Feasibility Study of Conventional Coagulants and Fenton Reagent for High Chemical Oxygen Demand Wastewater

Barwal A and Chaudhary R*

School of Energy and Environmental Studies, Faculty of Engineering Sciences, Devi Ahilya University, Takshashila Campus Khandwa Road, Indore, Madhya Pradesh, India

*Corresponding author: Rubina Chaudhary (Reader), School of Energy and Environmental Studies, Faculty of Engineering Sciences, Devi Ahilya University, Takshashila Campus, Khandwa Road, Indore, Madhya Pradesh, India, Tel: +91731-2460309; Fax: +91731-2460737; E-mail: rubina_chaudhary@yahoo.com

Abstract

Attempts were made in this study to examine the effectiveness of conventional chemical coagulation and flocculation process using ferrous sulphate, alum and Fenton process for the treatment of high chemical oxygen demand (COD) industrial wastewater. Removal of organic matter (expressed as COD) was investigated for highly organic wastewater having COD of 15000 mg/L. Also, the optimum conditions for coagulation/flocculation process, such as coagulant dosage, Fenton dosage and pH of solution were investigated using jar-test experiment. The results revealed that in the range of pH tested, the optimal operating pH was 7.5-8 for FeSO₄ and alum and 3 for Fenton process. Percentage removals of 26, 42 and 88 for COD was achieved by the addition of 1.0 g/L alum, 1.2 g/L of FeSO₄ and 1:20 Fe³⁺/H₂O₂ ratio, respectively. It can be concluded from this study that coagulation/flocculation may be a useful pre-treatment process for high organic load industrial wastewater prior to biological treatment.

Keywords: Alum dosing; Coagulation; Chemical oxygen demand; Fenton reagent; Wastewater

Introduction

In recent years, with an increase in the stringent water quality regulations due to environmental concerns, extensive research has focused on upgrading current water treatment technologies and developing more economical processes that can effectively deal with toxic and biologically organic contaminants in wastewater [1].

Industries manufacturing pharmaceuticals, cosmetics, organic dye-stuff, soaps and detergents, pesticides and herbicides, tanneries and leather, paper, brewery and fermentation industry generate wastewater containing high organic load, toxicity or presence of bio-recalcitrant compounds having various origins and properties. Such wastewater having poor biodegradability needs a strong pretreatment method, followed by a biological treatment process [2]. Usually, conventional chemical coagulation - flocculation methods like Alum, ferrous sulphate, polyelectrolyte etc. are very commonly used as a pre-treatment method to enhance the bio-degradability of wastewater during the biological treatment. Among these chemical processes, the advanced oxidation process (AOP) has been efficiently used to reduce the organic load or toxicity of different wastewater [3]. Fenton reagent is considered as one of the AOP and used for the treatment of both organic and inorganic substances [4]. The Fenton's reaction has a short reaction time among AOPs; therefore, it is used when a high COD removal is required [5].

Moreover, the reaction occurs at ambient temperature and pressure, involves easy and safe to handle reagents, no special equipment required, no mass transfer limitations, no energy involved and can be implemented with a great variety of compounds (6-8).

The Fenton's system consists of ferrous salts combined with hydrogen peroxide (H₂O₂) under acidic conditions. Ferrous ion reacts with hydrogen peroxide, producing hydroxyl radical 'OH mentioned below (reaction 1) [9-11].

\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot \text{OH} \]  

The 'OH free radical, having a very high oxidation potential (E°=2.80 V), is capable of reacting with many organic species through a series of chain reactions.

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

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

\[ \text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \cdot \text{OH} \]  …………….. (4)

Fe²⁺ produced can react with H₂O₂ and hydroperoxyl radical in the so-called Fenton-like reaction, which leads to regenerating Fe³⁺ (reactions 2 and 3). Fe²⁺ regeneration is also possible by reacting with organic radical intermediates (Reaction 4) [12].

It was also reported by Ivan et al. [13] that 'OH reacts unselectively within a millisecond with organic substances. H₂O₂ and Fe²⁺ also had a synergistic effect on the removal of colloidal organic residues by coagulation.

In Fenton treatment, the pH value should be near 2-4 during the reaction. After reactions are completed, precipitation of the oxidized iron as Fe(OH)₃ occurs by neutralizing or adjusting the pH to 7.5 - 8 [14,1]. Neyes et al. and Neyens et al. and Neyens and Baeyens [15,11] studied the effects of pH, temperature, reaction time and H₂O₂ concentration with considerable reduction inorganic concentration.

