

Title:

Enhancing CETP Wastewater Treatment through Electro-Fenton Process Optimization

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Abstract:

Common Effluent Treatment Plants (CETPs) have been established and are operational across several industrial clusters in India. However, a significant challenge associated with CETPs is their insufficient treatment efficiency due to the highly variable nature of wastewater generated by different industries connected to a single facility. In this study, electro-Fenton process used as an advanced oxidation process that combines electrochemical oxidation and Fenton chemistry to effectively degrade organic matter in wastewater.

The Electro-Fenton process was conducted in a laboratory-scale electrochemical reactor for the treatment of secondary treated wastewater from a Common Effluent Treatment Plant (CETP). In this experimental setup, Ferrous Sulphate was added externally, while Hydrogen Peroxide (H₂O₂) was generated in situ at the cathode using carbon-based electrodes. This study focused on optimizing key process parameters, including pH, applied voltage, ferrous ion concentration, and reaction time, to enhance hydrogen peroxide production and chemical oxygen demand (COD) reduction.

The optimal conditions for in situ hydrogen peroxide generation were identified as pH 6 and 1.5 volts. Under these conditions, the maximum COD removal efficiency reached 73.8% with a ferrous ion concentration of 3000 ppm and a reaction time of 60 minutes. Additionally, experiments were conducted without the addition of Ferrous Sulphate at the same voltage (1.5 V), across pH levels of 3, 5, and 6. Among these, the highest COD reduction of 48.85% was observed at pH 6.

Keywords: CETP wastewater, Advanced Oxidation Processes, Electro-Fenton Process, in-situ Hydrogen peroxide, Ferrous sulfate, COD Reduction

1. Introduction

India has one of the fastest growing populations with billions of people. The increase in population naturally leads to a rise in demand for various products. As people seek better standards of living the demands for goods and services increase, thereby industrial growth. There has been an exponential increase in industrial growth due to which there is an increase in demand of water, which leads to generation of more quantity of wastewater.

Industry has to spend a lot on wastewater treatment which is quite uneconomical for small and medium scale industries that cannot provide acceptable treatment to achieve the standards. The discharge of industrial wastewater into water bodies is a major constitutes a significant source of environmental pollution, particularly in river ecosystems. In India, most of the pollution is caused by small and medium scale industries.^[12] As a result, the discharge of large volume of wastewater into water bodies leads to adverse effect on human health, aquatic life and the overall quality of the environment^[22]

A Common Effluent Treatment Plant (CETP) is a treatment system designed to collectively process wastewater generated by small and medium-scale industries within an industrial cluster.^[2] CETP treats wastewater from various industries collectively. The quality of the treated wastewater is influenced by whether the CETP is homogeneous or heterogeneous. In homogeneous CETPs, the wastewater has similar characteristics, whereas in heterogeneous CETPs, the wastewater varies significantly in terms of its composition. The wastewater that is been treated in CETP has biodegradable as well as non-biodegradable refractory organic compounds. These treatment plants employ a combination of physical, chemical, and biological processes to treat wastewater. Commonly used treatment methods typically include sedimentation, chemical coagulation, biological degradation, and among others. The combination of these methods is determined by the specific contaminants present in the wastewater and the desired level of treatment for effective pollution control. The conventional treatment cannot achieve the desired discharge norms because of the presence of refractory organic compounds, which leads to the need for advanced treatment of wastewater.^[21]

Advanced Oxidation Processes (AOPs) of various types have been researched to effectively treat refractory pollutants from wastewater. Advanced Oxidation Processes (AOPs) are among the most effective methods for removing refractory organic pollutants. The principle of AOPs involves the generation of hydroxyl free radicals ($\text{HO}\cdot$), which can be produced through various agents such as hydrogen peroxide (H_2O_2), Fenton's reagent, ozone (O_3), and combinations like UV/ O_3 , UV/ H_2O_2 , and $\text{O}_3/\text{H}_2\text{O}_2$. Most of the Advanced Oxidation Processes including Fenton related processes are effective under acidic and neutral pH like Fenton-related process.^[15]

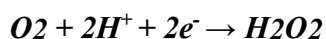
1.1. Theoretical Approach

H.J. Fenton has introduced the Fenton's process in 1894. It is among the AOPs using H_2O_2 as a precursor reagent of $\bullet OH$ radical. One of the advanced oxidation processes yields $\bullet OH$ Radical when reacts with iron (Fe^{2+}), which acts as a catalyst and a strong oxidant Hydrogen Peroxide.

