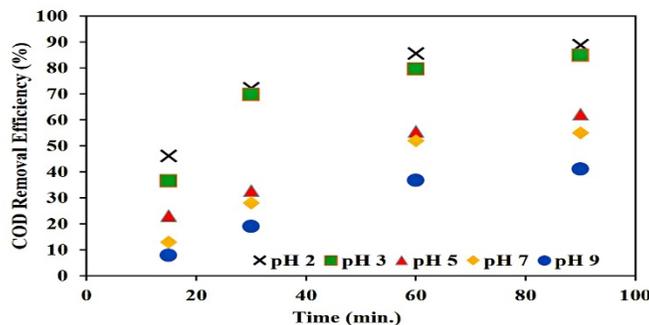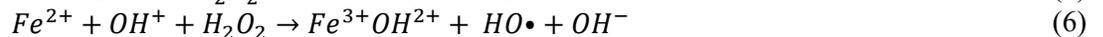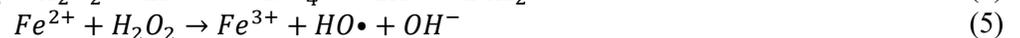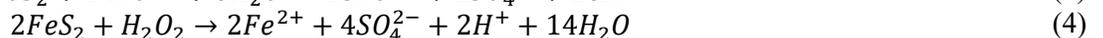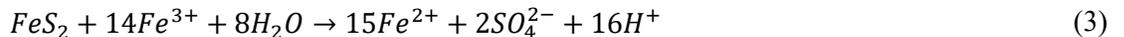

Fig.5: Effect of heterogeneous Fenton components on color removal

3.3. Effect of wastewater pH and time

At this stage, the effect of pH values of 2,3,5,7 and 9 on the COD removal efficiency was investigated. The experiments were carried out at a constant agitation speed of 200 rpm, 1.5 g/L FeS2 dosages, 15, 30, 60, and 90 min of reaction time, and 1.5 g/L H2O2. The results are shown in Fig.6. As can be seen from Fig.6, the highest removal efficiency (88.75%) was observed at pH 2. When the pH value increased from 2 to 3, the COD removal efficiency decreased slowly to 84.69%. The same trend was observed in subsequent pH values. This situation may be associated with the high oxidation potential of hydroxyl radicals at low pH values and decreasing potential of hydroxyl radicals at high pH values. Since the dissolution of FeS2 and the formation of Fe2+ increased in acidic environments[16] the highest yield was observed at pH 2 in this study. Fe3+ is formed as a result of the FeS2 and H2O2 reactions, and besides this, SO42− and H+ are formed (Eq. (2))[30]. This situation causes a decrease of the environment pH due to the nature of the reaction. In this study, it can be concluded that FeS2 and H2O2 have a good relationship for a heterogeneous fenton process, especially in pH-dependent walking steps.

$$FeS_2 + 7.5H_2O_2 \rightarrow Fe_{(aq)}^{3+} + 2SO_{4\,(aq)}^{2-} + H^+ + 7H_2O \tag{2}$$
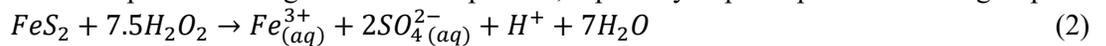
In the literature, in the heterogeneous fenton studies using FeS2, it was reported that the oxidation of pollutants generally took place in two ways [23], [31]–[33]. The first is the FeS2 oxidation indicated by Eqs.3-4, the second is described by Eqs. 5-6.

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{3}$$
$$2FeS_2 + H_2O_2 \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 2H^+ + 14H_2O \tag{4}$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^- \tag{5}$$
$$Fe^{2+} + OH^+ + H_2O_2 \rightarrow Fe^{3+}OH^{2+} + HO\bullet + OH^- \tag{6}$$

Fig.6: Effect of wastewater pH on COD removal efficiency

3.4. Effect of catalyst dosage

The effect of FeS2 dosage on COD removal was investigated for 0.5, 1, 2, 3, and 5 g/L. Experiments were carried out at a constant 200 rpm stirring speed, wastewater initial pH of 2, 90 min reaction time, and a fixed concentration of 2 mg/L H2O2. Results are shown in Table 1.