As per the literature review, no study has been performed for wastewater having extremely high COD value. Therefore, the objective of present study was to evaluate the efficiency of conventional coagulants and
Fenton’s reagent to remove COD from industrial wastewater characterized by its extremely high value of COD (approximately 15000 mg/L) and a low value of BOD, probably due to the presence of toxic compounds, which hamper a direct biological treatment and thus require a chemical pre-treatment. Effects of pH and the optimal dosages of conventional coagulants and Fenton reagent (Fe$^{3+}$/H$_2$O$_2$) were also determined.

**Material and Methods**

**Synthetic wastewater**

Synthetic industrial wastewater was prepared in the laboratory with tap water by mixing different chemicals containing organic carbon, macro and micro-nutrients. The composition of stock synthetic wastewater was adjusted in such a way that COD becomes approximately about 15000 mg/L. The working synthetic wastewater containing varying COD concentrations was prepared by diluting appropriate volume of stock synthetic wastewater with tap water. The composition of synthetic wastewater is mentioned in table 1.

**Experimental setup**

The coagulation, flocculation and Fenton system experiments were conducted using Jar Test equipment (Make- Jindal SM Scientific Instruments Pvt. Ltd., India), consisting of 6 jars of 1000 mL each whose contents were stirred with flat stirring paddles (25 mm × 75 mm) as shown in the figure 1.

**Analytical procedures**

Analytical procedures were monitored in accordance with standard methods [16]: COD removal efficiency (RE) was calculated by using the following equation 1:

\[
RE(\%) = \left( \frac{C_n - C_{ef}}{C_n} \right) \times 100 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ld...
37.5% (COD value 12385.6 and 3916.7 mg O₂/L respectively). However, above the dose of 1500 mg H₂O₂/L a slight decrease in COD removal was observed (Figure 4). This could be explained by the excess of hydrogen peroxide concentration, behaving as a hydroxyl radical's scavenger in the Fenton reaction. This finding is in line with the reports of Lin and Lo [18], Kang and Hwang [19] Ozdemir et al. [4].

**Effect of pH:** pH has been observed to significantly affect degradation of COD. The pH of the system was varied from 2.0-3.5 and the best removal efficiency was observed at pH 3.0 (Figure 5). At pH<3.0, there was reduction in the removal efficiency of COD. This may be due to the formation of Fe (II) complex which reacts more slowly with H₂O₂ produces fewer amount of °OH radicals thereby reducing the removal efficiency. Beyond pH>3.0, the COD removal efficiency also reduced due to decrease in the free Fe ions due to the formation of Fe (II) complex.

**Effect of Fenton (Fe²⁺/H₂O₂) dosing:** To investigate the optimum FeSO₄ dosage, five different Fe²⁺/H₂O₂ ratios (1:5, 1:10, 1:15, 1:20 and 1:25) were tested using optimized H₂O₂ concentration of 1500 mg/L (Figure 6). These results show that with an increase in Fe²⁺/H₂O₂ ratio from 1:5-1:20, COD removal efficiency significantly increases from 53% to 88%. However, above Fe²⁺/H₂O₂ ratio of 1:20, only slight changes in COD removal were observed and COD concentration kept almost the same level about 6946.6-1773.6 mg/L. Therefore, optimum ratio of Fe²⁺/H₂O₂ was observed to be 1:20.
Effect of reaction time for Fenton reagent: Reaction time for Fenton reagent is also considered as an important factor. The reaction time was extended to 2 h. The results demonstrated that COD removal efficiency was rapidly increasing within the first 30-45 minutes of reaction time. Maximum efficiency of COD removal (62.9%) was observed after 60 min. After this time, COD removal was diminished to 61.4% and 52.3% after 90 and 120 min. respectively (Figure 7). This could be explained by the formation of by-products more resistant to oxidation.

Conclusion

The process of coagulation-flocculation applied to the highly organic wastewater was found effective in COD removal using H₂O₂ and Fe²⁺. The best removal efficiency (88%) was obtained at pH 3.0 using a Fenton (Fe²⁺/H₂O₂) ratio of 1:20 with H₂O₂, doing of 1500 mg/L. The COD removal efficiency (62.9%) was found rapidly increasing at an optimum reaction time of 60 minutes. At acidic pH values, it has been shown that H₂O₂ decomposes to produce •OH radicals. When only conventional coagulants like alum and FeSO₄ were used, the COD removal efficiency was only 26 and 42% respectively. It is obvious that Fe²⁺/H₂O₂ has a strong synergistic effect on coagulation and achieve the best degradation in terms of COD removal and appears to be useful in increasing the biodegradability of wastewater that contains complex compounds. But, from economical point of view, Fenton process has higher cost if compared to other coagulants but this cost could be compensated by lower consumption of disinfecting agents and the lower costs of sludge handling and disposal.

References
