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COD Removal of Different Industrial Wastewater by Fenton Oxidation Process

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Abstract

Advanced oxidation processes are possibly one of the most effective methods for the treatment of wastewater containing organic products (effluents from chemical and agrochemical industries, the textile industry, paints, dyes, etc.).Fenton process is a one of advanced oxidation process. Fenton's process have been extensively used for the removal of COD, TOC, dyes, phenolic compounds other organic chemicals from industrial and municipal wastewater. In this study, the laboratory scale batch experiments were performed to analyze the COD reduction of three different industrial wastewater samples by using Fenton Process. Various amounts of H2O2 and Fe+2 were taken in order to optimize the COD reduction.

Keywords: Advanced Oxidation Process, Fenton reagent, textile wastewater, dye wastewater, pharmaceutical wastewater, COD

Introduction

Water is the basic need of every living organism. But a continuous increase in multifarious activities by human beings like industrialization, urbanization etc. has led to pollution of our water resources. Numerous industries like textile, paper, pulp, dyeing and printing industries are throwing their effluents into water bodies causing water pollution. Biological treatment is the most common process used to treat organics-containing wastewaters [A. Christensen (2009)]. The biological processes are frequently employed since they are more economic and environ-mental friendly, using optimized natural pathways to actually destroy pollution, not only transform it into another form [A.Z. Gotvajn (2005)]. However, some refractory compounds persist after the biological treatment and chemical oxidative processes arise as good methods to treat the remaining recalcitrant organic matter.

Biological treatment is not appropriate for these wastewaters due to their low bio-degradability [S. Cheng (1996)]. The effluent after biological treatment still contained high concentration of organic nitrogen and dissolved chemical oxygen demand (DCOD) in the effluent [C.C. Wang (2001), M.A. Aparicio (2007)] and therefore further chemical treatment is necessary in order to meet the effluent standard. An alternative advanced oxidation methods which is very efficient and less expensive compared to adsorption is required to treat wastewater.

Advanced wastewater treatment is defines as the additional treatment needed to remove suspended, colloidal, and dissolved constituents remaining after conventional secondary treatment. [Metcalf & Eddy, 4th edition]. Advanced Oxidation processes are used to oxidize complex organic constituents found in wastewater that are difficult to degrade biologically into simpler end products.

Among chemical processes, the advanced oxidation process (AOP) has been used to reduce the organic load or toxicity of different waters and wastewaters [M. Pérez (2002), L. Guzzella (2002), and I.A. Alaton (2002)]. AOPs are based on the generation of hydroxyl free radicals, which have a high electrochemical oxidant potential. The generation of hydroxyl radicals involves the combination of classical oxidants, such as H_2O_2 or O_3 with UV radiation or a catalyst. The formed radicals react with organic materials breaking them down gradually in a stepwise process. The generation of hydroxyl radicals can be achieved by a variety of reactions, such as ozone/UV, hydrogen peroxide/UV, Fenton oxidation, photo-Fenton or titanium dioxide/hydrogen peroxide/solar radiation [Antoni Sánchez Ferrer(2003)]. The advantage of AOPs is that they effectively destroy the organic compounds, converting them mainly to carbon dioxide and water.

Among AOPs, the Fenton's reagent [H.J.H. Fenton (1894)] has been efficiently used as a chemical process for wastewater treatment and pre-treatment. The Fenton's system consists of ferrous salts combined with hydrogen peroxide under acidic conditions. This reaction allows the generation of hydroxyl radicals as shown in reaction (1):

$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH^{\blacksquare}$ …… (1)

Fe^{+3} produced can react with H_2O_2 and hydroperoxyl radical in the so-called Fenton-like reaction, which leads to regenerating Fe^{+2} (reactions (2) and (3)). Fe^{+2} regeneration is also possible by reacting with organic radical intermediates (reaction (4)) [P.C. Vendevivere (1998)].

