

Removal of organic pollutants from produced water using Fenton oxidation

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Abstract. Produced water (PW) is the largest stream of wastewater from oil and gas exploration. It is highly polluted and requires proper treatment before disposal. The main objective of this study was to investigate the effectiveness of Fenton oxidation in degradation of organic matter in PW. The role of operating factors viz., H₂O₂ concentration (0.12×10^{-3} moles/L to 3 moles/L), [H₂O₂]/[Fe²⁺] molar ratio (2 to 75), and reaction time (30 to 200 minutes), on COD removal was determined through a series of batch experiments conducted in acidic environment at room temperature. The experiments were conducted with 500 mL PW samples in 1L glass beakers covered on the outside with aluminum foil to protect them from sunlight. Pre-decided amounts of ferrous sulfate heptahydrate (FeSO₄·7H₂O) and hydrogen peroxide (H₂O₂) were added to initiate the Fenton reaction. An increase in COD removal was observed with increase in reaction time and [H₂O₂]/[Fe²⁺] molar ratio. COD removal also increased with H₂O₂ concentration up to 0.01 moles/L; further increase in H₂O₂ concentration decreased the COD removal efficiency. Over 90% COD removal was achieved under optimum reaction conditions. The study indicates that Fenton oxidation is effective for remediation of PW in terms of organic matter removal.

1 Introduction

In recent years, an increasing concern about monitoring water quality has been reflected in many studies. The amount of freshwater on Earth is limited and its quality is being constantly threatened due to various types of pollutions. Hence there is a demand for the protection of water resources, in order to prevent their contamination by toxic compounds and pathogenic agents [1].

Organic compounds especially persistent organic pollutants (POPs) may enter the environment by either natural or anthropogenic sources. The former includes volcanic eruptions and forest fires. However, the largest fraction is produced by the latter, namely, by incomplete combustion of fossil fuels, petrochemical processing, automobile exhausts, and tobacco smoke [2-4]. These compounds provoke adverse effects in the ecosystems, even at low concentrations (ng/L-µg/L). They are toxic and persistent, some of them show bioaccumulation effects [5], and are endocrine disrupting as well as tumorigenic substances

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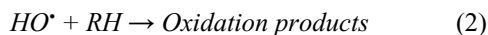
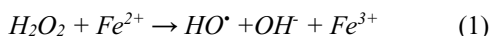
[6]. In addition, a class of organic compounds i.e. aromatic hydrocarbons with four or more rings are carcinogenic and mutagenic as a result of their ability to undergo metabolic transformations [7].

Like many production activities, a large volume of liquid waste is produced from oil and gas exploration. This liquid waste is termed Produced water (PW). Produced water is the water that exists in subsurface formations and is brought to the surface during oil and gas production. One of the causes of the harmful characteristics of produced water is the presence of toxic organic compounds. The most abundant organic pollutants in produced water are water-soluble low molecular weight organic acids, monocyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and dissolved hydrocarbons like BTEX and high molecular weight alkyl phenols [8,9].

In recent years, research and development of enhanced options to more effectively treat produced water and particularly to remove toxic organic compounds have received growing interests in order to meet the increasingly stringent regulations.

The removal of organic compounds from wastewater can be performed through physical, chemical and biological processes. Physical processes such as volatilization and adsorption [10] can greatly reduce the amount of persistent organic compounds in the wastewater, but they do not solve the problem of pollution due to their inability of contaminant degradation [11]. Conventional phase separation techniques will not remove the water-soluble organics from the aqueous phase. Thus, various biological [12, 13] and chemical [14] oxidation methods have been used to treat produced water. By far, biological degradation has been considered as the most cost-effective treatment method [15,16] However, conventional biological systems exhibited limited ability to remove aromatic hydrocarbons from PW [10,17] due to the bio-recalcitrance, toxicity and high chemical stability of the fused benzene rings [18]. Since some organic compounds are quite resistant to the first steps of biological oxidation [19], chemical oxidative treatment, such as advanced oxidation processes (AOPs), can be employed as an alternative approach for their remediation. AOPs are oxidative technologies by which the hydroxyl radicals are generated to degrade organic contaminants. Among the AOPs, the Fenton method is one of the most promising treatments, due to its high performance, technological simplicity, and moderate cost [20–23].

