

Treatment of Spent Caustic from Ethylene Plant Using Electro-Fenton Technique

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Abstract

The treatment of sulfidic spent caustic produced from ethylene plant by electro fenton technique using iron and stainless steel electrodes was investigated. The effect of operating conditions such as current density, H₂O₂ concentration, reaction time, initial pH and H₂O₂ feeding mode on the efficiency of electro fenton method was studied. The results show that maximum COD removal of 83.4% was achieved at current density = 3.3 mA/cm², H₂O₂ concentration = 1875 mg H₂O₂/L and initial pH=3. Multi steps and continuous addition mode were employed; it was found that a highest COD removal achieved 89.7% at continuous addition of H₂O₂. It is demonstrated that electro fenton method can effectively treat spent caustic.

Keywords

Spent Caustic, Electro-Fenton, Wastewater Treatment, COD Removal

1. Introduction

Refineries and Petrochemical companies are under more stringent environmental regulations to better monitor and control their wastewater streams. One of the most problematic wastewater streams is originated in the process to extract hydrogen sulfide, mercaptans and organic acids from hydrocarbon streams. Diluted caustic (NaOH) solutions are often used in the petrochemical industry for the removal of acidic compounds, e.g. volatile (organic) sulfur compounds from gaseous streams and LPG. The use of caustic leads to the formation of a waste product referred to as spent caustic [1]. This stream has a high content of chemical oxygen demand (COD) and biological oxygen demand (BOD). Current levels of removal of the pollutants from water which can be achieved using the conventional water treatment technologies are often not sufficient, especially when wastewater streams contain significant amounts of hardly biodegradable chemicals [2]. The integration between chemical and biological oxidation allows designing more effective and economical processes [3]. Spent caustic characteristics can greatly vary from refinery to refinery. It may contain high concentrations of sulfides, disulfides, mercaptans, phenolic, amines, hydroxides, and other hydrocarbons depending upon its origin [4], moreover

it's highly variable and depends on a number of factors such as feed stock and furnace operation condition. Spent caustic streams may also have other characteristics that can create issues with conventional biological processes such as noxious odors, pH swings, foaming, or poor settling of biological solids [5]. Due to its noxious odor, toxicity, and hazardous characteristics, spent caustic is classified as hazardous waste according to the US Resource Conservation and Recovery Act [6].

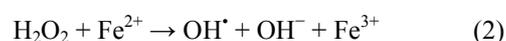
Several efforts have been made in recent decades to develop a better option to treat spent caustic. Marco de Graaff et al. [7] demonstrates the feasibility and advantages of a 2-step process for the biological treatment of sulfidic spent caustics under halo-alkaline conditions (i.e. pH 9.5; Na⁺ = 0.8 M). Experiments with synthetically prepared solutions were performed in a continuously fed system consisting of two gas-lift reactors in series operated at aerobic conditions at 35 C. The detoxification of sulfide to thiosulfate in the first step allowed the successful biological treatment of total-S loading rates up to 33 mmol In the second, biological step, the remaining sulfide and thiosulfate was completely converted to sulfate by haloalkaliphilic sulfide oxidizing bacteria. Seok-YoungOh et al. [8], investigated the oxidation of spent caustic, strong alkaline liquid waste from refinery and petrochemical plants, by hydrogen oxide and persulfate activated with zero-valent iron

(Fe(0)) as an alternative treatment process. TOC removal from the spent caustic was not successfully achieved by treatment with hydrogen peroxide or persulfate only; spent caustic was mineralized when Fe(0) was added. The optimal Fe(0)-to-hydrogen peroxide/persulfate molar ratio was 1:5. Shih-hsiung sheu *et al.* [9], investigated the treatment spent caustic from olefin plants containing much H₂S and some mercaptans, phenols and oil. A new treatment process of spent caustic by neutralization followed by oxidation with Fenton's reagent (Fe²⁺/H₂O₂) was successfully developed. Over 90% of dissolved H₂S were converted to gas phase by neutralization at pH = 5 and T = 70 °, and the vent gas stream could be introduced to sulfur recovery plant. Ichrak Ben Hariz *et al.* [10], studied electrocoagulation technology to remove sulfide and organics from refinery spent caustic wastes. The performance of electrocoagulation in the removal efficiency of sulfide and organic compounds was investigated. Several working parameters, such as solution pH, current density and electrode nature were studied in an attempt to achieve a higher removal capacity. The optimum electrocoagulation time, initial pH, current density were found to be 30 min, pH 9 and 21.2 mA/cm² for initial sulfide concentration of 34,517 mg L⁻¹ and COD of 72,450 mg L⁻¹ respectively. Under the optimum conditions established, removal efficiency of sulfide and organics expressed as COD was greater than 80%. Yanxin Wei *et al.* [11], performed an experimental study on regeneration sodium hydroxide (NaOH) from the spent caustic by bipolar membrane electro dialysis (BMED). The effects of operation parameters, such as concentration of electrolyte, current density and initial base concentration, on regeneration were investigated. The results indicate that low energy consumption and high current efficiency can be achieved with the concentration of electrolyte in the range of 0.20–0.30 mol/L, initial concentration of the base in range of 0.10–0.2 mol/L and current density in the range of 30–60 mA/cm². Yu Zheng-zhe *et al.* [12] studied the performance of UV/H₂O₂, UV/O₃ and UV/H₂O₂/O₃ oxidation systems for treating spent caustic from an ethylene plant. In UV/H₂O₂ system, with increase of H₂O₂ dosage, removal efficiencies of COD and the ration of biochemical oxygen demand (BOD) to chemical oxygen demand (COD) of the effluent were increased and better performance was obtained than with H₂O₂ alone. In UV/H₂O₂ system, removal efficiency of COD reach 68% under the optimum condition, and BOD/COD ratio was significantly increased from 0.22 to 0.52. In UV/O₃ system, with increase of O₃ dosage, removal efficiency of COD and BOD/COD ratio were increased, and a better performance was obtained than the O₃ system alone. Under the optimum condition, removal efficiency of COD was 54%, and BOD/COD ratio was significantly increases from 0.22 to 0.48. In UV/H₂O₂/O₃ system, COD removal efficiency was found to be 22% higher than UV/O₃. Sharifah Hanis *et al.* [13] investigated comparison the performance of Fenton and photo-Fenton oxidation processes in the treatment of sulfidic spent caustic wastewater. Response surface methodology, particularly central composite design was used to investigate the effect of