$Fe^{+3} + H_2O_2 \rightarrow Fe^{+3} + HO_2{}^{\blacksquare} + H^+$ ……. (2)

$Fe^{+3} + HO_2{}^{\blacksquare} \rightarrow Fe^{+2} + O_2 + H^+$ ……….. (3)

$Fe^{+3} + R^{\blacksquare} \rightarrow Fe^{+2} + R^+$ ………………….. (4)

The Fenton's reaction has a short reaction time among AOPs; therefore, Fenton's reagent is used when a high COD removal is required [V. Sarria (2001)]. A wide variety of Fenton's reagent applications have been reported, such as treatment of textile wastewaters [M. Pérez (2002), P.C. Vendevivere(1998), S.F. Kang (2002)], treatment of 1-amino-8-naphthol-3,6-disulfonic acid manufacturing wastewater [Z. Wanpeng (1996)], reduction of polynuclear aromatic hydrocarbons in water [F.J. Beltrán(1998)], improvement in dewatering of activated sludge , removal of AOX from pharmaceutical wastewater [C. Hölf (1997)], treatment of brines or treatment of paper pulp manufacturing effluents [M. Pérez (2002)].

In this work, the Fenton's reagent is used to remove COD from an industrial wastewater characterized by its extremely high value of COD and a low value of BOD, probably due to the presence of toxic compounds, which hamper a direct biological treatment.

Experimental

Collection of wastewater sample

The wastewater is sample is collected from different industries like dye, pharmaceutical and textiles located in different areas of Gujarat.

Experimental Chemicals & Equipment

Hydrogen Peroxide (50% m/w), Ferrous sulphate, Magnetic stirrer, Sulphuric acid, Sodium hydroxide, pH meter, Beaker, COD apparatus

Preparation of Fenton solutions

In which the Fenton procedure, hydrogen peroxide and ferrous sulphate are used. 50% m/w hydrogen peroxide is give best result of producing hydroxyl radicals. Ferrous solutions are prepared by dissolve 150 gm of ferrous sulphate in crystal form in 500 ml distilled water

Experimental Setup and Procedure

The procedure of Fenton's reaction was as follows: the wastewater was put into beaker of 1- liter volume, and then acidified with H_2SO_4, if necessary. Fenton's reaction is only effective in the acidic pH range. Hence, when the initial pH of wastewater was above 7-8, the samples were acidified to the selected value, in the pH range of 3.0–4.0, in order to estimate the pH effect on COD removal.

After that, the various amounts of hydrogen peroxide solutions and $FeSO_4 \cdot 7H_2O$ (in a solid state) were added with continuous magnetic stirring. After appropriate time the wastewater was neutralized with solution of NaOH up to about pH 7. After sedimentation, the residual amount of H_2O_2 was removed by using Na_2SO_3 because the effect of H_2O_2 on $K_2Cr_2O_7$ and they showed linear relationships between concentrations of H2O2 and COD. COD was determined in accordance with standard methods [APHA, 1992], while pH was measured using a pH meter.

Fig 1. Experimental setup of waste water

Results and Discussion

Results

In the first part of the investigations, optimization of Fenton's reaction was carried out for the three types of wastewater like dyes, textile and pharmaceutical wastewater. Different doses of H_2O_2, as well as concentrations of Fe^{+2} ions and pH was reduced from 8-10 to 3-4 and residences time about 60 min.