Commonly, it takes place at temperatures between 20 to 40 Celsius [24] and no energy input is necessary to activate hydrogen peroxide [25]. In Fenton initiation reaction, Fe^{2+} catalyses the decomposition of hydrogen peroxide to generate the hydroxyl radical ($OH\bullet$) (Equations 1 and 2), which is a strong and relatively non-specific oxidant (with redox potential E of 2.8 V) [26]. It is the main oxidizing specie that can degrade most refractory organics including persistent organic pollutants e.g. PAHs [27]. The reaction between $OH\bullet$ and hydrocarbons is very fast, and the rate constants can be as high as 10 mol /L s [24].



Literature reveals that Fenton's reagent is one of the most efficient compositions based on hydrogen peroxide. This method can be effectively used to degrade various contaminants owing to the activity of hydroxyl radical which allows it to oxidize nearly all organic pollutants [28], e.g. phenol ketone, alcohol, benzene, nitrobenzene, perchloroethylene, toluene, p-toluene, aniline, p-nitrophenol, humus compounds etc. Fenton's reagent was also shown to be useful for destabilizing oil emulsions and decomposition of the oxidizing ethyl-t-butyl ether (ETBE) in water petrol extracts [29].

The present work evaluates the feasibility of organic matter degradation in produced water by applying Fenton's reagent at room temperature. The effect of variables (initial

concentrations of hydrogen peroxide, reaction time and $[H_2O_2]/[Fe^{2+}]$ molar ratio) that influence the Fenton degradation of organic matter will be determined.

2 Materials and methods

2.1 Produced water and reagents

Produced water was obtained from a local Crude Oil Terminal and used without further treatment before experiments. Table 1 shows the characteristics of PW. Hydrogen peroxide (30%) and $FeSO_4 \cdot 7H_2O$ were purchased from R & M chemicals Ltd. The pH of the produced water was adjusted by the addition of 98% H_2SO_4 and 98% NaOH solution.

Table 1. Characteristics of PW.

Parameters	Values
pH	7.81
COD	3200 mg/L
TOC	891 mg/L

2.2 Method

To understand the role of different factors influencing Fenton oxidation in COD removal, batch experiments were carried out at room temperature and acidic environment. The experiments were conducted in a 1L glass beaker serving as a reactor. The outside of the reactor was covered with aluminium foil to protect it from light. Homogeneous mixing was provided using a magnetic stirrer. In each of the experimental runs, 500 ml of produced water was stirred in the glass reactor at room temperature. After the adjustments of pH up to 3 using H_2SO_4 , a calculated amount of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was added as the source of Fe^{2+} . After $FeSO_4 \cdot 7H_2O$ was completely dissolved in PW, necessary amount of H_2O_2 was added cautiously into the reactor to start the reaction. Time zero coincided with the H_2O_2 addition. After the pre-decided reaction times, which ranged from 30 to 200 minutes, Fenton reaction was seized by increasing the pH of the reacting solution up to 9 by adding NaOH solution. Aliquots were taken from the reactor at measured time intervals and immediately analyzed for COD [30].

2.3 Analysis

The COD concentrations of treated produced water samples were determined by using HACH DR 2800 spectrophotometer under Program 430 using the USEPA Method 8000. TOC measurement of the PW sample was carried out using Shimadzu TOC-VCSH- TOC analyser following the standard operating procedure for the analysis of dissolved and Total organic carbon CCAL 20A.0.

3 Results and discussions

All the experiments were carried out at room temperature. The initial pH of each sample was adjusted at 3.5. Effects of concentration of H_2O_2 , $[H_2O_2]/[Fe^{2+}]$ molar ratio and reaction time on COD removed were studied during the experimentation. Details of these experiments are discussed below.

3.1 Effect of H_2O_2 concentration

The concentration of H_2O_2 for Fenton's treatment of produced water was varied in the range of 0.12 mmol/L to 3 mol/L to determine an experimental condition for further research. Results from the experiments are outlines in Fig.1. In all experiments, it was observed that the maximum COD removal was achieved after 120 minutes. On the other hand, the increase in hydrogen peroxide concentration from 1.2 mmol/L to 0.01 mol/L yielded rising removal efficiencies and the percentage of COD removal increased from 76% to 91.6% (Fig. 1). The increase of H_2O_2 dosage leads to an increase in the generation of hydroxyl radical species responsible for the degradation of organic matter, thus increasing the removal efficiency of COD. However, higher concentrations of H_2O_2 lead to lower degradation rates due to the fact that in the presence of excess amount of hydrogen peroxide, chemical oxidation of organics can be inhibited due to the formation of oxygen bubbles instead of hydroxyl radicals [31].