Fe/H₂O₂ and H₂O₂/COD in assessing treatment process efficiency. Empirical models were developed to describe the relationship between the factors and responses. The models were validated through analysis of variance and were further used in process optimization. The best solution for Fenton process was found to be at Fe/H₂O₂ and H₂O₂/COD ratio of 0.07 and 2.52 correspondingly. On the other hand, lower H₂O₂/COD ratio of 1.84 was achieved in photo-Fenton process. Removal of COD and sulfide up to 97% and 100% was observed with photo-Fenton process.

Jan Sipma *et al.* [14] focused on the biological treatment of sulfidic spent caustics from refineries, which contain mainly hydrogen sulfide, methanethiol (MT) and ethanethiol (ET). Also various organic compounds can be present such as BTEX. Biological oxidation of 2.5 mM MT in batch experiments occurred after MT was first auto-oxidized into dimethyl disulfide (DMDS) whereafter oxidation into sulfate was completed in 350 h. DMDS as sole substrate was completely oxidized within 40 h. Therefore, DMDS formation seems to play an important role in detoxification of MT. Biological oxidation of ET and butanethiol was not successful in batch experiments. Complete oxidation of MT and ET was observed in flow-through reactor experiments. Simultaneous oxidation of sulfide and MT was achieved when treating a synthetic spent caustic, containing 10 mM sulfide and 2.5 mM MT, in a bubble column reactor with carrier material at a hydraulic retention time of 6 h. Addition of 7.5 mM phenol, a common pollutant of spent caustics, did not adversely affect the biological oxidation process and phenol was completely removed from the effluent. Finally, three different spent caustics solutions from refineries were successfully treated. Alaa Hawari *et al.* [15] studied the treatment of spent caustic produced from an ethylene plant. In the case of neutralization alone it was found that the maximum removal of sulfide was at pH values below 5.5. The higher percentage removal of sulfides (99% at pH = 1.5) was accompanied with the highest COD removal (88%). For classical oxidation using H₂O₂ the maximum COD removal percentage reached 89% at pH = 2.5 and at a hydrogen peroxide concentration of 19 mM/L. For the advanced oxidation using Fenton's process it was found that the maximum COD removal of 96.5% was achieved at a hydrogen peroxide/ferrous sulfate ratio of (7:1).

In this study, Electro-Fenton method investigates the effectiveness of COD reduction of sulfidic spent caustic using iron and stainless steel electrodes. The system consists of hydrogen peroxide as an oxidant and ferrous ion as a catalyst. Only hydrogen peroxide is added from outside and Fe²⁺ is provided from sacrificial iron anode. The oxidation ability arises from generation of hydroxyl radical which is the second most powerful oxidant after fluorine. Hydroxyl radical is generated according to the following reactions.



Where, the main reaction at cathode is hydrogen evolution

as in eq.3 and the ferric ions can be directly reduced as in eq.4.



2.1. Materials and Methods

2.1. Spent Caustic

The sulfidic spent caustic used was obtained from Sidi Kerir petrochemicals company, located in Alexandria, Egypt. Chemical analysis of sulfidic spent caustic was carried out according to standard method of analysis [16]. results are indicated in Table 1.

Table 1. Spent caustic characteristics.

Parameters	Values
COD	24,000 mg/L
Conductivity	1120 $\mu\text{s}/\text{cm}$
pH	12.8
NaOH	2.8 – 3.8 wt %
Na ₂ S	3.3 – 3.9 wt %
NaCO ₃	2.7 – 4.9 wt %

2.2. Chemicals

The main chemical used for electro fenton process is hydrogen peroxide (H₂O₂) 30%; w/w). The initial pH was adjusted to a desired value using sulfuric acid (98%, Loba chemie). In addition, potassium dichromate (AR, BDH), ferrous ammonium sulphate (not less than 98%, M & B), silver sulfate (99.5%) and mercury sulfate (99%) were used.

2.3. Analytical Method

Chemical oxygen demand (COD) of samples was measured by closed reflux method according to ASTM D1252-95[16].The samples were tested using COD digestion vials (Hach), where the sample is placed within digestion vials, heated at 150°C for 2 hours. Digestion vials were then allowed to cool naturally to ambient temperature before measuring COD, The COD removal percentage was defined as:

$$\text{COD Removal, \%} = \frac{C_i - C_f}{C_i} * 100 \quad (5)$$

Where; C_i is the initial COD concentration (mg/l), C_f is the final COD concentration (mg /l).