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Table 1: Result of Lab Scale Experiment

Industrial Waste water	Fe^{2+} (ml)	H_2O_2 (ml)	pH	Temp. (°C)	Time (min.)	Collection W ast	COD removal	Wastewater Raw	after Fenton
Dyes (Ahmedabad)	11	8	8.0	36	60	Primary Tank	82%	3600	640
	15	12	8.55	32	60	Primary Tank	81%	5800	1100
Textile (Surat)	3	1.8	7.0	30	60	Primary Settling	74%	920	240
Pharmaceutical (Vapi)	33	23	10.0	38	60	Collection Tank	71%	10000	2970
	27	19	9.0	32	60	Equalization	83%	9400	1580
	33	23	10	38	30	Collection Tank	61%	10000	3910

The wastewater sample is collected from primary tank or collection tank or equalization tank. The optimum COD reduction by this process is in the range of 60% to 85%. The comparison between raw water COD and after Fenton Process can be visualized by the following chart

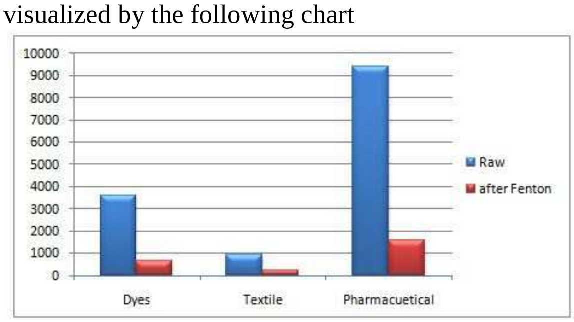

Fig.2 COD removal in different waste water

Discussion about Fenton Process:

Figure 3 shows that COD removal with respect to time, in this maximum COD removal after 20 min to 30 min is observed. Here we use pharmaceutical waste water.

From above graph and from experiment we can see that the ratio of Fenton's reagent doesn't matter because the reduction of COD during 0.5:1 fenton ratio (H2O2 :Fe+2) and 2:1 fenton ratio is almost same So we can use 0.5:1 fenton ratio and it is beneficial.

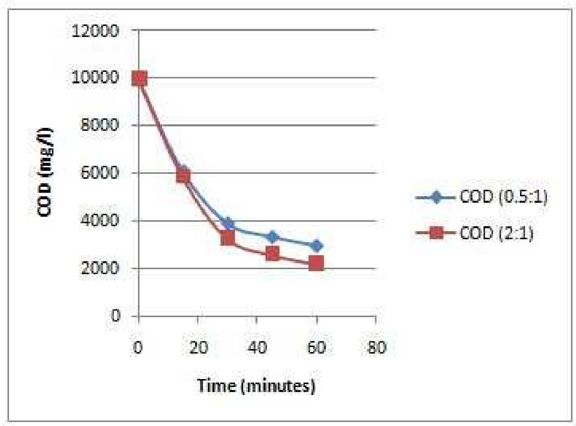

Fig.3 COD reduction by Fenton process (Pharmaceutical waste water)

In Dye waste water we can show that the COD reduction is maximum during 10 min to 30 min. In Dye waste water we also see that the reduction of COD during both ratios it is almost same. So we can achieve our goal of COD reduction.

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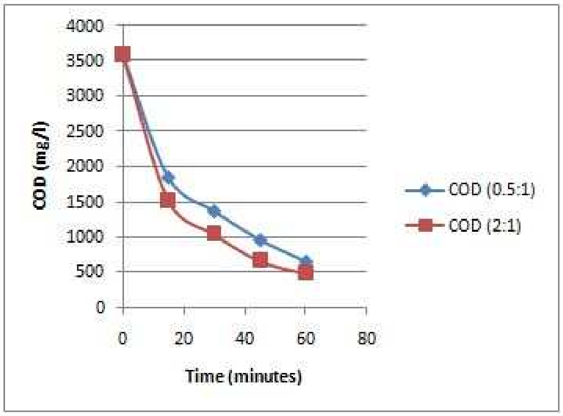

Fig.4.COD reduction by Fenton process (Dye waste water)

In Textile waste water we use only one ratio and it is 0.5:1. In this sample the COD is reducing gradually during 20 minutes to 60 minutes.

