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Fenton Process for Removing Organic Pollutants from Industrial Wastewater

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ABSTRACT:
The fenton process is one of the most studied advanced oxidation processes, due to its efficiency, low reaction time and easy application. In the present study, fenton process is used to remove the organic pollutants from industrial wastewater. The process parameters like pH and reaction time were studied using 1:10 ratio of $FeSO_4$ and H_2O_2 with a 500ml working volume of sample. The most favourable circumstances were determined at a pH level of 7 with a reaction duration of 3 Hours. Finally, chemical oxygen demands (COD) and chlorides, before and after fenton process were measured to ensure the entire destruction of organics during their removal from industrial wastewater. The experimental results shown that the fenton process effectively achieved removal efficiency of 80%.

Keywords: Industry wastewater, Fenton process, Chemical oxygen demand (COD), chlorides.

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I. Introduction

In modern years, there has been a crucial necessity to build up effective technologies to remove an increasing number of persistent pollutants, especially from water and wastewater. The natural environment, particularly aquatic ecosystems, is especially sensitive to anthropogenic changes. The development of industry, agriculture, and the development of civilisation and the increase in consumption contribute to the spread and increase in concentrations of a wide range of anthropogenic pollutants in the environment [Popenda *et.al.,* 2018; Kudlek and Dudziak, 2018; Pochwat, 2022]. In recent years, special attention has been paid to the research and implementation of advanced oxidation processes. The common feature of these methods is that they enable the generation of highly reactive hydroxyl (·OH) radicals, which react with almost all organic compounds. Owing to the high effciency in the degradation of most organic micropollutants, advanced oxidation methods are now increasingly considered as the most promising alternative treatment methods compared to conventional methods. The Fenton process is an advanced oxidation method [Sabina Ziembowicz et.al. 2022]. Currently, the treatment of highly toxic organic substances found in wastewater is receiving increased attention due to their detrimental impact on the environment. During the last decades, Fenton's process has been studied to optimize its efficiency in the depuration of liquid effluents [M Pera-Titus *et al.*, 2004; P Bautista *et al.*, 2008]. This Advanced Oxidation Process (AOP) is capable of reacting and eliminating organic matter by producing the potent oxidant hydroxyl through the decomposition of hydrogen peroxide in the presence of iron ions in acidic conditions., [*M Kitis et al., 1993*]. Furthermore, the catalytic breakdown of hydrogen peroxide follows a radical mechanism utilizing hydroperoxyl radicals. Radical chain oxidations will be then initiated by the hydroxyl radicals that will react non-selectively with the organic matter present in the wastewater [*E Neyens et al., 2003*]. The primary benefit of this method lies in the fact that the reaction occurs under room temperature and pressure conditions, making the treatment more cost-effective. Moreover, short reaction times are necessary, thus it required easy-to-use reagents [*A Guedes et al., 2003*]. The Fenton's process has an important role [*F Rivas et al., 2001; A Vlyssides et al., 2004*], either to promote the wastewater treatment to accomplish the parameters standard The objective is to ensure a secure release into natural waterways, reduce the toxicity of the effluent, and improve its biodegradability for effective post-biological purification in municipal wastewater treatment facilities. The wastewater toxicity and biodegradability were also measured to predict the possibility of using this chemical oxidation as a pre-treatment to obtain an effluent suitable to be further biologically depurated [*I A Balcioglu et.al., 2003; U E Cokgor et.al., 2004; E Neyens et.al., 2003; C M Miller* *et.al., 1996; W Z Tang et.al., 1997,* Pochwat, *et.al.,* 2022].

The occurrence of numerous organic contaminants in wastewater stems from industrial wastewater discharge and leaks from storage of hazardous compounds. The presence of these organic substances in water poses a significant danger to public health, as many of them are toxic. As a result, it is crucial to eliminate them from the contaminated water. The treatment methods such as biological processes are ineffective due to the stubborn nature of the contaminants present. Therefore, oxidation processes are favored to break down these present organic substances.