2.4. Experimental Setup

Batch experiments were performed in cylindrical cell (Pyrex glass beaker 1 liter) with 800 ml working volume of sulfidic spent caustic equipped with stainless-steel cylindrical screen used as cathode while iron rod act as anode with diameter of 1 cm and anode effective surface area was 45.5 cm². The cell was operated in constant current (I) mode of 100, 150, 200, 250 mA by using DC power supply. These corresponds to current densities of 2.2, 3.3, 4.4, 5.56 mA/cm² respectively. Hydrogen peroxide was added at desired

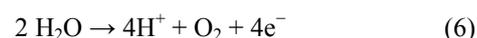
concentrations, 800, 1200, 1875, 2200 mg H₂O₂/l. All the experiments were performed at room temperature of 25±1 °C. A magnetic stirrer was used to homogenize the liquid composition. The schematic of the experimental setup is shown in fig.1. Samples were taken at pre-selected time intervals. For each run 800 mLs of the sulfidic spent caustic were used. The pH was adjusted by the addition of 25 wt % H₂SO₄ solutions. A given volume of H₂O₂ 30% (w/w) was added to start electro fenton reaction. Direct current from the DC power supply was passed through the solution during reaction period. Samples were drawn periodically during each experiment at every 15 minutes interval, withdrawn samples were diluted 200 times with distilled water and then COD was measured.

The electrodes were washed with 25 wt % H₂SO₄ solutions before each run in order to remove any adhering scales or oxides and then washed with distilled water prior to use.

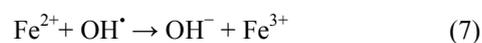
3. Results and Discussion

3.1. Effect of Current Density

One of the critical parameters in the electro fenton processes is the electrical current which is responsible for the generation of metal ions within the electrochemical cell. This parameter directly determines the extent of anodic dissolution of iron electrode. Applied current plays the role of ferrous ion as a catalyst in the electro fenton process. The main goal of ferrous ion as a catalysts is to release hydroxyl radical from hydrogen peroxide. Experiments were applied at current density from 2.2 to 5.56 mA/cm² at constant concentration of sulfidic spent caustic effluent, pH and H₂O₂ concentration. As seen in fig. 2, it was found that COD removal increased with increasing electrical current. This is due to that at higher applied current more ferrous ion can be generated according to Faraday's law, in electro fenton process which in turn, increases the generation of hydroxyl radicals, which are highly reactive and responsible for the degradation. Furthermore, due to higher electro regeneration of ferrous ion from ferric ion at cathode according to eq. (4). The maximum COD removal observed was 83.4 % at current density 3.3 mA/cm². However, the efficiency of electro fenton will be less at higher current density of 4.4 and 5.56 mA/cm² as shown in fig. 3. This is due to the competitive electrode reactions in electrolytic cell. The discharge of oxygen at anode as indicated in eq. (6) and the evolution of hydrogen at cathode as indicated in eq. (3) at high current which inhibit main reaction and leading to decrease in efficiency of electro fenton.



Moreover, at higher current density leads to lower COD removal. This decrease in COD removal happens due to the scavenging effect of ferrous ion as indicated in eq. (7) .In this reaction ferrous ions consume hydroxyl radicals.



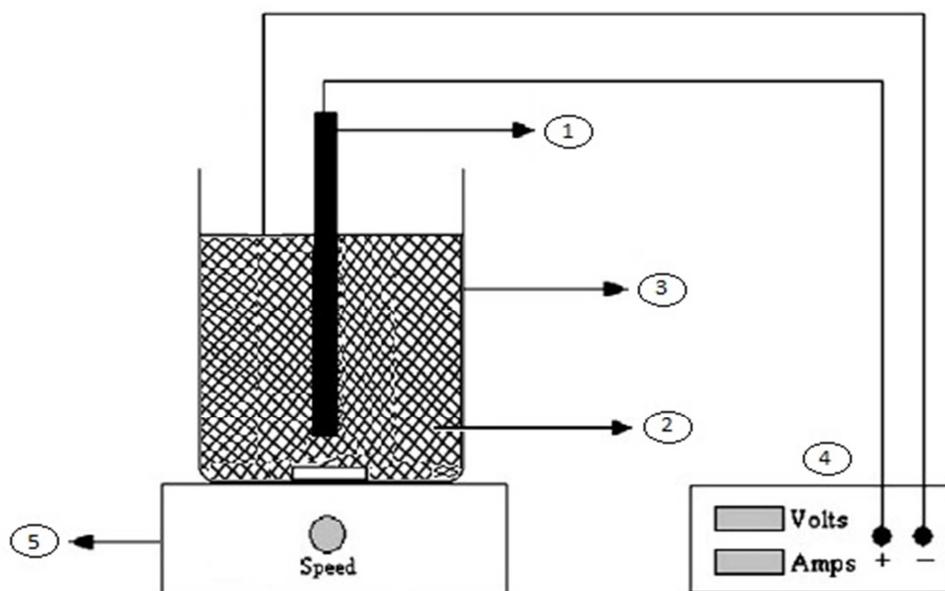


Fig. 1. Experimental schematic diagram.

1- Iron anode, 2-st. steel cathode, 3- electrolytic cell, 4- D.C power supply, 5- Magnetic stirrer