Table 1: Effect of FeS_2 dosage on COD removal

FeS_2 Dosage (g/L)	COD removal efficiency (%)
0.5	54.39
1	75.58
1.5	94.7
3	84.25
5	78.06

As can be seen from Table 1, while the FeS2 dosage increased from 0.5 g/L to 1.5 g/L, COD removal efficiency increased rapidly. This situation may be attributed to the higher amount of Fe2+ due to the increasing FeS2 dosage. Increasing Fe2+ may have accelerated the oxidation of pollutants in parallel with the mechanism in Eqs.5 and 6. This situation was reflected as an increase in removal efficiency. However, a slow decrease in COD removal efficiency is observed at the FeS2 dosage of 3 g/L and 5 g/L. It may be explained by the fact that the excessive amount of aqueous Fe2+ participating in the reaction consumes HO• unwantedly which acts as an oxidizer (Eq. (7))[23], [31], [34]–[36]. This situation is generally interpreted as a "scavenging effect" in the literature[37], [38].

$$Fe^{2+} + HO• \rightarrow Fe^{3+} + OH^- \tag{7}$$

According to the data obtained, it can be concluded that the optimum FeS_2 dosage for COD removal is 1.5 g/L for this study.

3.5. Effect of H₂O₂ concentration

The effect of H2O2 concentration on COD removal was investigated at 0.5, 1, 2, 3, and 5 g/L values. The experiments were carried out at a constant 200 rpm stirring speed, wastewater initial pH 2, the reaction time of 90 min, and a constant dosage of 1.5 g/L FeS2. Results are shown in Table 2.

Table 2: Effect of FeS_2 dosage on COD removal

H_2O_2 Dosage (g/L)	COD removal efficiency (%)
0.5	42.13
1	90.46
2	94.7
3	74.52
5	68.88

It is clear from Table 2 that while the H2O2 dosage increases from 0.5 to 2 g/L, COD removal efficiency increases effectively. The increased removal efficiency with increasing H2O2 concentration can be explained by the formation of a greater amount of hydroxyl radicals[39] and thus more pollutants being oxidized. Similar findings were reported[40]. It is observed that COD removal efficiency decreases at 3 g/L and 5 g/L dosages. The mechanisms are shown in Eq.8 and 9 [41] can explain this situation. Using more than the optimum amount of H2O2 reacted with the oxidative HO• and reduced its amount, and had a scavenging effect. On the other hand, OOH• has less oxidation capacity compared to HO•. Thus, the remaining less amount of hydroxyl radicals in the reactor and the formation of OOH• with low oxidation capacity resulted in a decrease in the oxidation of pollutants. Similar situations have been reported in the literature[42].

$$HO• + H_2O_2 \rightarrow OOH• + H_2O \tag{8}$$
$$OOH• + HO• \rightarrow H_2O + O_2 \tag{9}$$

Salehi et al.[43] explained the reduced pollutant oxidation at excessive H_2O_2 concentrations in the pyrite-assisted heterogeneous Fenton process with Eq.10 [41], [43], [44].

$$HO\bullet + HO\bullet \rightarrow H_2O_2 \qquad\qquad (10)$$

This may cause excessive H_2O_2 production in the system and contribute to the HO$\bullet$ scavenging effect of H_2O_2 at Eq.8, which may have reduced the oxidation of pollutants in this cycle. In the light of the data obtained, it can be said that the optimum H_2O_2 concentration for this study is 2 g/L.

4. Conclusion

Pyrite, which can be synthesized in the laboratory, is a waste as a result of mining activities, is handled as an ore, was used as a natural iron source in this study. The effects of major operational parameters such as H_2O_2 concentration, catalyst dosage, and initial pH value on COD removal from aqueous solutions containing mixed dyes were investigated by the heterogeneous fenton process using FeS_2 as a catalyst. According to the results of XRD, SEM/EDX, and FTIR, it was determined that FeS_2 ore densely contains (wt. %) Fe (44.87%) and S (51.02%), its morphological structure is irregular and well crystallized. H_2O_2 concentration and catalyst dosage affected the process efficiency with the same trend. While COD removal increased with increasing dosages, a decrease in COD removal was observed at dosages higher than optimum. The optimum conditions were determined for pH, catalyst dosage, and H_2O_2 dosage as 2, 1.5 g/L, and 2 g/L, respectively. Under optimum conditions, COD removal efficiency was observed as 94.7%. Consequently, it can be said that FeS_2 is an effective candidate catalyst for the removal of COD from dye mixture solutions and can be used as a promising catalyst in future heterogeneous fenton studies by expanding its catalyst property.

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