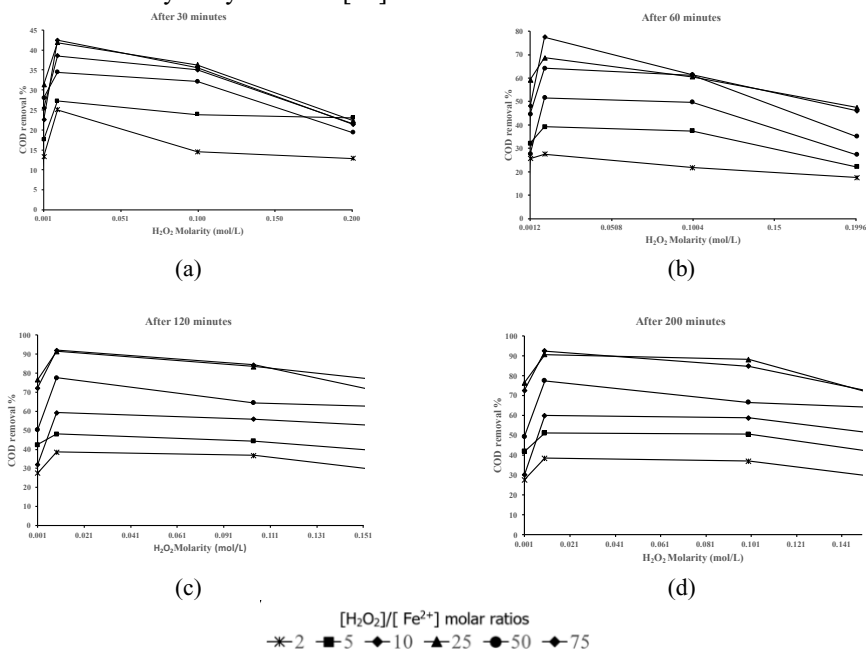


Fig. 1. COD removal with respect to varying H_2O_2 concentrations at different $[H_2O_2]/[Fe^{2+}]$ molar ratios.

3.2 Effect of $[H_2O_2]/[Fe^{2+}]$ molar ratio

To study the role of Fe^{2+} concentration on Fenton treatment of produced water, a series of experiments were conducted with different Fe^{2+} concentrations by keeping the dosage of H_2O_2 at 0.01 mol/L, reaction time 120 minutes and pH was adjusted to the value of 3.5. As

by applying these experimental conditions, COD removal efficiency achieved was the highest under the present study. Based on six different $[H_2O_2]/[Fe^{2+}]$ molar ratios, the results obtained are presented in Fig. 2.

During Fenton oxidation, OH^\bullet and Fe^{2+} ions both enter a series of reactions that lead to the oxidation of organics. The $[H_2O_2]/[Fe^{2+}]$ molar ratio of 1:5 to 1:25 has been reported in literature [32]. According to the results, it is evident that the maximum COD removal was achieved between $[H_2O_2]/[Fe^{2+}]$ molar ratios of 10 to 25. In Fenton oxidation, Fe^{2+} species act as catalyst which are accountable for speeding up the formation of OH^\bullet radicals. In experiments where the amount of Fe^{2+} is in low concentrations, the degradation of organic compounds due to Fenton oxidation is slower due to the unavailability of sufficient amount of catalyst (Fe^{2+}) for the oxidant. Though, under the present study, the removal efficiency of organic compounds decreased by increasing Fe^{2+} concentration due to the scavenging effect exhibited by high concentration of Fe^{2+} . Moreover, if the amount of Fe^{2+} used is too high, there would be production of large quantities of ferric based sludge, which further muddles the oxidation process due to the necessity of its handling and disposal [33].

Bearing in mind the potential generation of sludge and its handling and disposal, the molar ratio of 10 was thought to be suitable to achieve effective reduction of COD in present experimental conditions.