Fenton's reaction involves the interaction of hydrogen peroxide (H_2O_2) with Ferrous Salts in an acidic condition, leading to the generation of hydroxyl radicals ($\bullet OH$). The basic reaction chemistry of the Fenton process,

1. Electrochemical Reduction of Oxygen to Hydrogen Peroxide (Cathode Reaction):

In the Electro-Fenton process, the reaction starts at the cathode, where oxygen (O_2) from the surrounding solution is reduced by gaining electrons through electrochemical reduction. This reaction produces hydrogen peroxide (H_2O_2).



This reaction occurs in the process reactor, typically under acidic conditions which helps stabilize the hydrogen peroxide. Hydrogen peroxide is essential because it can be further decomposed to form hydroxyl radicals ($\bullet OH$), which are highly reactive and capable of oxidizing organic pollutants. ^[13] The active species, $\bullet OH$ is a strong oxidizing agent that can efficiently degrade organic substances into harmless compounds through dehydrogenation. ^[10]

2. Fenton's Reaction (Decomposition of Hydrogen Peroxide):

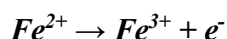
The critical step occurs when Hydrogen Peroxide (H_2O_2) reacts with Ferrous ions (Fe^{2+}), which are typically added to the system or already present to catalyze the reaction. This happens in an acidic medium, as Fenton's reaction is most efficient under acidic conditions.



Hydroxyl radicals ($\bullet OH$) are produced during this reaction. These radicals are extremely reactive and are capable of breaking down complex and recalcitrant organic compounds, making them the primary agents for pollutant degradation. The reaction also produces ferric ions (Fe^{3+}) and hydroxide ions (OH^-), which are byproducts of the reaction.

3. Oxidation of Ferrous Ions (Anode Reaction):

At the anode, ferrous ions (Fe^{2+}) are oxidized to ferric ions (Fe^{3+}), releasing electrons:



The electrons produced at the anode flow through the external circuit and participate in the

reduction of oxygen at the cathode, where hydrogen peroxide is generated. The overall efficiency of the process is affected by operating parameters like pH, Temperature, H_2O_2 and Fe^{2+} dosage, and reaction time.

In this process, basic Fenton process reactions are commonly accepted mechanisms including in situ generation of H_2O_2 on the cathode and sacrificial production of Fe^{3+} on the anode. No matter whether the Fenton's reagents are externally applied or in situ generated in a sacrificial anode and cathode, the homogeneous Fenton reaction produces the active oxidizing agent OH^- .

In particular, the in-situ electro-generation of hydrogen peroxide, obtained by oxygen reduction on carbon electrodes. In this process, H_2O_2 is electro generated and ferrous sulphate is externally added into the cell, where Fe^{2+} is produced by cathodic reduction of ferrous salts.

The efficiency of H_2O_2 generation is highly dependent on the operation parameters and cathode material for their appropriate electrochemical prosperities towards DO reduction, low catalytic activity for H_2O_2 and high over potential for hydrogen evolution.

In this experimental study, Electro-Fenton treatment is carried out for in-situ generation of hydrogen peroxide and evaluate the treatment of CETP (dye and dye intermediates based) wastewater. The aim of this study to reduce COD of secondary treated CETP wastewater using Electro-Fenton process through in situ generated hydrogen peroxide in Electro-Fenton reactor. There are health hazards like skin burns, eye damage, respiratory irritation, and fire hazards associated with Hydrogen peroxide.^[2]

In situ hydrogen peroxide (H_2O_2) generation offers numerous advantages in diverse applications, prioritizing safety, cost-efficiency, and sustainability. Hydrogen peroxide's reactivity and susceptibility to decomposition due to heat and light necessitate on-site production to mitigate risks linked to transportation and handling. The Electro-Fenton process is to reduce the organic pollutants. Reducing COD in CETP wastewater is essential to minimize environmental pollution, ensuring compliance with environmental regulations and sustainable water management.