Fenton oxidation was studied extensively by many researchers for the treatment of wastewater containing organic compounds [*C M Miller et.al., 1996; W Z Tang et.al., 1997*]. The treatment of wastewater generated by the pharmaceutical industry has consistently been a challenge in achieving desired effluent standards due to the diverse range of products produced in a drug manufacturing facility, thus fluctuations simultaneously of pollutant concentration will occur. The substances synthesized in a pharmaceutical industry are structurally complex organic chemical that are resistant to biological degradation [*I A Balcioglu et.al., 2003*]. Due to that, conventional treatment methods are usually inappropriate for the treatment of pharmaceutical wastewaters and hence there is a need for advanced oxidation methods [*U E Cokgor et.al., 2004*]. Recently, the Fenton reaction has been effectively employed in the wastewater treatment process to remove numerous hazardous organic substances from wastewater. Recently, in a comprehensive review, Neyens and Baeyens [*E Neyens et.al., 2003*] indicated that Fenton's oxidation is very effective method in the removal of many hazardous organic pollutants from wastewaters. Fenton's oxidation can also be an effective pre-treatment step by transforming constituents to by-products that are more readily biodegradable and reducing overall toxicity to microorganisms in the downstream biological treatment processes [*P Bautista et.al., 2008*]. Fenton's oxidation is one of the best-known metal catalyzed oxidation reactions of water-miscible organic compounds. The Fenton's reagent has not only oxidation function but also coagulation by the formation of ferric-hydroxo complexes [*E Neyens et.al., 2003; A Guedes et.al., 2003*]. Recently, the Fenton reaction has been effectively employed in the wastewater treatment process to remove numerous hazardous organic substances from wastewater. [*Nora San et.al., 2003; Nese Ertugay et.al., 2013*]. The traditionally accepted Fenton mechanism is represented by following equations [*A R Dincer et.al., 2008*].

Eqn (1) is recognized as Fenton reaction and implies the oxidation of ferrous to ferric ions to decompose H_2O_2 into hydroxyl radicals. It is often considered the foundation of Fenton chemistry:

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH$, K = 40 – 80 L/mols Eqn (1)

The generated ferric ions can be reduced by reaction with excess hydrogen peroxide to form again ferrous ion and more radicals as shown in Eqn (2).

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\cdot}O_2H + H^+$, K = 9.1 x 10-7 L/mols Eqn(2)

This reaction is called Fenton-like reaction and slower than Fenton reaction and allows Fe^{2+} regeneration in an effective cyclic mechanism. In Fenton like reaction, apart from ferrous ion regeneration, hydroperoxyl radicals (HO^{2-}) are produced. Hydroperoxyl radicals may also target organic contaminants, however, they are less reactive than hydroxyl radicals. It should be noted that, the iron added in small amount acts as a catalyst while H_2O_2 is continuously consumed to produce hydroxyl radicals.

The Fenton chemistry involves the following reactions.

$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^-$, K = 2.5-5 x 108 L/mols Eqn(3)

$Fe^{2+} + {}^{\cdot}O_2H \rightarrow Fe^{3+} + HO^{2-}$, K = 0.72 – 1.5 x 106 L/mols Eqn(4)

$Fe^{3+} + {}^{\cdot}O_2H \rightarrow Fe^{2+} + O_2 + H+$, K = 0.33 – 2.1 x 106 L/mols Eqn(5)

Fenton process is encompassing hydrogen peroxide (H_2O_2) with iron ion's reaction to form active oxygen species that oxidize organic or inorganic compounds [*Huseyin Tekin et.al., 2006*].

In recent years, some typical reviews [*Ipek Gulkay et.al., 2006; E. Brillas et.al., 2009; R. Chand et.al., 2009; G.M.S. Elshafei et.al., 2014; C.K. Wang et.al., 2015; R. Carta et.al., 2013; X.J. Yang et.al., 2014; C. Zhang et.al., 2015; D. Wang et.al., 2014; M. Cat et.al., 2015; Z.P. Wang et.al., 2015; Y. Yang et al., 2009; P. Yan et al., 2014; L. Yu et al., 2014; P. Bautista et al., 2008; G. Pliego et al., 2014*] have been published regarding different aspects of the introduction of Fenton/Fenton-like processes. Pliego et al. [*G. Pliego et al., 2015*], in their review, presented various methods that can enhance Fenton-like processes, such as radiation, electrochemistry, and heterogeneous catalysts; Bautista et al. 2008, provided detailed information on the application of the Fenton process for the treatment of industrial WW. Brillas *et.al.,* 2006 gave a profound introduction to the electro-Fenton processes and the related electrochemical technologies. In our review, the significant impact parameters such as pH, H2O2 dosage, catalyst dosage, temperature, etc. are thoroughly discussed, followed by a presentation of physical field/phenomenon-assisted Fenton-like processes.