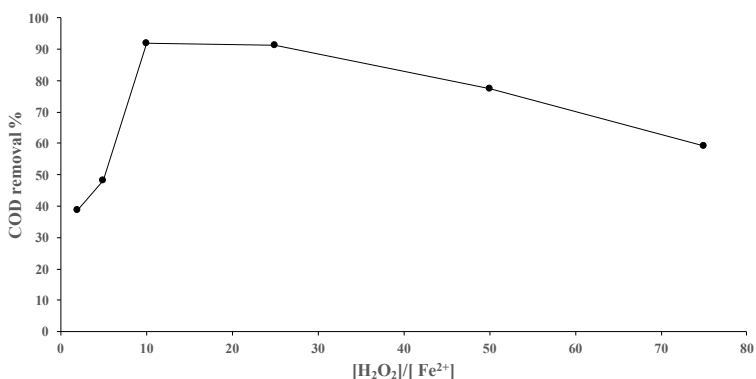


Fig. 2. COD removal at different $[H_2O_2]/[Fe^{2+}]$ molar ratios by keeping H_2O_2 at 0.01 mol/L and reaction time 120 minutes.

3.3 Effect of reaction time

The reaction time of Fenton's reagent with produced water was varied in the range of 30-180 minutes. The highest COD removal of almost 90% was observed at 120 minutes as shown in Figure 3, with initial pH of produced water adjusted at 3.5, dosage of H_2O_2 at 0.01 mol/L and $[H_2O_2]/[Fe^{2+}]$ molar ratio at 10. Reaction time beyond 120 minutes did not give any further COD removal. Hence 120 minutes was considered to be ideal with the aforementioned conditions.

It can be seen from the graph that the COD reduction of PW was very rapid in the first 60 minutes of Fenton oxidation, after which the COD reduction became gradual up to 120 minutes. After 120 minutes there was only a slight increase in COD reduction which became steady after 180 minutes. Even though the reaction was seized after 200 minutes, but no further COD removal was achieved after 180 minutes. Since in Fenton oxidation OH^\bullet is the key oxidizing species and its production is very quick and vigorous. Thus, in the

present study, Fenton reaction of organics initiated immediately as soon as H_2O_2 was mixed with Fe^{2+} .

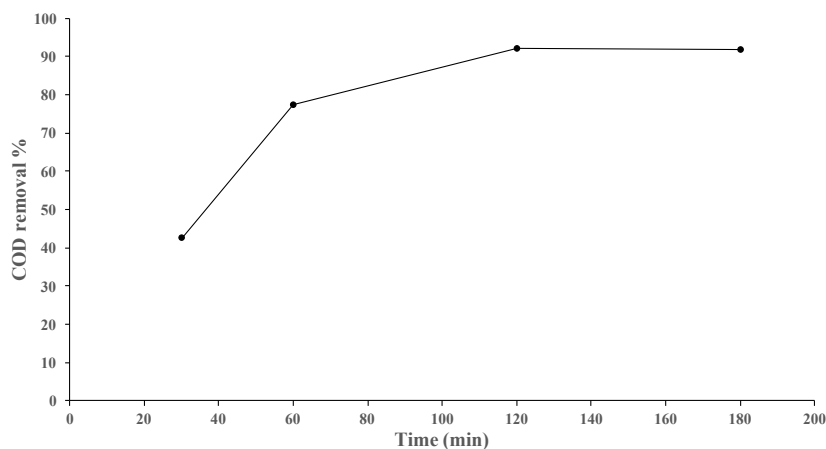


Fig. 3. COD removal at different reaction times by keeping H_2O_2 at 0.01 mol/L and $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ molar ratio at 10.

4 Conclusions

This paper studied the degradation of organic compounds in produced water by Fenton's reagent at room temperature to make the treatment process more economical. Maximum COD removal efficiency of up to 91% was achieved. Results showed that chemical degradation of organics was highly dependent on Fe^{2+} and H_2O_2 dosage as well as the reaction time. The hydrogen peroxide played an important role during the oxidation as changing hydrogen peroxide concentration changes the $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ molar ratio, although the degradation of organics increased with the increasing H_2O_2 concentration, at high concentrations of the oxidant COD removal was reduced. With an initial concentration of 0.01 mol/L, up to 91% COD removal was achieved while with 0.1 mol/L only 50% COD removal was observed. The same effect was observed for the concentration of Fe^{2+} ions.

This study demonstrates that Fenton oxidation process is effective for the remediation of produced water in terms of COD removal without increasing the temperature of PW. COD removal percentage may have been higher than the present results if the temperature of PW was increased, but the goal of the study was to make Fenton oxidation efficient as well as economical at the same time, so no heating was provided. It could be considered a promising technology for treatment of produced water.

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