2. Materials and Methods

2.1. Secondary treated wastewater from Common effluent treatment plant

In this experimental study, secondary treated wastewater from mainly dye and dye intermediates industrial wastewater containing CETP effluent was collected. CETP treats wastewater from 674 industries, 70% of which are dye and dye intermediate industries, and the rest are textile processing-based industries. So the wastewater carries a larger amount of refractory organics, which are highly toxic and not Vulnerable to biological processes. The characteristics of wastewater were determined and are listed in **Table 1**.

Table 1: Characteristics of Secondary treated wastewater from CETP

Parameters	Values	GPCB Prescribed limit
pH	7.71	6.5 to 8.5
COD (mg/L)	410	250
BOD (mg/L)	8	30
TSS (mg/L)	120	100

Chemicals for experiment

The analytical grade sulfuric acid was used to maintain the required pH, and Sodium Sulfate, and Ferrous Sulfate Heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were used to conduct the experimental runs of the electro- Fenton process. The analytical grade potassium permanganate (KMnO_4) and starch was used as titrant and indicator, respectively, to measure the moles of generated hydrogen peroxide. The analytical grade chemicals were used to prepare the reagents for conducting the analysis of COD as per method 5220 of standard methods for analysis of water and wastewater.

Electrodes

Carbon material-based electrodes were used in the electrochemical reactor. The anode was of a mixed metal oxide electrode (14 cm×4 cm×1 mm), and the cathode was made of graphite (14 cm×4 cm×1 cm).

Experimental Setup

A batch electro-Fenton experiment was conducted to oxidize the refractory COD in CETP wastewater using a lab-scale model. The pH of wastewater was adjusted to the desired level by adding sulfuric acid and Ferrous Sulfate Heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was introduced as a source of Fe^{2+} .

In situ generation of hydrogen peroxide (H_2O_2) was generated using carbon-based electrodes within the electrochemical reactor. The anode and the cathode were placed at a 5 cm distance, with an active electrode area of 22.5 cm². A 0.5 mM Na_2SO_4 electrolyte solution was used. For maintaining the effective mixing, stirring at 200-300 rpm was maintained throughout the experiments using a magnetic stirrer. Samples were collected at 5 minute intervals for the first 30 minutes, followed by sampling every 15 minutes up to a total reaction time of 60 minutes during the electro- Fenton reaction.

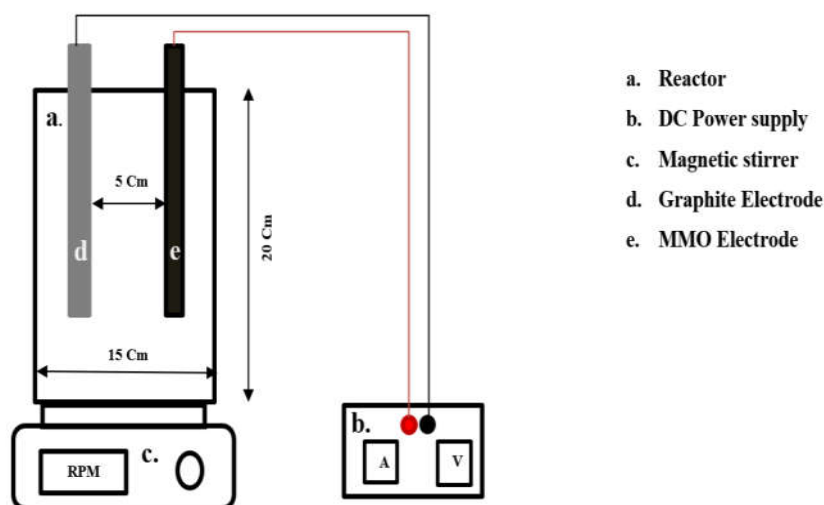


Figure 1: Schematic Diagram of Lab-Scale Model

2. Results and Discussions

Various pH values, dosages of ferrous sulphate, and applied voltages were systematically varied in a laboratory-scale model to determine the optimal conditions for in-situ hydrogen peroxide generation and COD reduction.