Fenton-like processes consist of heterogeneous and homogeneous Fenton-like processes. Heterogeneous Fenton-like processes can be established by replacing Fe^{2+} in the Fenton reagent with a solid catalyst, while homogeneous Fenton-like processes are due to a combination of other metal ion(s)/metal ion-organic ligand complexes and H_2O_2 [*G. Pliego et al., 2015*]. In Fenton-like systems, pH, H2O2 dosage, catalyst dosage, and reaction temperature have received extensive study due to their significant impact on the oxidation capacity of the Fenton-like agent. Thus, the systematic introduction and analysis of these parameters is necessary.In the present study, fenton process is used for treating industrial wastewater. The process parameters like pH and reaction time were studied using 1:10 ratio of $FeSO_4$ and H_2O_2 with a 500ml working volume of sample.

II. Materials and Methodology

2.1 Wastewater Characterization

The industrial wastewater sample was collected from the Isnapur industrial site, Hyderabad, (17.29.43N 78.23.34E) Telangana, India. The physicochemical characterization of wastewater samples was carried using “standard methods for examination of water and wastewater 21st addition-2005, APHA” [*Jotin R et al., 2012; Bhagawan D et al., 2017, Sabina et.al., 2022*]. The initial characterization of chloro pesticide intermediate industrial wastewater sample was given in Table1

Table 1 Initial characterization of chloro pesticide intermediate industrial wastewater sample

S. No	Parameter	Concentration
1	pH	1.29
2	EC	103.8ms/cm
3	COD	90,000mg/l
4	Chlorides	34,450mg/l
5	Total Solids (TS)	75,500mg/l
6	Total Dissolved Solids (TDS)	55,000mg/l
7	Suspended Solids (SS)	20,500mg/l
8	Sulphates	1,685mg/l
9	Total Organic Carbon (TOC)	42,390mg/l

2.2 Fenton Process for treating chloro pesticide intermediate industrial wastewater

According to theoretical calculations, the required quantity of hydrogen peroxide and iron sulphate (1:10 ratio) were added to 300ml working volume of sample and kept it in a shaker under closed conditions. The samples were collected for every 1hr till 3hrs of reaction time and then again kept it in a shaker for 24hrs to check the degradability of the sample. The samples were filtered with Whatmann filter paper and analyzed using standard methods (APHA 2005) [*Ashok KC et al., 2013*, Pochwat, 2022 & Sabina 2022].

2.3 Removal Percentage Calculation

The quantitative reduction of pollutants was measured according to the APHA standard methods [APHA 2005] and the percentage removal was calculated using Eqn-6.

$$\% \text{ Removal} = (C_0 - C_t) \times 100/C_t \quad \text{Eqn (6)}$$

Where C0 represents the initial concentration and Ct represents the final concentration.

III. Results and Discussions

3.1 Initial physicochemical characterization of chloro pesticide intermediate industrial wastewater

The initial physicochemical characterization of chloro pesticide intermediate industrial wastewater sample was performed and shown in Table 2.

Table 2 Initial physicochemical characteristics of chloro pesticide intermediate industrial wastewater sample

S. No	Parameter	Initial Concentration	Central Pollution Control Board (CPCB) Limits
1	pH	<2	6.0-9.0
2	Electrical Conductivity [EC]	103.8ms/cm	NA
3	Chemical Oxygen Demand	90,000mg/l	250mg/l
4	Sulphates	1,685mg/l	400mg/l

7	Total Solids [TS]	75,500mg/l	NA
8	Total Dissolved Solids [TDS]	55,000mg/l	NA
9	Chlorides	34,450mg/l	NA
10	Total Organic Carbon [TOC]	42,390mg/l	NA

Note: All the parameters were expressed in mg/l, except pH, EC. EC expressed in Milli Siemens and NA-Not Applicable.

