Fenton Oxidation Process of Refractory Organics in Gas Processing Wastewater

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In current research, treatment of gas-associated wastewater (3,100 m³/d) from a gas production company located at Alexandria was carried out. The produced wastewater was found to be contaminated with high organic and inorganic pollutants, characterized by high COD (chemical oxygen demand) 55000 mg/L, low BOD (biochemical oxygen demand) 9500 mg/L, TSS (total suspended solids) 385 mg/L and total phenols of 0.8 mg/L. The BOD/COD ratio of 0.17 proves that wastewater has hazardous organics that are hardly biodegradable. Due to the low TSS concentration, conventional coagulation precipitation method is not considered adequate. A Fenton reagent [Fe²⁺/H₂O₂] is proposed for degradation of existing soluble organics in the wastewater. Optimum operating conditions were: H₂O₂ in concentration of 1.6 M/L (one Stoichiometry with COD), 80 mM/L of Fe²⁺ ions, at pH around 3 and optimal time of 30 minutes. A corresponding residual concentration of COD and BOD were 11000 and 4000 mg/L and a complete removal of phenols. Results concluded that, Fenton reagent was found suitable to improve the biodegradability of the raw gas processing wastewater, BOD/COD increased from 0.17 to 0.36 and a complete removal of phenols has been achieved, making it feasible to be treated biologically in effective manner.

Keywords: Gas, Dehydration, Wastewater, Refractory, Organics, Removal and Fenton.

Natural-gas processing starts near their producing wells. Natural-gas components contain varying amounts of: low molecular weight hydrocarbon compounds; including methane (CH₄), ethane (C₂H₆), propane (C₃H₈) and butane (C₄H₁₀). These hydrocarbons exist in a liquid state at earth high pressure (1-3). Furthermore; natural gas contains acid gases, water vapor and some salts. To avoid the formation of methane hydrates within the gas production plant or through the sales gas pipeline, natural gas must be...
Glycol Dehydration presented an example of absorption dehydration process. A highly contaminated wastewater is produced from glycol dehydration process which characterized by high chemical oxygen demand (COD), hardly biodegradable, highly toxic and carcinogenic.

The hazardous organics found in wastewater can cause effects on all sensory organs, respiratory system, gastrointestinal system, nervous system, and immune system. These effects pushed to a mandatory removal of these organics from industrial wastewater before reaching water streams.

The advanced oxidation processes (AOPs) may be suitable methods, which may result in satisfactory elimination of soluble organics. Moreover, they represent an interesting alternative, since they can be employed as a pre-treatment before the biological treatments for wastewater remediation, increasing the biodegradability through partial oxidation.

Many researchers in literature have used the following processes for handling gas processing wastewater; Fenton, photo Fenton, wet air oxidation and ozonation-modified Fenton. Fenton reaction, equation (1) is one effective mechanism of Fenton; iron-salt-dependent decomposition of hydrogen peroxide, producing the highly active hydroxyl radical, which has a nonselective oxidation properties for organic compounds. Haber and Weiss suggested the Fe$^{2+}$ regeneration by through formation of superoxide radical as indicated in equations 2 and 3.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^- \quad (1)
\]

\[
\text{HO}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{H}_2\text{O} + \text{OO}^- \quad (2)
\]

\[
\text{Fe}^{3+} + \text{OO}^- \rightarrow \text{Fe}^{2+} + \text{O}_2 
\]

AOPs provided a high oxidation capacity for petroleum wastewater in oil industries, since they allowed the reuse of water. A persistent delineation for reducing the cost is the integration of the Fenton with bio-technologies (aerobic and anaerobic treatments).

The present work aims to treat the natural gas processing wastewater by Fenton oxidation process to enhance its biodegradability, for further facilitating its biological treatment.

**Materials and Methods**

Natural gas wastewater represents hazardous refractory wastewater which was selected for this study. Natural gas production factory is located at Alexandria, Egypt and discharges its wastewater into the sea. Dark Fenton treatment was carried out.
**Fenton process**

The use of Fenton reagent; Ferrous sulfate heptahydrate (FeSO\(_4\)·7H\(_2\)O) and Hydrogen peroxide (H\(_2\)O\(_2\)), [Fe\(^{2+}\)/ H\(_2\)O\(_2\)] at pH near (3) as catalytic oxidation was investigated. All experiments were performed at room temperature (25°C ± 2) in a Jar Test apparatus used for stirring the reactants. Needed dose of catalyst Ferrous sulfate was added into the reaction vessel to start the experiments and the pH was adjusted at the desired value (around 3) by addition of H\(_2\)SO\(_4\) (30%) and kept stable during the reaction. The required amount of H\(_2\)O\(_2\) (30%) was fed under continuous stirring of the wastewater using the Jar test method. This method was preceded by rapid mixing of the wastewater at 120 rpm for the desired time. When the set time is reached, the reaction was stopped and the residual hydrogen peroxide was eliminated by raising the pH to 12 through the addition of NaOH (20%). Under alkaline conditions, the iron got precipitated and was then removed by sedimentation. After 30 min settling time, the supernatant was withdrawn and neutralized to pH around 7.0 for chemical analysis.