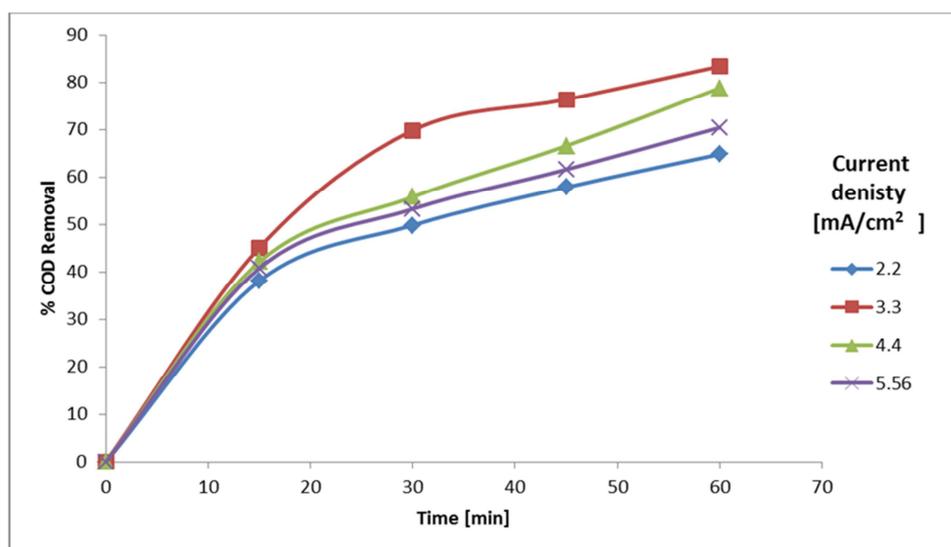
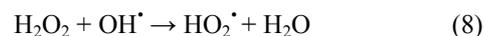


Fig. 2. Effect of current density on the percentage of COD removal (H_2O_2 Concentration = 1875 mg/L, pH = 3, Temperature = 25°C and time=60 min).

3.2. Effect of Hydrogen Peroxide Concentration

The initial concentration of H_2O_2 plays an important role in the electro fenton process. Progress of COD removal with time at different H_2O_2 dosage (800, 1200, 1875, 2200 mg/l H_2O_2) and constant current density and pH values are shown in fig. 4. From the results observed that the maximum COD removal was 83.4 % for 1875 mg/l H_2O_2 . When dosage increase from 800 to 1200 mg/l H_2O_2 the COD removal increased from 64.9 % to 76.3%. The increase in removal efficiency was due to the increase in hydroxyl radical

concentration as a result of increasing the concentration of hydrogen peroxide as indicated in eq. (2). However, when the dosage increased to 2200 mg/l H_2O_2 , the COD removal decreased to 60.8%, this is due to the side reaction between hydrogen peroxide and hydroxyl radical.



This reaction results in the consumption of hydrogen peroxide as well hydroxyl radical and the production of hydroperoxyl radical, a species with much weaker oxidizing power compared with hydroxyl radical. Therefore, there existed an optimum H_2O_2 so that the consumption of

hydroxyl radical would be in minimum.

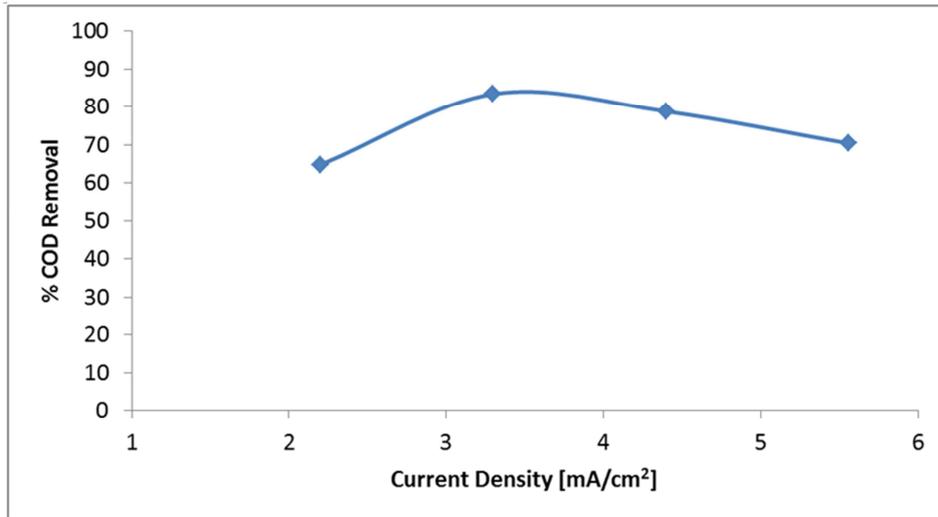


Fig. 3. Effect of current density on the percentage of COD removal at pH = 3 and H₂O₂ Concentration = 1875 mg/L.

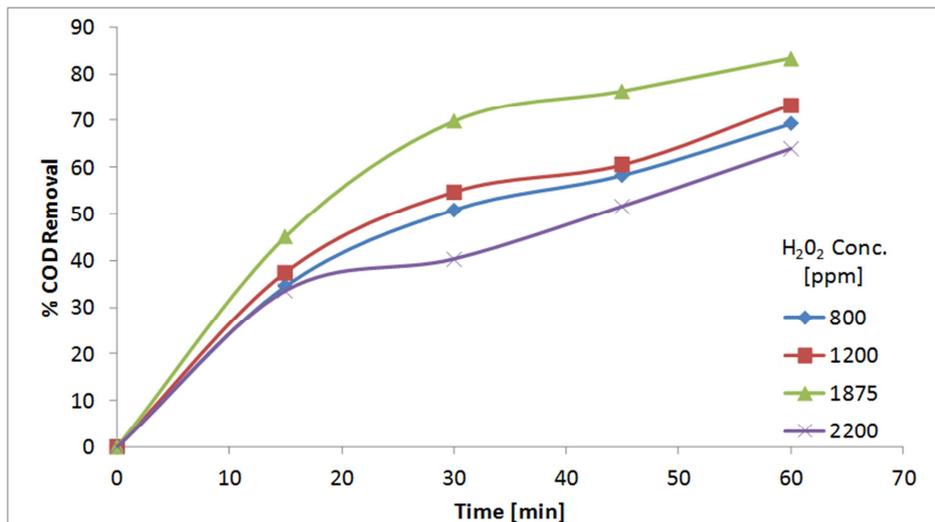


Fig. 4. Effect of different H₂O₂ Concentration on the percentage of COD removal (pH = 3, C.D. = 3.3 mA/cm², Time = 60 min).

