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# Electrochemical Generation of Fenton's Reagent to Treat Spent Caustic Wastewater

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**Abstract:** This work shows the results of four Electro-Fenton laboratory tests to reduce the chemical oxygen demand in spent caustic solutions. The treatment consisted of i) a pH reduction followed by ii) an Electro-Fenton process, which was analyzed in this work. The efficiency of the Electro-Fenton process was analyzed as the COD reduction in pure phenol and sulphide solutions and real spent caustic samples. Close to 97% COD removal was achieved for sulphide treatment, and around 81% for phenol treatment. In the real spent caustic sample, 93% COD reduction was obtained. The sulphide content is lowered by both a pH reduction and the Electro-Fenton process, whereas the phenol concentration is not affected by the pH reduction – only by the Electro Fenton process.

**Keywords:** Electrochemical oxidation, ferrous iron, hydrogen peroxide, hydrogen sulphide, phenol

## INTRODUCTION

An important wastewater stream from oil refineries is the spent caustic. Caustic solutions are used as scrubbing agent during the desulphurisation process to eliminate sulphur and mercaptans from oil and gasses. Spent

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**Table 1.** Characteristics of two types of spent caustic

| | Sulphidic spent caustic | Phenolic spent caustic |
|---|---|---|
| Initial NaOH | 5% | 12–18% |
| $S^{2-}$ | 2–5 g $L^{-1}$ | 10–25 g $L^{-1}$ |
| Mercaptans | 5–10 g $L^{-1}$ | 10–30 g $L^{-1}$ |
| Phenols | 1–5 g $L^{-1}$ | 10–40 g $L^{-1}$ |

caustic is classified as D003 (reactive sulphide) hazardous waste under the US Resource Conservation and Recovery Act (RCRA) (1).

Spent caustic is a highly specific effluent. Generally, there is exists two types of spent caustic waste streams depending on the origin – sulphidic spent caustic from scrubbing operations and phenolic spent caustic from heavy gasoline sweetening. In Table 1 is given compositions of caustic produced in oil refineries (2). Typically, relatively small volumes (0.1 to 8 $m^3/h$) are discharged, and these vary depending on the refinery's size and layout. The harmful effects are considerable due to the concentration in $S^{2-}$ and phenols. Around 550 t of spent caustic is produced when processing 1 Mt of crude oil.

Different ways to treat spent caustic wastewater have been suggested. The conventional method is an acid neutralization followed by steam stripping. After neutralization, stripping removes residual hydrogen sulphide and mercaptans (2). Residual mercaptans and sulphides in the treated caustic generate odours that may be noticeable even when diluted with other plant wastes. The liquid effluent has high BOD and COD concentrations because the major portion of the organic constituents is unaffected by the stripping process.

Another conventional method is the wet air oxidation (WAO), which is a high pressure treatment (25–90 bar) at elevated temperatures (200–300°C) (3–5). Here the oxidation agent is the oxygen present in the air, which is introduced into the spent caustic as steam. For example a 40,000 mg $L^{-1}$ COD concentration can be reduced to lower than 1000 mg $L^{-1}$ in 60 min at 202°C and 28 bar. However, the process is very expensive, and due to severe reaction conditions, safety is a major concern. Some test with low pressure has been carried out without remarkable success (6).

An efficient COD reduction can be achieved by oxidation with Fenton's reagent (7,8). Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants or waste waters. Mixing iron and hydrogen peroxide in the right manner, it results in the generation of highly reactive hydroxyl radicals ($^{\bullet}OH$) or peroxide radicals ($^{\bullet}OOH$). Ferrous iron(II) is oxidized to ferric iron(III) by hydrogen peroxide to a hydroxyl radical and a hydroxyl anion.

In order to have an efficient process, the procedure requires:

a. adjusting the wastewater to pH 3–5,
b. adding the iron catalyst (for example as a solution of $FeSO_4$), and
c. adding slowly the $H_2O_2$.