3.2 Effect of Fenton process for the treatment of chloro-pesticide intermediate industrial wastewater

3.2.1 Effect of reaction time and pH

Effect of reaction time is one of the effecting parameters in treatment of chloro pesticide intermediate industrial wastewater using fenton process. The effect of reaction time (30, 60, 90, 120, 150, 180Min & 24hr) studied at different pHs (<2, 3 & 7) and which were shown in the following figures. The maximum removal has been observed at reaction time of 3hr. This might be due to sufficient dosage and after 3hr of reaction time, it maintained constant. Hence, to avoid excess operational cost the reaction time is optimized to 3hr of reaction time.

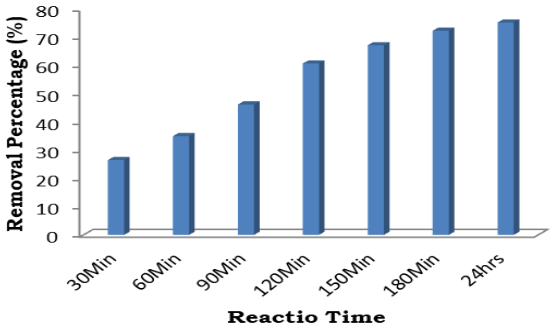

Fig.1 Removal Percentage of Chlorides at pH <2

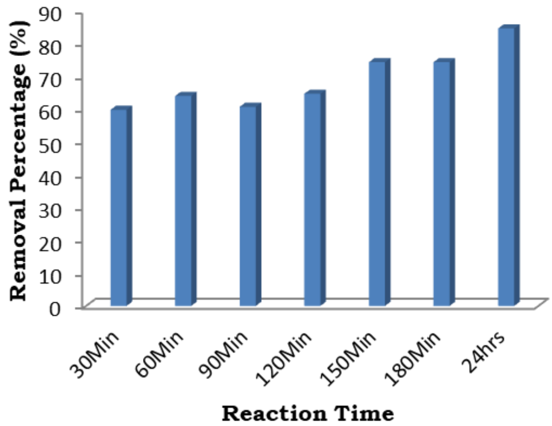

Fig.2 Removal Percentage of Chlorides at pH 3

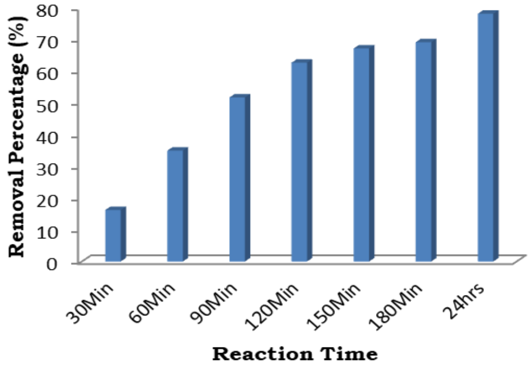

Fig.3 Removal Percentage of Chlorides at pH 7

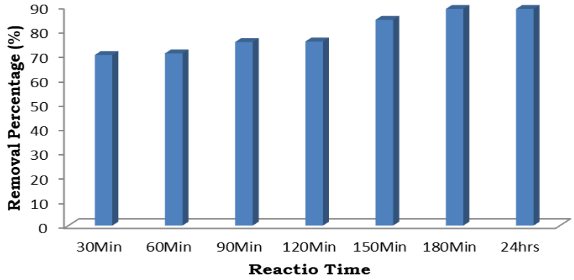

Fig.4 Removal Percentage of COD at pH <2

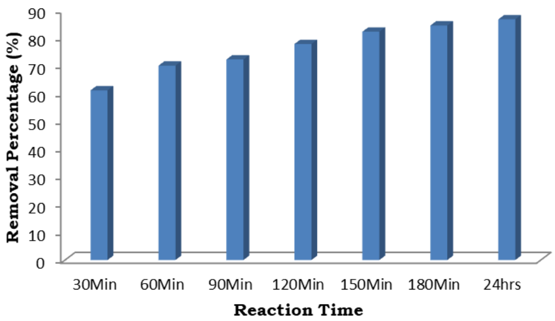

Fig.5 Removal Percentage of COD at pH 3

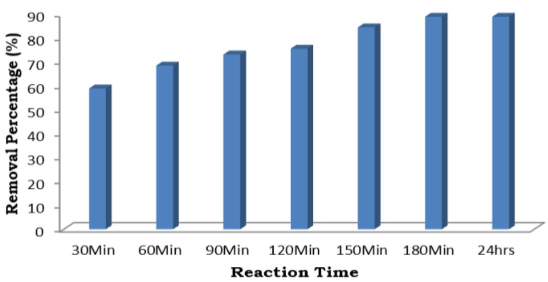

Fig.6 Removal Percentage of COD at pH 7

From Fig 1, 2, 3, 4, 5 and 6, we observed that the removal percentage of COD and chlorides increased with increasing the pH and reaction time. The maximum removal achieved at pH 7. At this pH, the removal % of COD and chlorides are 80 and 78% respectively at 180Min of reaction time.