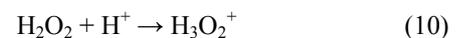
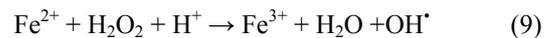
3.3. Effect of Reaction Time

Reaction time influences the treatment efficiency of the electro fenton process. The effects of reaction time on the pretreatment performance were investigated at H₂O₂ of 1875 mg/L, current density of 3.3 mA/cm² and pH 3. It can be seen from the fig. 5, that COD of spent caustic is decreased to 69.8% of its original value within 30 min and after 60 min decreased to 83.4%. Generally hydroxyl radicals produced by the catalytic decomposition of H₂O₂ are considered to be the main oxidizing species in electro fenton oxidation process, it is the source for producing hydroxyl radicals. So that we can discharge treated spent caustic to biological treatment.

3.4. Effect of Initial pH

pH is one of the major factors that limits the performance of electro fenton process, as it affects on decomposition of hydrogen peroxide. Initial pH control in the electro fenton

process is achieved by using sulfuric acid. As seen in fig. 6, pH affects on electro fenton reaction on COD reduction of spent caustic. In this study pH varied in the range 2 to 5. The maximum COD removal is 83.4% at pH 3. A lower pH is favored for the production of OH[•] according to equation (9). At initial pH < 3, hydrogen peroxide would remain steady according to formation of oxonium ion (H₃O₂⁺) as in equation (10) and also slow down the regeneration of Fe²⁺ from Fe³⁺ as indicated in equation (11) therefore electro fenton become less effective .



In addition, at pH > 3, electro fenton process become less effective due to iron species begin to precipitate as ferric

hydroxides, hindering the regeneration of Fe^{2+} . At higher pH values especially $\text{pH} > 5$, the efficiency of electro fenton decreases dramatically, this is due to the fact that H_2O_2 is

unstable in basic solution and rapidly decomposes to water and oxygen. These results are in accord with previously published works [17, 18, 19].

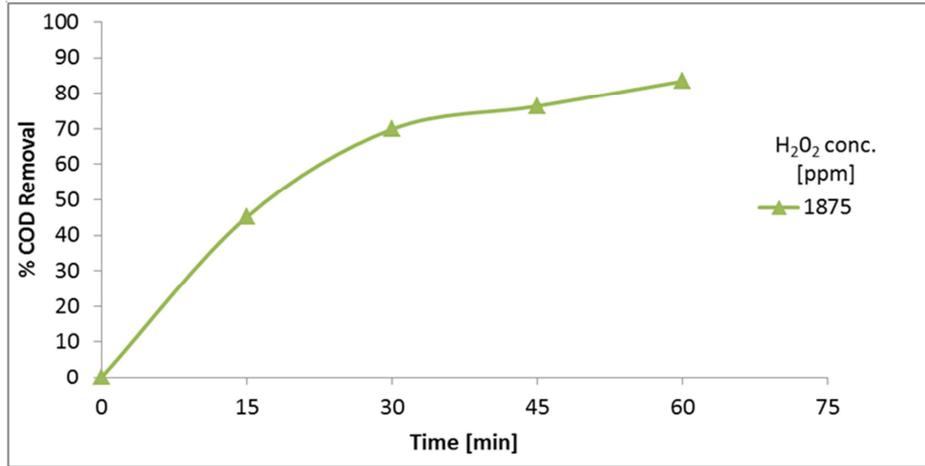


Fig. 5. Effect of electrolysis time on the percentage of COD removal ($\text{H}_2\text{O}_2 = 1875 \text{ mg/L}$, $\text{C.D.} = 3.3 \text{ mA/cm}^2$, $\text{pH} = 3$).

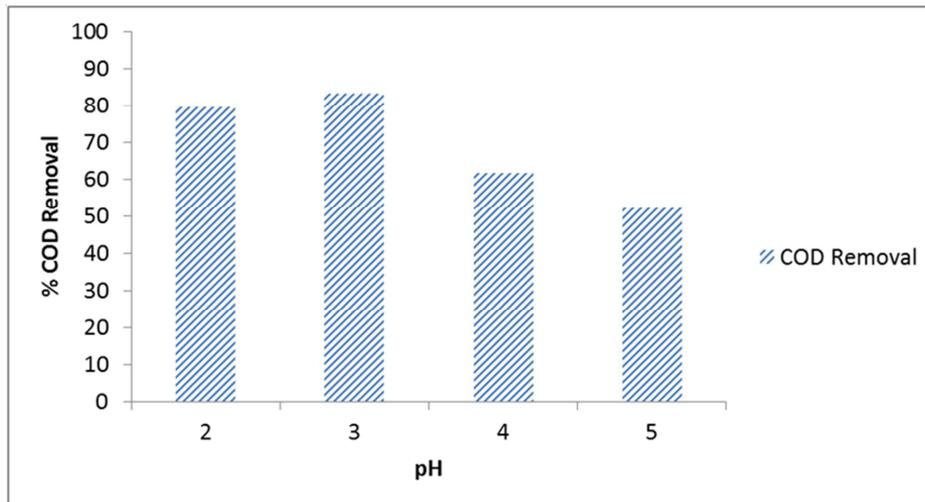


Fig. 6. Effect of the pH Values on the percentage of COD Removal ($\text{H}_2\text{O}_2 = 1875 \text{ mg/L}$, $\text{C.D.} = 3.3 \text{ mA/cm}^2$, and time=60 min).