If the pH is too high, the iron precipitates as $Fe(OH)_3$ and catalytically decomposes the $H_2O_2$ to oxygen. The Fenton's reagent can be generated electrochemically (electro-Fenton), where the ferrous iron is produced in-situ at the anode together with a chemical addition of $H_2O_2$. Different organic compounds have been oxidized by the electro-Fenton process such as phenols (9), 2,4,6-trinitrotoluene (10) and herbicides (11). Synthetic spent caustic wastewaters have been treated by the electro-Fenton process in a labyrinth type cell (12).

The purpose with this work is to design, build, and test an electrochemical cell that would be able to produce $Fe^{2+}$ by in-situ anodic dissolution of iron into the wastewater during turbulent conditions at room temperature. In the cell an air flow between two concentric cylinder electrodes will generate the turbulent mixing. Hydrogen peroxide would then simultaneously be added to the wastewater solution. During the process different parameters should be tested such as pH, temperature, electric current density, and $H_2O_2$ addition rate.

## BACKGROUND

In order to treat the spent caustic efficiently, an oxidation of $S^{2-}$ and organic carbon is necessary:

$$2S^{2-} + 2O_2 + H_2O \longrightarrow S_2O_3^{2-} + 2OH^-$$

$$S_2O_3^{2-} + 2O_2 + 2OH^- \longrightarrow 2SO_4^{2-} + H_2O$$

$$\text{Mercaptans: e.g. } CH_3CH_2SH + 5O_2 + 2OH^- \longrightarrow 2CO_2 + 4H_2O + SO_4^{2-}$$

$$\text{Phenols: e.g. } C_6H_6O + 7O_2 \longrightarrow 6CO_2 + 3H_2O$$

Hydrocarbons, mercaptans, and phenols are difficult to oxidize with oxygen alone, and elevated temperatures or pressures are necessary. A way to enhance the oxidation is to use the stronger oxidant called Fenton's Reagent. Fenton's reagent has been used to destroy/oxidize a variety of organic compounds in wastewater treatment such as very toxic trichloroethylene and perchloroethylene (7,8). Mixing iron and hydrogen peroxide in the right manner, it results in the generation of highly reactive hydroxyl radicals ($^{\bullet}OH$) or peroxide radicals ($^{\bullet}OOH$). Ferrous iron(II) is oxidized to ferric iron(III) by hydrogen peroxide to a hydroxyl radical and a hydroxyl anion. Iron(III) is then reduced back to iron(II) by the same hydrogen peroxide to a peroxide radical and a proton:

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

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + {}^{\bullet}OOH + H^+$$

The hydroxyl radicals have a relative oxidation power of 2.06 times compared to chlorine, and 1.58 times compared to hydrogen peroxide alone (8).

In order to have an efficient process, the procedure requires:

- adjusting the wastewater to pH 3–5,
- adding the iron catalyst (for example as a solution of $FeSO_4$),
- adding slowly the $H_2O_2$. If the pH is too high, the iron precipitates as $Fe(OH)_3$ and catalytically decomposes the $H_2O_2$ to oxygen.

The main idea is to produce Fenton's reagent by electrochemical oxidation of iron(0) and adding $H_2O_2$ simultaneously:

Anodic reaction:

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

$Fe^{2+}$ will then catalyze the production of hydroxyl radicals as mentioned above.

Cathodic reactions:

$$\text{a) } Fe^{3+} + e^- \rightarrow Fe^{2+}$$

$$\text{b) } 2\,H^+ + 2e^- \longrightarrow H_2$$

The occurrence of cathodic reactions is depending on process conditions but reaction a) is preferred in order to maintain constant acidic conditions and to have high concentration of $Fe^{2+}$ in solution.

If iron plates are used in an electrolytic cell, continuous anodic oxidation of iron will occur at the plate surface and liberate the catalyst for Fenton's reagent. The advantages with the electrochemical in-situ production of $Fe^{2+}$ are:

- No generation of residual products. For example when using $FeSO_4$ as catalyst, the sulphate has to be removed from the wastewater.
- The process do not need to be heated.