The pH value plays a decisive role in determining the oxidation potential of OH. radicals due to its reciprocal relation of the oxidation potential to the pH value. Furthermore, the concentration of inorganic carbon and the hydrolytic speciation of Fe (III) species are strongly affected by the pH value. Therefore, the role of pH in the Fenton reaction must be determined. The same as in Fenton and Fenton-like reactions have a maximum catalytic activity at pH of about 2.8–3The pH value affects the formation of OH. radicals and thus the oxidation efficiency. For pH values above 6, the degradation significantly decreases as iron precipitates as a hydroxide derivative, reducing the availability of Fe (II) and hindering the transmission of radiation. Another factor contributing to the inefficiency of removal at pH > 3 is the dissociation and self-decomposition of H2O2.

3.2.2 The removal percentage of chlorides

The removal percentage of chlorides at pH 1.29, 3 and 7 were given in following figures 7, 8 & 9. With increasing the reaction time, removal percentage of Chlorides also increased.

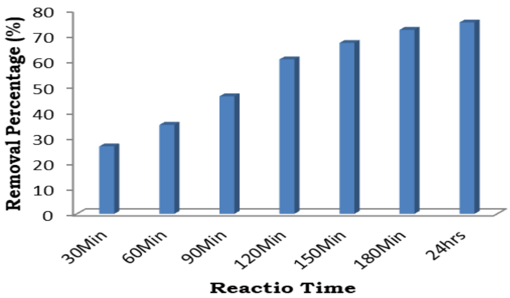

Fig.7 Removal Percentage of Chlorides at pH 1.29

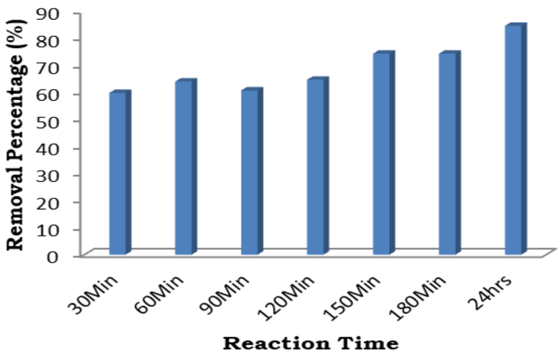

Fig.8 Removal Percentage of Chlorides at pH 3

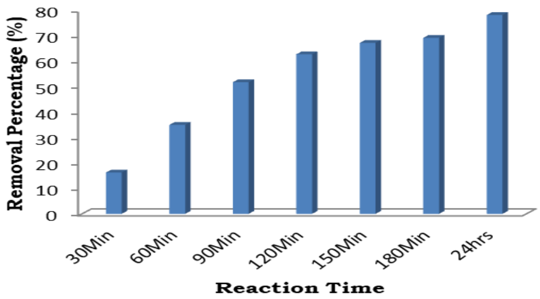

Fig.9 Removal Percentage of Chlorides at pH 7

IV. Conclusions

The Fenton process is advanced process which is used to remove the contaminants from water and wastewater, and it has wide application on an industrial scale. The maximum removal percentage of chlorides and COD obtained with fenton process at pH.

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