3.5. Effect of H_2O_2 Feeding Mode

Effect of H_2O_2 addition mode on COD reduction was investigated. A specific volume of H_2O_2 was added in multiple steps in two steps (at 0, 30 min), and in three steps (at 0, 20, 40 min) and continuous mode to the cell at constant current density = 3.3 mA/cm^2 and $\text{pH} = 3$. As seen in fig. 7, the efficiency of electro fenton increases and the highest COD removal was achieved when continuous addition mode was employed. It was found that COD removal for multiple steps in two and three steps was 85.2% and 87.1% respectively, and 89.7% for continuous feeding mode. This is due to it minimize effects of side reaction and reducing the effect of hydroxyl radical scavenging eq. (8) [20, 21, 22].

3.6. Electrical Energy Consumption and Electrode Consumption

In order to assist in assessing the economic feasibility of electro fenton in comparison with other techniques, the

energy consumption and iron metal consumption were calculated as follows :

$$\text{Energy consumption (kWh/g COD removed)} = \frac{EIt_{\text{EF}}}{(C_o - C_t)V} \quad (12)$$

Where:

E is the cell voltage (Volt),

I is the current (A),

t_{EF} is the electro fenton time (h),

C_o is the initial COD concentration (mg/l),

C_t is the COD at time t (mg/l),

V is the treated volume (L).

The amount of Fe metal consumed in electro fenton was calculated using Faraday's law:

$$\text{Fe consumption (g Fe/g COD removed)} = \frac{ItM}{ZFV(C_o - C_t)} \quad (13)$$

Where:

M is the molecular weight of Iron (55.8 g/mol)

Z is the number of electron transfer ($Z_{Fe} = 2$).

F is Faraday's constant ($96,500 \text{ C mol}^{-1}$).

The variation of electrical energy consumption and electrode consumption with current density, Hydrogen Peroxide concentration and pH Values were presented in Figures (8 to 10).

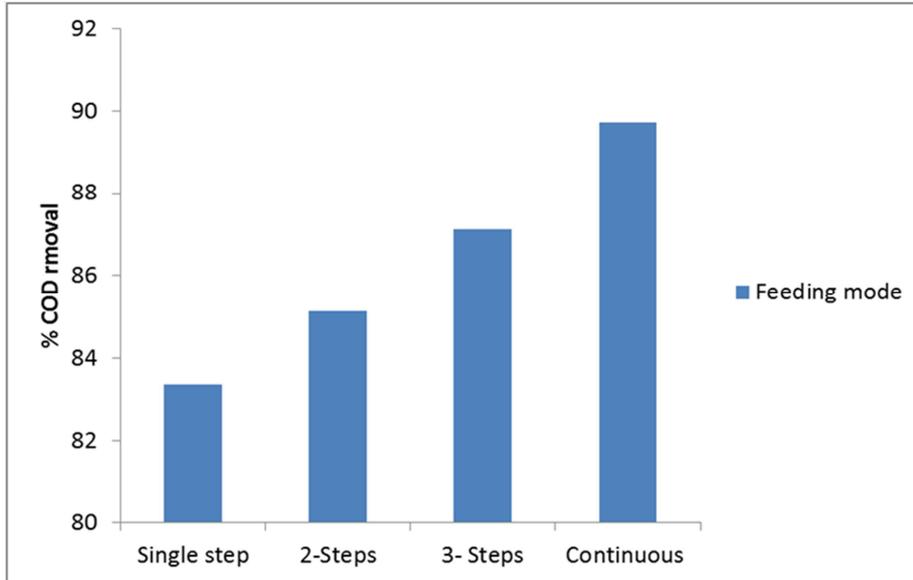


Fig. 7. Effect of H₂O₂ Feeding mood on the percentage of COD Removal at (C.D. = 3.3, pH = 3).

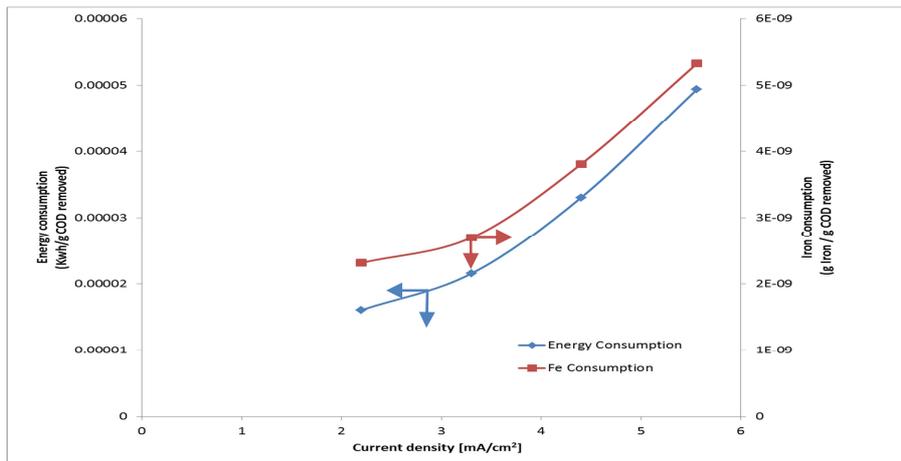


Fig. 8. Effect of current density on the energy consumption and Fe consumption, (H₂O₂ = 1875 mg/L, pH = 3).