Series sets of experiments were carried out to determine the optimum time of reaction and to examine the effect of H\(_2\)O\(_2\) and Fe\(^{2+}\) doses on the efficiency of Fenton process.

Also, one drop of Na\(_2\)S\(_2\)O\(_3\) (0.1N) was added to each sample to decompose any residual hydrogen peroxide and prevent further Fenton degradation of organic substrate during the analysis.

Optimum operating conditions for Fenton process (H\(_2\)O\(_2\) dose, Fe\(^{2+}\) dose & contact time) were determined as follows: the optimum H\(_2\)O\(_2\) dose was worked out in the sequence: 0 M/L, 0.2 M/L, 0.4 M/L, 0.8 M/L, 1.6 M/L, 3.2 M/L and 6.4 M/L, while the other two variables were fixed at values taken from previous Fenton studies \(^{(19)}\). The optimum Fe\(^{2+}\) was worked out at 0 mM/L, 2 mM/L, 4 mM/L, 8 mM/L, 12 mM/L, 20 mM/L, 28 mM/L, 40 mM/L, 60 mM/L, 80 mM/L, 100 mM/L and 120 mM/L using the predetermined optimum H\(_2\)O\(_2\) dose whereas the time remaining variables was fixed as before. The above steps were repeated in the same order to obtain the optimum contact time at 2, 10, 15, 20, 30, 40 and 50 minutes.

The analysis was carried out according to the standard method for examination of water and wastewater (APHA, 2012)\(^{(14)}\).

**Results and Discussions**

*Natural gas industry wastewater sources*

The industrial wastewater is a complicated in nature produced through the processing of gas cleaning unit. Figure 1 shows the source of wastewater.
Wastewater characterization

The target wastewater of this study results from glycol dehydration process. Its representative characteristics are summarized in Table 1. Characteristics of industrial wastewater investigated in this study in terms of COD, BOD, TSS and total phenols were 55000, 9500, 385 and 0.8 mg/L, respectively. The wastewater was nearly acidic in nature, the pH varied between 4.5 and 4.9. The wastewater contains considerable amounts of nitrogen with an average value of 43 mg N/L while total phosphorus was limited and records only 13 mg/L on average. It has to be mentioned that the locally allowable limits for industrial wastewater discharge into the sea are fixed at 100, 60 and 60, 0.015 mg/ L for COD, BOD, TSS and total phenols, respectively. As observed, the values of COD and BOD, TSS and phenols in Table 1 exceed these limits. Thus, a treatment capable of reducing the organic load as well is required.

The ratio of BOD/COD in wastewater is usually used to represent the biodegradability of the wastewater, when the value of BOD/COD is greater than 0.3, the wastewater has a better biodegradability. Whereas the quotient of BOD/COD is less than 0.3 indicates that the wastewater inhibits the metabolic and respiration activities of microorganism due to their noxious or refractory peculiarities and it is difficult to be biodegraded.15

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Average*</th>
<th>Law4/1994</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
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<td>4.7±0.2</td>
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</tr>
<tr>
<td>Chemical oxygen demand(COD)</td>
<td>mg/L</td>
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<tr>
<td>Biochemical oxygen demand(BOD₅)</td>
<td>mg/L</td>
<td>9500</td>
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</tr>
<tr>
<td>Total suspended solids (TSS)</td>
<td>mg/L</td>
<td>385</td>
<td>60</td>
</tr>
<tr>
<td>Total kjeldahl nitrogen (TKN)</td>
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</tr>
<tr>
<td>Oil and grease</td>
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<tr>
<td>Settleable solids at 30 min</td>
<td>mL/L</td>
<td>ND**</td>
<td>ND</td>
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<tr>
<td>Total sulfides</td>
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<td>2</td>
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<tr>
<td>Phenols</td>
<td>mg/L</td>
<td>0.8</td>
<td>0.015</td>
</tr>
<tr>
<td>Cyanides(CN)</td>
<td>mg/L</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

*Average of 5 samples  ** Not detected

Data in Table 1 showed that the ratio of BOD/COD for natural gas wastewater is less than 0.17. Therefore, an effective wastewater pretreatment has to be conducted. Dark Fenton treatment was carried out as shown in Fig. 1.
Treatment of wastewater using Fenton process

It has been demonstrated that, Fenton oxidation process is able to destroy hydrocarbons in water media and participate in removing a large amount of (COD) in industrial wastewater \(^{(16)}\).