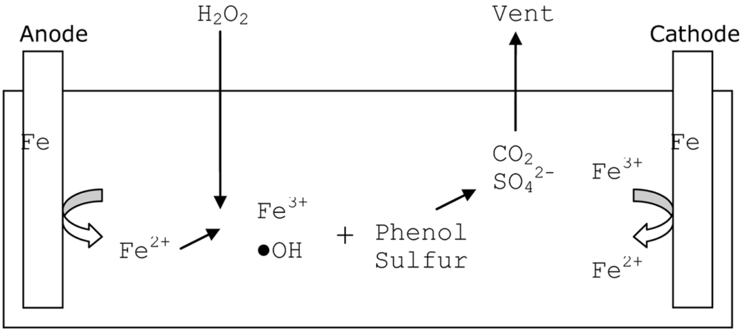


***Figure 1.*** Electro-Fenton process principle.

- Better dosage of $Fe^{2+}$ by controlling the electric current.
- Less operational costs (no addition of chemicals).

Figure 1 shows the principle in this method to produce Fenton's Reagent – the so-called Electro-Fenton.

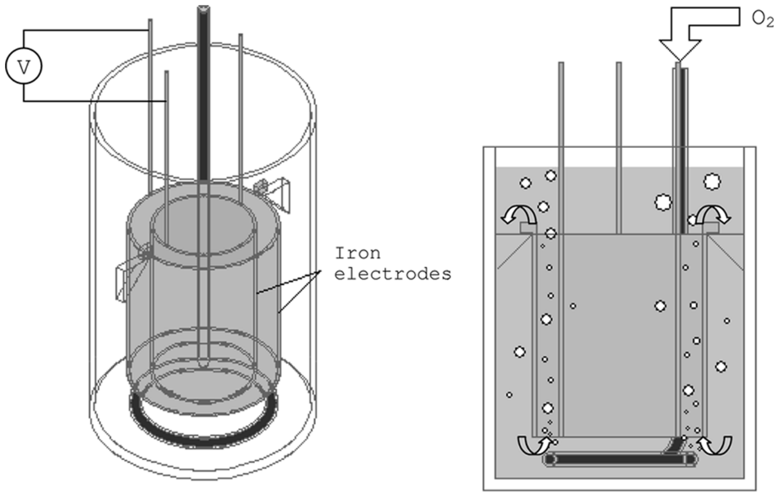
## EXPERIMENTAL DETAILS

### Analytical Methods

The chemical analyses were done according to Chilean standards (NCh). The COD was measured according to NCh 2313/24 Of. 97 (13), the sulfur content was measured according to NCh 2313/17 Of. 97 (14), and the phenol content was measured according to NCh 2313/19 Of. 98 (15).

### Experimental Setup

Figure 2 shows the experimental setup. The glass reactor of 1.2 [L] volume was set up as two concentric steel cylinders, which functioned as sacrificial anodes. The inner and outer cylinders had diameters of 5 and 8 cm, respectively. The thickness of the cylinders was 3 mm. An airflow passing upwards in-between the cylinders provided the stirring in the reactor - generating turbulent conditions. 30% $H_2O_2$ was added consciously as drops at the top of the cell. The $Fe^{2+}$ produced by the anode reaction acted as source for Fenton's reagent together with added $H_2O_2$.



(a) (b)

***Figure 2.*** Airlift reactor for electrogeneration of Fenton's reagent. (a) general view, (b) side view.

## Experimental Plan

Four series of experiments were carried out. The initial concentrations and conditions are given in Table 2. Each experiment consisted of

1. a pH reduction until 4 and
2. an oxidation by electro generated Fenton's reagent.

In the latter case the oxidation was carried out for 60 minutes. The $H_2O_2$ solution was added as drops at the top of the reactor. The total amount of $H_2O_2$ added was calculated as the stoichiometric amount needed for total reaction of the COD: Samples were taken initially, after the neutralization step and after 15, 30, 45, and 60 minutes of electro oxidation. The

**Table 2.** Experimental conditions

| | COD (mg $L^{-1}$) | Phenol (mg $L^{-1}$) | Sulphide (mg $L^{-1}$) | pH |
|---|---|---|---|---|
| Exp. 1 (Only sulphide) | 5025 | – | – | 10.1 |
| Exp. 2 (Only phenol) | 5056 | – | – | 9.6 |
| Exp. 3 (Sulphide and phenol) | 9984 | – | – | 9.9 |
| Exp. 4 (Real spent caustic sample) | 125800 | 1619 | 21494 | 10.2 |

samples were analyzed for COD (exp. 1–3) or for COD, phenol, and sulphide in the case of the real spent caustic sample. The current during the electro oxidation was 1 A. The reactor was placed in a thermostatic bath and the temperature was kept at 70°C during experiments.