Figure 2 detail the results of in-situ hydrogen peroxide (H_2O_2) generation at 1.5 volts under varying pH conditions 6, 5, and 3 respectively. at pH 6, H_2O_2 concentrations increased from 0.65 mg/L at 5 minutes to 1.8 mg/L at 60 minutes, with corresponding moles of H_2O_2 ranging from 0.03×10^{-3} to 0.96×10^{-3} g/mole. at pH 5, H_2O_2 concentrations peaked at 1.2 mg/L after 60 minutes, with moles of H_2O_2 ranging from 0.04×10^{-3} to 0.93×10^{-3} g/mole and at pH 3, concentration of H_2O_2 varied between 0.01 mg/L and 0.65 mg/L during the 90-minute duration with moles of H_2O_2 varying from 0.016×10^{-3} to 0.30×10^{-3} g/mole.

These results illustrate the impact on pH on the effectiveness of hydrogen peroxide generation under controlled voltage conditions, indicating the successful and efficient in situ production of hydrogen peroxide within the electrochemical cell.

The maximum in-situ generation of hydrogen peroxide was observed at a voltage of 1.5 V and a pH of 6, as mentioned above. Very less production of hydrogen peroxide is observed at 5 and 10 minutes. After 10 min generation rate was increased up to 60 minutes but after that hydrogen peroxide was degraded. The degradation of hydrogen peroxide concentration after 60 minute occurs due to its natural decomposition into water, which is accelerated by factors such as fluctuation in pH, the presence of catalyst and electrode degradation. These factors collectively lead to a reduction in, in situ generated hydrogen peroxide after 60 minutes.

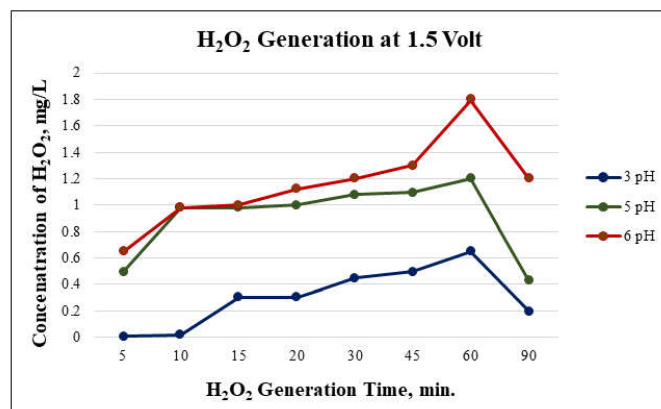


Figure 2: In-situ Hydrogen Peroxide Generation

2.1 Optimization of pH

First, varying voltage and ferrous sulfate doses, we optimized pH values to determine their optimal interaction in the experimental setup.

Figure 3 (a) illustrates that the COD reduction achieved within the voltage range of 0.5 to 3 volts at a pH of 3 varied from 1% to 55%. The maximum reduction of 51% was observed at 1.5 volts. An extended experimental run of 90 minutes yielded a COD reduction of 50%, which was not significantly different from the reduction observed at 60 minutes. Thus, a 60-minute contact time was determined to be the optimal duration for the Electro-Fenton (EF) process, as no significant improvement in COD reduction was observed beyond this period.

As shown in Figure 3 (b), the reduction in COD at voltages ranging from 0.5 to 3 volts at a pH of 5 varied between 2.5% and 60%. The highest COD reduction of 56.16% was achieved at 1.5 volts after 60 minutes, while the lowest reduction of 2.43% occurred at 3 volts. These results indicate that the efficiency of COD reduction is influenced by both the applied voltage and the reaction time, with optimal performance observed at specific conditions.