Determination of the optimum dose of H\(_2\)O\(_2\)

The effect of H\(_2\)O\(_2\) on the COD reduction has been studied. It is expected that as the molar ratio of H\(_2\)O\(_2\) to pollutant is increased, more hydroxyl radicals are available to descent the organic pollutants and therefore accelerate their decadence. The doses of H\(_2\)O\(_2\) were based on their stoichiometry with respect to COD which then represented in M/L.

To obtain the optimum H\(_2\)O\(_2\) dose, investigations were carried out using different H\(_2\)O\(_2\) doses ranged between (0 to 6.4 M/L).

The results indicated that at H\(_2\)O\(_2\) dose = 0.2M/L the COD was 51000 mg/L, at H\(_2\)O\(_2\) dose =0.4 M/L the COD was 46000 mg/L. At H\(_2\)O\(_2\) dose =0.8 M/L the COD was 43000 mg/L. The results indicated significant enhancement of the COD removal at H\(_2\)O\(_2\) dose of 1.6 M/L. Therefore the dose of (1.6 M/L) has been selected as shown in Fig. 2. The increase in COD removal is comparable to the results presented by Gulkaya \textit{et al.} \(^{(17)}\) and Kang \textit{et al.} \(^{(18)}\). This may be due to the fact that increased amount of H\(_2\)O\(_2\) reacts with more FeSO\(_4\) and produces more amount of hydroxyl radical leading to more organic degradation. One more point could be the production of ferric sulphate, which acts as coagulant and helps in enhancing COD reduction. In this study it was observed that for 16% COD reduction the H\(_2\)O\(_2\) dose was 0.4 M/L, whereas for 41.8% COD reduction the H\(_2\)O\(_2\) was 1.6 M/L.

Adding of H\(_2\)O\(_2\) in amount overrides the stoichiometric ratio of COD: H\(_2\)O\(_2\)=1:1 (55 g/L H\(_2\)O\(_2\)) did not improve the respective maximal organic degradation. This may be due to auto-decay of H\(_2\)O\(_2\) to oxygen and water (Eq. 4) and the recombination of OH radicals (Eq. 5) or play as a scavenger for the OH radicals according to Haber and Weiss \(^{(12)}\) (Eq. 2).
\( \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \) \hspace{2cm} (4) \\
\( 2\text{OH}^* \leftrightarrow \text{H}_2\text{O}_2 \) \hspace{2cm} (5)

Since the OH radical reacts with \( \text{H}_2\text{O}_2 \), the \( \text{H}_2\text{O}_2 \) itself plays as the \( \text{OH}^* \) scavenger \(^{(19)} \). Therefore, the \( \text{H}_2\text{O}_2 \) should be optimally added to achieve the best degradation.

![Fig. 2. Effect of different hydrogen peroxide doses on COD removal and BOD/COD ratio.](image)

**Determination of the optimum dose of Fe\(^{2+}\)**

To obtain the optimum (Fe\(^{2+}\)) dose, investigations were carried out using different Fe\(^{2+}\) doses ranged between 2 mM/L and 120 mM/L. The results presented in Fig 3 indicated a little refinement in the quality of the treated wastewater produced by incremental increase of Fe\(^{2+}\) doses from (2 mM/L) to (120 mM/L). The corresponding COD concentration decreased from 51000 mg/L to 9600 mg/L at Fe\(^{2+}\) dose of (2 mM/L) and Fe\(^{2+}\) dose of (120 mM/L). The COD removal was 7.2 and 82.5 % at Fe\(^{2+}\) dose of (2 mM/L) and (120 mM/L) respectively.

The results indicated significant enhancement of the COD removal at Fe\(^{2+}\) doses of (80 mM/L). Therefore this does of Fe\(^{2+}\) has been selected.

Hence it may be stated that higher ferrous concentration causes generation of additional OH\(^*\) radicals and speeds up the redox reaction. Another important thing is that Fe\(^{2+}\) converts into Fe\(^{3+}\) as shown in Eq. (1), which acts as coagulant resulting in improved COD reduction. The results indicated that increasing Fe\(^{2+}\) does did not enhance COD reduction significantly, which indicates that OH\(^*\) generation is hindered in the presence of extra FeSO\(_4\) concentration. In addition, according to De Laat and Gallart (1999) the Fe\(^{3+}\) formed can react with \( \text{H}_2\text{O}_2 \) to

generate Fe\(^{2+}\) and hydroperoxyl radicals [HO\(_2^\cdot\)] in the reaction medium (Eq. 6).