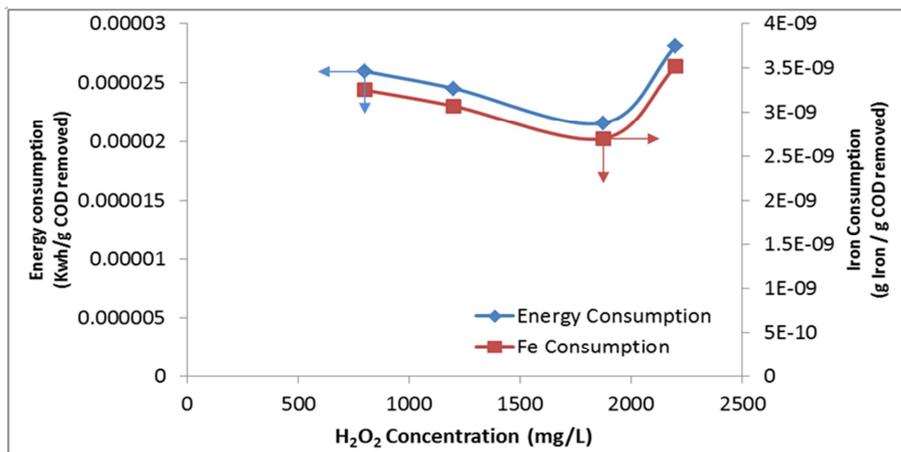


Fig. 9. Effect of H₂O₂ Concentration on the energy consumption and Fe consumption, (C.D = 3.3 mA/cm², pH = 3).

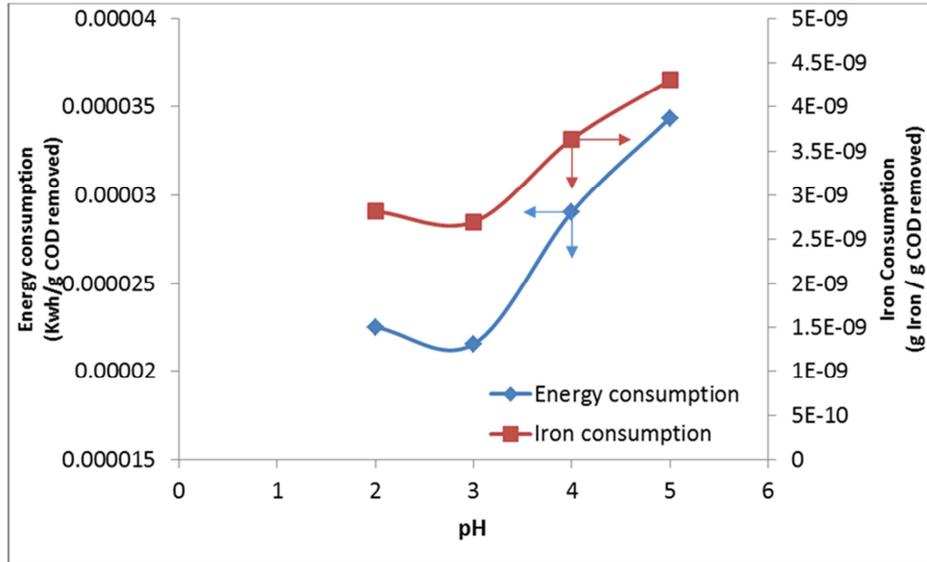


Fig. 10. Effect of pH Values on the energy consumption and Fe consumption, ($H_2O_2 = 1875 \text{ mg/L}$, $C.D. = 3.3 \text{ mA/cm}^2$).

It is clear that a technically efficient process must also be feasible economically. The major operating cost of electro fenton is associated with electrical energy consumption during process. Electrical energy consumption was calculated using the Eq. (12). According to the results presented energy consumption values ranged from 2.2E-05 to 3.4E-05 kWh/g COD removed and Fe consumption from 2.8E-09 to 4.3E-09 g Fe/g COD removed at different current density, It can be concluded that the higher voltage of the system applied, the weight of the electrode consumed in the process has been increased and also the higher the concentrations of the Fe^{2+} in the solution which is responsible for H_2O_2 activation. And also lead to high anode consumption at higher current density.

3.7. Kinetics of Electro-Fenton

The kinetic study is an important issue in order to examine the order of the reaction. It was assumed that the process takes place according to pseudo first order mechanism, which

can be expressed by:

$$\ln\left(\frac{C_0}{C_t}\right) = Kt \tag{14}$$

where

- C_0 is the initial concentration, (mg/l),
- C_t is the concentration at time t, (mg/l),
- K is the rate constant, (min^{-1}),
- t is the time, (min.).

To investigate the kinetics of COD Reduction , electrolysis were performed with different parameters effect. A pseudo-first-order kinetics model was applied to investigate the kinetics of degradation. Figures 11 to 13 show the effect of current density, H_2O_2 concentration and pH value on the kinetics of the reaction. Apparent rate constant value was determined analytically with Equation (14) from the slope of $\ln(C_0/C)$ vs. time.

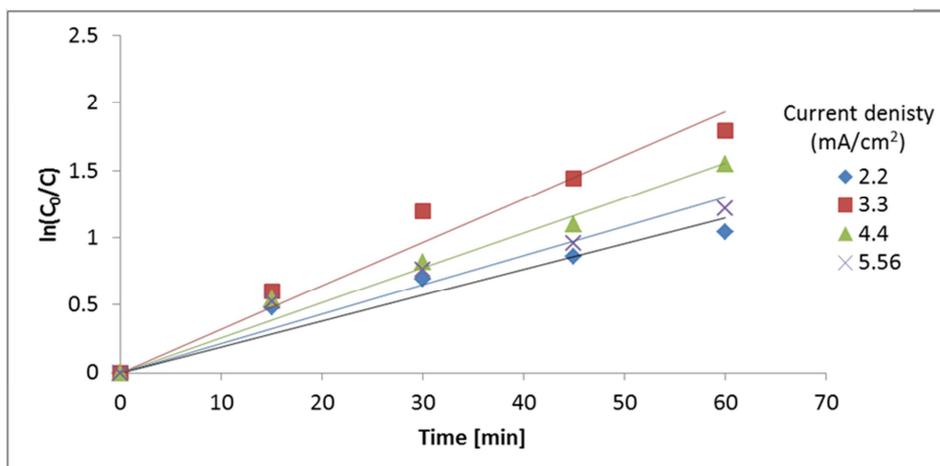


Fig. 11. Effect of current density on the kinetics of the reaction, ($H_2O_2 = 1875 \text{ mg/L}$, $\text{pH} = 3$, $\text{Time} = 60 \text{ min}$).