As illustrated in Figure 3 (c), the COD reduction at a pH of 6 ranged from 3% to 65% for voltages between 0.5 and 3 volts. The maximum COD reduction of 63% was observed at 1.5 volts after 60 minutes, while the minimum reduction of 3.65% occurred at 2.5 volts. These results suggest that the efficiency of COD reduction varies with both voltage and reaction time. Comparative analysis of COD reduction across different pH levels (3, 5, and 6) at 1.5 volts reveals that the EF process is more effective at pH 5 and 6, achieving reductions of 56% and 63% respectively, compared to a lower efficiency at pH 3. Consequently, no further experiments were conducted at pH 3. Additionally, at higher voltages (2.5 and 3 volts), ferrous ions accumulated on the graphite electrode surface due to electrostatic interactions, necessitating the reversal of the anode and cathode in subsequent experiments and the discontinuation of further runs at 2, 2.5, and 3 volts.

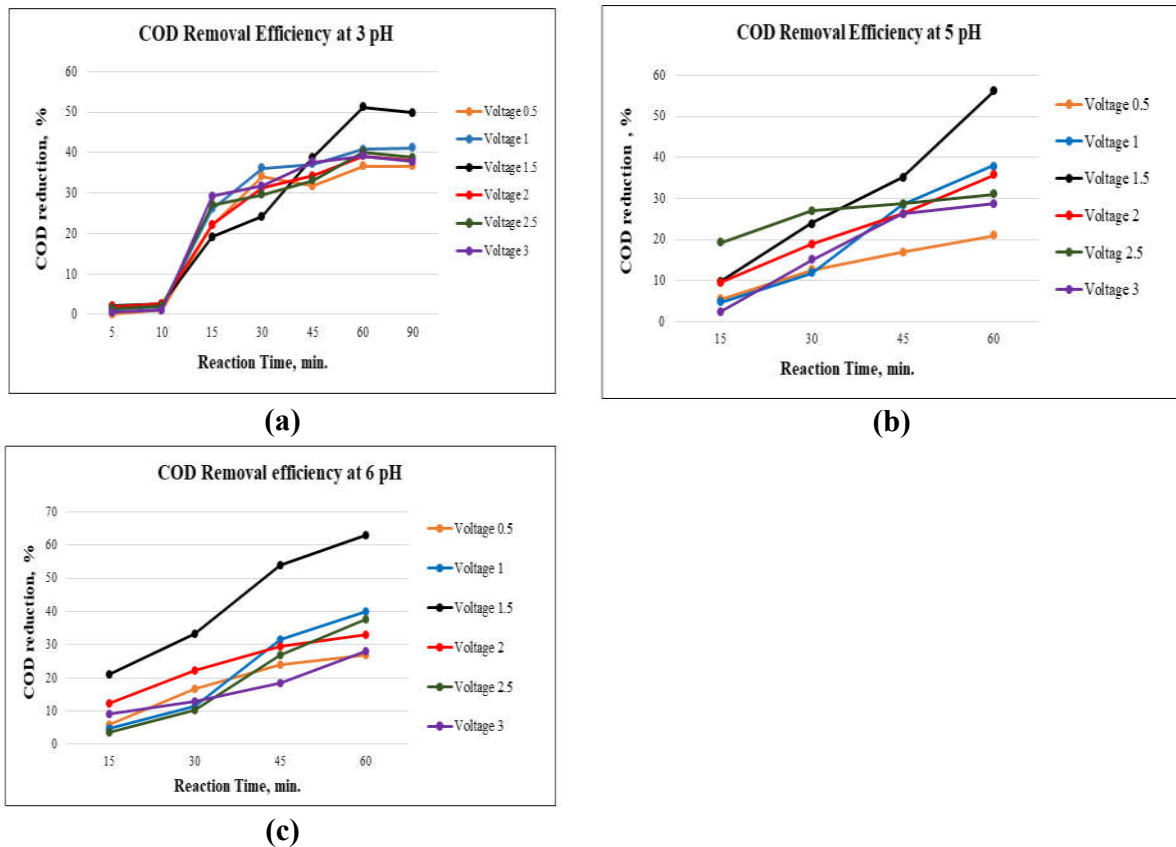


Figure 3: COD Reduction Efficiency at Fe^{2+} : 1000 ppm

2.2. Optimization of Voltage

As shown in Figure 4 (a), the reductions in COD observed at 1 to 2 Volts were 2 % to 55 % at 5 pH. The highest COD reduction observed at 1.5 Volt was 37.25 % at reaction time 60 minutes and lowest COD reduction observed at 1 volt was 5 % for 15 minutes of reaction time and for 60 minutes of reaction time. This suggests that when voltage is increases the COD reduction efficiency was vary with reaction time.