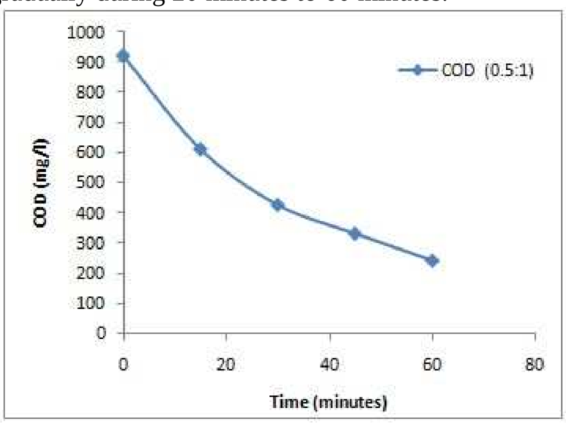

Fig.5 COD reduction by Fenton process (Textile waste water)

Optimized parameters, efficiency of COD removal are shown in Table. In all cases COD of raw wastewater was very high. After Fenton's reagent was used, a decrease in COD from 70%-80% was observed.

Effect of Iron Concentration

In the absence of iron, there is no evidence of hydroxyl radical formation when, for example, H2O2 is added to a phenolic wastewater (i.e., no reduction in the level of phenol occurs). As the concentration of iron is increased, phenol removal accelerates until a point is reached where further addition of iron becomes inefficient. This feature (an optimal dose range for iron catalyst) is characteristic of Fenton's Reagent, although the definition of the range varies between wastewaters. Three factors typically influence its definition:

1. A minimal threshold concentration of 3-15 mg/L Fe which allows the reaction to proceed within a reasonable period of time regardless of the concentration of organic material;
2. A constant ratio of Fe:substrate above the minimal threshold, typically 1 part Fe per 10-50 parts substrate, which produces the desired end products. Note that the ratio of Fe:substrate may affect the distribution of reaction products; and
3. A supplemental aliquot of Fe which saturates the chelating properties in the wastewater, thereby availing unsequestered iron to catalyze the formation of hydroxyl radicals.

Iron dose may also be expressed as a ratio to H_2O_2 dose. Typical ranges are 1 part Fe per 5-25 parts H_2O_2 (wt/wt).

Effect of Iron Type (Ferrous or Ferric)

For most applications, it does not matter whether Fe^{2+} or Fe^{3+} salts are used to catalyze the reaction -- the catalytic cycle begins quickly if H_2O_2 and organic material are in abundance. However, if low doses of Fenton's Reagent are being used (e.g., < 10-25 mg/L H_2O_2), some research suggests ferrous iron may be preferred. Neither does it matter whether a chloride or sulfate salt of the iron is used, although with the former, chlorine may be generated at high rates of application.

It is also possible to recycle the iron following the reaction. This can be done by raising the pH, separating the iron floc, and re-acidifying the iron sludge. There have been some recent developments in supported catalysts that facilitate iron recovery and reuse.

Effect of H_2O_2 Concentration

Because of the indiscriminate nature by which hydroxyl radicals oxidize organic materials, it is important to profile the reaction in the laboratory for each waste to be treated. For example, in a typical application the following series of reactions will occur:

Substrate →	**Oxidized Intermediate "A"**	**→Oxidized Intermediate "B"**	**→Oxidized Intermediate "C"**	**→Oxidized Intermediate "D"**	**→Oxidized Intermediate "E"**	**→CO_2**

Each transformation in this series has its own reaction rate and, as the case of phenolics illustrates, there may occur build-up of an undesirable intermediate (quinones), which requires sufficient H_2O_2 to be added to push the reaction beyond that point. This is frequently seen when pretreating a complex organic wastewater for toxicity reduction. As the H_2O_2 dose is increased, a steady reduction in COD may occur with little or no change in toxicity until a threshold is attained, whereupon further addition of H_2O_2 results in a rapid decrease in wastewater toxicity.