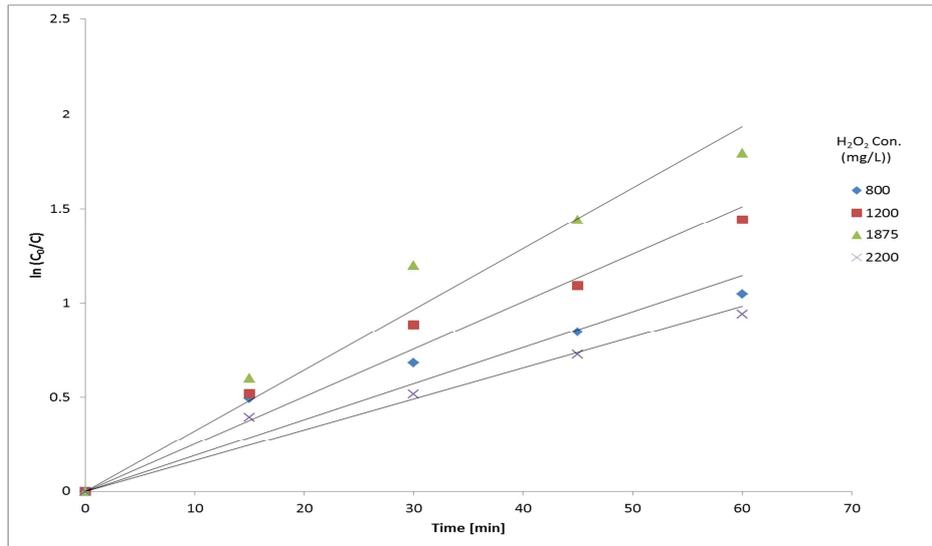


Fig. 12. Effect of H_2O_2 concentration on the kinetics of the reaction, ($pH = 3$, $C.D. = 3.3 \text{ mA/cm}^2$, $\text{Time} = 60 \text{ min}$).

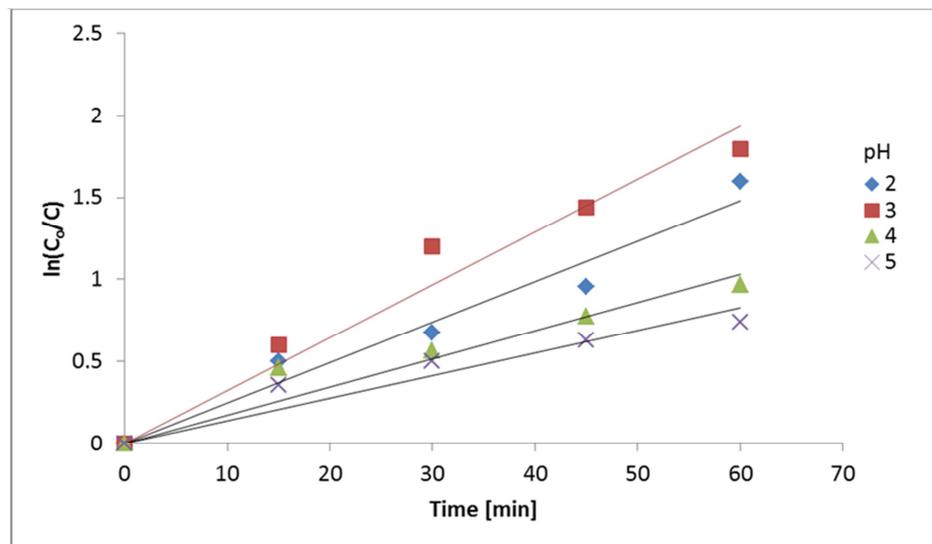


Fig. 13. Effect of pH values on the kinetics of the reaction, ($H_2O_2 = 1875 \text{ mg/L}$, $C.D. = 3.3 \text{ mA/cm}^2$, $\text{Time} = 60 \text{ min}$).

4. Conclusions

The COD removal of sulfidic spent caustic by the electro fenton method has been studied. It has shown that electro fenton method could effectively reduce COD of sulfidic spent caustic. The effects of operation parameters, such as, reaction time, current density, H_2O_2 concentration, initial pH and H_2O_2 feeding mode were investigated. The present study has revealed that :

- COD removal efficiency increased with the increasing current density, but further increase of current density would reduce the removal efficiency.
- COD removal increases with increasing H_2O_2 concentration, but further increase in the concentration of hydrogen peroxide, COD removal will be decreased.
- Initial pH is one of the most important factors for electro fenton process. It was found that the optimum pH for electro fenton was 3.

- The continuous addition of hydrogen peroxide was more effective than the addition of hydrogen peroxide in a single step.

About 83.4 % of initial COD was removed at initial $pH=3$, initial H_2O_2 concentration = 1875 mg/l and current density = 3.3 mA/cm^2 after 60 min, while COD removal increased to about 89% with continuous addition of hydrogen peroxide. The results show that electro fenton is an effective method for COD reduction in industrial wastes with low capital cost. The application of electro fenton has received increased attention in the last decade to treat spent caustic. Overall, electro fenton method is promising technology for application in wastewater treatment.

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