As shown in Figure 4 (b), the reductions in COD observed at 1 to 2 Volts were 4 % to 40 % at 5 pH. The highest COD reduction observed at 1.5 Volt was 38.5 % for 60 minutes of reaction time and lowest COD reduction observed at 1 volt was 4.76 % for 15 minutes of reaction time. This result indicates that the COD reduction efficiency may vary with time intervals.

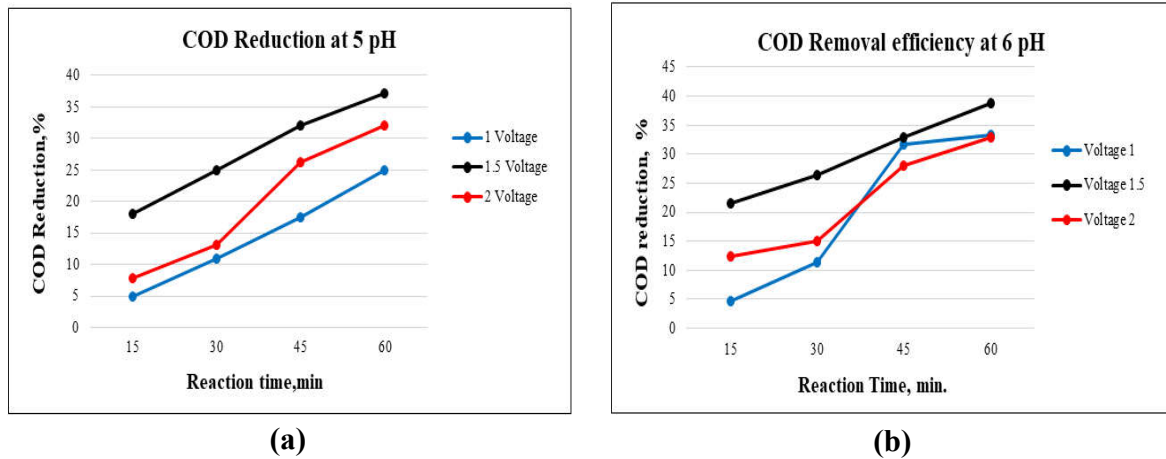


Figure 4: COD Reduction Efficiency at Fe^{2+} : 2000 ppm

As illustrated in Figure 5 (a), the reductions in COD at a pH of 5 exhibited significant variation when the applied voltage ranged from 1 to 2 volts. The reduction efficiency spanned from 5% to 55%, with the highest reduction of 52% observed at 1.5 volts for a reaction time of 60 minutes. In contrast, the lowest reduction of 2.43% occurred at 2 volts with a shorter reaction time of 15 minutes. These results highlight the influence of both voltage and reaction time on COD reduction efficiency, demonstrating optimal conditions at 1.5 volts for a longer duration.

As shown in Figure 5 (b), the reductions in COD observed at 1 to 2 Volts were 20 % to 80 % at 6 pH. The highest COD reduction observed at 1.5 Volt was 73.80 % for 60 minutes of reaction time and lowest COD reduction observed at 1 volt was 20.97 % for 15 minutes of time. This indicates that COD reduction may vary with reaction times and voltages.

By comparing all results of Table 4.15 the maximum COD reduction efficiency achieved at 6 pH was 73.8% at 1.5 voltages for 60 minutes of reaction time. So, the optimum conditions of COD reduction in these experiments were 6 pH and 1.5 voltages. So, further runs for optimize the Fe^{2+} doses can be carried out at pH 6 and 1.5 voltage.