Both synthetic and real wastewater samples were tested. Synthetic solutions of $H_2S$ (exp. 1) and phenol (exp. 2) were prepared in distilled water and then added the NaOH solution in such a way that the "initial" COD was around 5000 mg $L^{-1}$ and the pH around 10 for each solution. In exp. 3 the solution was prepared as a 50–50% mixture (in mass) of $H_2S$ and phenol so the initial COD was around 10000 mg $L^{-1}$. The real spent caustic sample (exp. 4) was sampled at ENAP petroleum refinery in Concon, 5th Region of Chile and measured initially to have $125800 \pm 5000$ mg $L^{-1}$ COD.

## RESULTS AND DISCUSSION

Table 3 shows the results for the neutralization/acidification and oxidation of the sulphide, phenol and real spent caustic samples. It can be seen that the combined process of pH reduction and oxidation by Electro Fenton does reduce the COD efficiently in all cases. In the case of sulphides, the pH reduction to around 4 reduces the concentration of sulphides due to the reaction:

$$H^+ + HS^- \Longrightarrow H_2S$$

which will be favored at low pH. The gas released from the wastewater sample should be collected and treated separately. This neutralization/

Table 3. COD, phenol and sulphide reduction after neutralization and oxidation with Electro Fenton

| | | Exp. 1 | Exp. 2 | Exp. 3 | Exp. 4 | | |
|---|---|---|---|---|---|---|---|
| | Time (min) | COD (mg $L^{-1}$) | COD (mg $L^{-1}$) | COD (mg $L^{-1}$) | COD (mg $L^{-1}$) | Sulphide (mg $L^{-1}$) | Phenol (mg $L^{-1}$) |
| Initial | | 5025 | 5056 | 9984 | 125800 | 21492 | 1619 |
| Neutralization/acidification | 0 | 1475 | 5056 | 4664 | 22872 | 5840 | 1619 |
| Oxidation by electro-Fenton | 15 | 756 | 2770 | 3768 | 18000 | 3800 | 1150 |
| | 30 | 206 | 2134 | 2248 | 14000 | 2300 | 800 |
| | 45 | 192 | 1704 | 2144 | 10500 | 1100 | 500 |
| | 60 | 166 | 987 | 968 | 8308 | 564 | 310 |

acidification is a required operation to reduce the concentration of sulphur compounds. According to results obtained by Weng and Sa (13) in the neutralization of spent caustic, the reduction in sulphide concentration is significant when reducing the pH to around 4–5. Decreasing the pH below 4 does not reduce the sulphide concentration further. In exp. 1 and exp. 4 the COD reduction due to acidification only was 71% and 82%, respectively. This point is considered as $t = 0$ min. Hereafter, the electric current is switched on (releasing $Fe^{2+}$) and $H_2O_2$ added drop wise. The phenol concentration was found not to be affected by the pH reduction—only by the Electro Fenton process—maintaining the same concentration in the sample before and after the pH reduction.

The COD reduction after 60 min by the Electro-Fenton oxidation (considering $t = 0$ min as the initial COD level) was in the four cases: 89% (exp. 1), 80% (exp. 2), 79% (exp. 3) and 64% (exp. 4). The latter case was the real spent caustic sample. It could indicate that the oxidation process is slower in the real wastewater than in synthetic samples due to presence of other substances. The combined process reduced the COD by 93% in the real wastewater sample, though. Comparing the results obtained in this work with earlier results (10) using the Electro-Fenton process in a rectangular labyrinth-shaped reactor it can be concluded that the COD reductions in synthetic spent caustic samples are similar.