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{HO}^\cdot + \text{Fe}^{2+} + \text{H}^+
\]  (6)

The oxidation capacity of HO\(_2^\cdot\) is less comparable to OH\(^\cdot\), which affects the overall COD reduction. It is desirable that the ratio of H\(_2\)O\(_2\) to Fe\(^{2+}\) should be as small as possible, so that the recombination can be avoided and the sludge production from iron complex is also reduced.

![Graph showing effect of Fe\(^{2+}\) dose on COD removal and BOD/COD ratio.](image)

**Fig. 3. Effect of different Fe\(^{2+}\) doses on the COD removal and BOD/COD ratio.**

**Determination of the optimum contact time**

Different contact times ranging from 2 min to 40 min were investigated. The doses of H\(_2\)O\(_2\) and Fe\(^{2+}\) were kept constant at (1.6 M/L) and (80 mM/L) respectively at pH around (3). Figure 4 shows that the optimum contact time was 30 min where the higher COD removal (65.4 \%) has occurred.

**Efficiency of Fenton treatment process**

The wastewater was treated at the pre-determined optimum operating conditions of: H\(_2\)O\(_2\) of (1.6 M/L), Fe\(^{2+}\) of (80 mM/L), improvement of the biodegradability of gas processing wastewater is achieved. These results are lower than those obtained by Aken et al. (21) who obtained BOD/COD ratio of 0.4 when treating halogenated organic compounds. These results are comparable to those obtained by Diya’uddeen et al. (22) who used Fenton process for the treatment of petroleum refinery effluent BOD/COD ratio of (0.14) and increased biodegradability ratio to (0.37). The results are higher than those obtained by Martins et al. (23) who treated phenolic acids and obtained BOD/COD ratio of 0.3 at 42 min. L, in reaction time of (30 min) and at pH around (3). The results indicated that the BOD/COD ratio has risen to around (0.36).
Results are matched with the research works presented by many authors who stated that; AOPs are suitable methods, resulted in satisfactory elimination of soluble organics (22-28).

![Graph](image)

**Fig. 4. Effect of reaction times on the removal of COD and BOD/COD ratio.**

The results presented in Fig. 5 and Table 2 show that the quality of treated effluent is quite satisfactory. The concentration of COD, BOD, TKN, TSS, TP, Oil and grease, and phenols was reduced from 55000 to 11000, 9500 to 4000, 43 to 7, 385 to 50 , 13 to 1.7, 75 to 5 and 0.8 to 0 mg/L, respectively. The corresponding removal efficiency was 80, 57.8, 83.7, 87, 86.9, 93.3 and 100, respectively. Characteristics of the treated effluent were not complying with the permissible limits for wastewater discharge into sea but the biodegradability (BOD/COD ratio) improved from 0.17 to 0.36 ± 0.02 in 30 min. Hence, this facilitates the subsequence biological treatment.
Fig. 5. Efficiency of Fenton process on the treatment of gas processing wastewater at optimum operating conditions.

TABLE 2. Characteristics of the treated wastewater using Fenton treatment at the optimum operating conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
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<tr>
<td>pH</td>
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<td>6-9</td>
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<tr>
<td>Chemical oxygen demand (COD)</td>
<td>mg/L</td>
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<td>100</td>
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<td>Biochemical oxygen demand (BOD₅)</td>
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<td>Total suspended solids (TSS)</td>
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<tr>
<td>Total kjeldahl nitrogen (TKN)</td>
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<tr>
<td>Oil and grease</td>
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<td>mg/L</td>
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*Average of 5 samples  ** Not detected

Conclusions

1- Gas processing wastewater was chemically characterized and found to be highly polluted with soluble, hazardous, and non-biodegradable organic hydrocarbons that are difficult to treat directly through conventional biological treatment methods.

2- Conventional coagulation-precipitation treatment method is not adequate to remove these soluble organics since the TSS concentration in the gas processing wastewater is very low.

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Using Fenton oxidation process was found adequate to oxidize and remove these soluble, hazardous, and non-biodegradable organic hydrocarbons from gas processing wastewater.

The optimal operating conditions achieved were: H₂O₂ in 1.6 M/L (1-stoichiometry of COD), Fe²⁺ ions in 80 mM/L at pH around 3 and at 30 min reaction time with continuous stirring at 120 rpm.

The Fenton process application proved to be adequate as the treated effluent removal of COD, BOD, TSS and phenols were 80%, 57.8%, 87% and 100, respectively at optimum operating conditions.

The BOD/COD ratio has risen to around 0.36, this means that the improvement of the biodegradability of gas processing wastewater is achieved. Fenton oxidation treatment process, therefore, represents an effective pretreatment solution of gas processing wastewater.

References


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