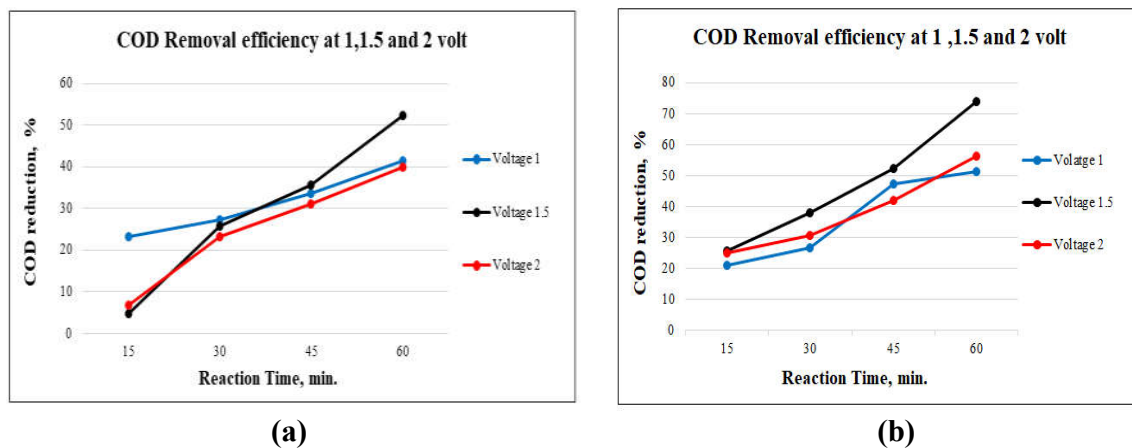
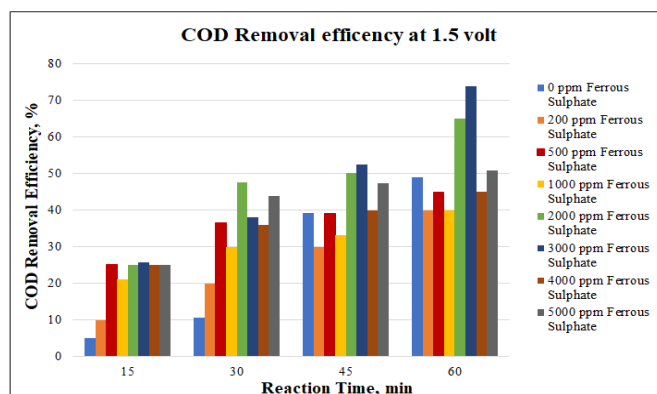


Figure 5: COD Reduction Efficiency at Fe^{2+} : 3000 ppm**2.3 Optimization of Ferrous iron Dosages**

As illustrated in Figure 6, the COD reduction is observed at different dosing of Fe^{2+} . The highest COD reduction observed at 3000 ppm Fe^{2+} dose was 73.80 % and lowest COD reduction observed at without Fe^{2+} dose was 5 %.

**Figure 6: COD Reduction Efficiency at Different Ferrous Sulphate Dosages**

By applying various dosages of ferrous sulphate for different time intervals the optimum ferrous sulphate required for the Electro-Fenton process was identified as 3000 ppm and the optimum reaction time was 60 min was 73.8%.

2.4 Conclusion

The Electro-Fenton (EF) process has been proven to be a robust and effective technique for reducing COD through the in situ generation of hydrogen peroxide. This study elucidated optimal operating conditions, highlighting a ferrous ion (Fe^{2+}) dosage of 3000 ppm and a reaction time of 60 minutes as yielding the highest COD reduction efficiency, reaching up to 73.8%. The process demonstrated sensitivity to operational parameters such as applied voltage, pH levels, and Fe^{2+} concentration, underscoring the need for careful optimization to maximize treatment efficacy.

Despite its promising performance, one notable operational challenge was observed when employing graphite as the cathode and Mixed Metal Oxide (MMO) as the anode. The accumulation of Fe^{2+} ions on the graphite electrode surface due to electrostatic interactions posed a significant issue, potentially limiting the process efficiency over sustained operation. This phenomenon highlights the importance of electrode material selection and configuration in mitigating ion accumulation and ensuring sustained performance in EF applications.

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