Figure 3 shows the COD reduction due to oxidation by Electro Fenton alone (from $t = 0$ to 60 min) for exp. 1–3. It can be seen that in the pure sulphide sample (exp. 1), the COD was reduced to a level around $200\,\mathrm{mg\,L^{-1}}$ after 30 min and thereafter maintained this level during the rest of the treatment. On the other hand it seems that phenols are oxidized more rapidly than sulphides by this process since the decreasing

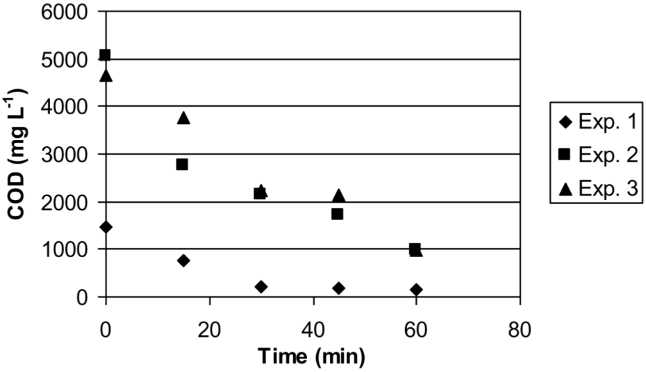


***Figure 3.*** COD versus time during the Electro-Fenton process.

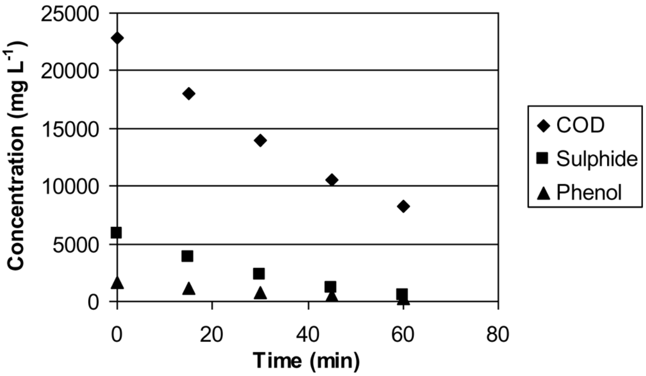


***Figure 4.*** The concentration vs. time during the Electro-Fenton process for exp. 4 (real spent caustic sample).

slope of COD reduction represented by phenols is steeper than the COD-sulphide slope.

Figure 4 shows the COD, phenol and sulphide contents in the real wastewater sample (exp. 4) with considering only the oxidation by Electro Fenton (from t = 0 to 60 min). From the figure it can be observed that all contents are lowered with time. In addition, it seems that after 60 min still large amount of organic compounds could be oxidized since the curves have not reached a minimum. The presence of other organic compounds such as olefins in the real wastewater should be considered too, meaning that a real spent caustic wastewater would be oxidized slower than a synthetic solution only containing phenols and sulphurs.

In this work, the $H_2O_2$ was added according to stoichiometric oxidation of the present COD. Further investigations should include experiments with excess $H_2O_2$ in order to speed-up the oxidation. Still further COD reduction is needed if the process should be feasible. For downstream treatment at the ENAP petroleum refinery in Concon, Chile, the concentration of COD in the spent caustic should be reduced to around 300 – 500 mg $L^{-1}$ before entering the general biological treatment plant.

## CONCLUSIONS

A specially designed process including a pH reduction followed by an Electro-Fenton's reactor demonstrated to be a useful tool for reducing COD in spent caustic. Its advantages regarding safety and costs make it a process that has to be considered in petroleum refineries. A cylindrical batch airlift reactor that generated in-situ $Fe^{2+}$ for Fenton's reagent was tested for oxidation of both synthetic sulphide and phenol samples and real spent caustic solution from a petroleum refinery.

The organic contaminant removal in the form of COD reduction was significant in all cases with more than 95% COD reduction when treating sulphide samples. For real wastewater treatment, 93% COD reduction was obtained.

The sulphide content was highly affected by both the pH reduction and the oxidation by Fenton's reagent. On the other hand, the phenol concentration was only reduced by the Fenton's reagent oxidation.

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