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Effect of Temperature

The rate of reaction with Fenton's Reagent increases with increasing temperature, with the effect more pronounced at temperatures < 20 °C. However, as temperatures increase above 40-50 °C, the efficiency of H_2O_2 utilization declines. This is due to the accelerated decomposition of H_2O_2 into oxygen and water. As a practical matter, most commercial applications of Fenton's Reagent occur at temperatures between 20-40 °C.

Applications of Fenton's Reagent for pretreating high strength wastes may require controlled or sequential addition of H_2O_2 to moderate the rise in temperature which occurs as the reaction proceeds. This should be expected when H_2O_2 doses exceed 10-20 g/L. Moderating the temperature is important not only for economic reasons, but for safety reasons as well.

Effect of pH

The effect of pH on reaction efficiency is illustrated below:

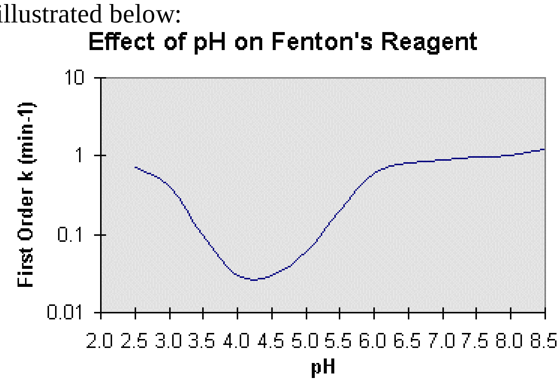

Fig. 6 Effect of pH

The optimal pH occurs between pH 3 and pH 6. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In the latter form, iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals. There have been some recent developments using nonradical scavenging sequestering agents (e.g., NTA and gallic acid) to extend the useful pH range to pH 8-9, but no commercial applications are known. The drop in efficiency on the acid side is less dramatic given the logarithmic function of pH, and is generally a concern only with high application rates.

In highly concentrated waste streams (>10 g/L COD), it may be necessary to perform the oxidation in steps, readjusting the pH upwards to pH 4-5 after each step so as to prevent low pH from inhibiting the reaction.

Effect of Reaction Time

The time needed to complete a Fenton reaction will depend on the many variables discussed above, most notably catalyst dose and wastewater strength. For simple phenol oxidation (less than ca. 250 mg/L), typical reaction times are 30 - 60 minutes. For more complex or more concentrated wastes, the reaction may take several hours. In such cases, performing the reaction in steps (adding both iron and H_2O_2) may be more effective (and safer) than increasing the initial charges.

Determining the completion of the reaction may prove troublesome. The presence of residual H_2O_2 will interfere with many wastewater analyses. Residual H_2O_2 may be removed by raising the pH to e.g., pH 7-10, or by neutralizing with bisulfite solution. Often, observing color changes can used to assess the reaction progression. Wastewaters will typically darken upon H_2O_2 addition and clear up as the reaction reaches completion.

Effect of Post Treatment

As a result of degrading complex organic materials into organic acid fragments, the pre-oxidized effluent is generally more amenable to conventional treatment, e.g., flocculation and biotreatment. The presence of iron in the reaction mixture makes it particularly suited to subsequent lime flocculation. In many cases, it may be possible to remove up to 80% of the wastewater COD through a combination of Fenton's Reagent and lime flocculation. Significantly, this may be achieved with an H_2O_2 dose of 50-75% of the stoichiometry.

Conclusion

The main advantage of Fenton's reagent over other OH· systems are its simplicity, the components are commonly available and there is no need for special equipment. The basic advantages of this method include the high efficiency of the oxidation reaction, low cost, easily available substrates and the simplicity of the procedure. From above discussions Fenton process is an efficient method for treatment of the different types of industrial wastewater which were tested. Nevertheless, although COD was generally decreased by chemical oxidation, high efficiency of organic components degradation is not always followed by reduction of COD to an acceptable level. Therefore, in order to optimize Fenton's reaction special care should be taken not only to remove organic constituents (COD or TOC) but also to reduce toxicity, BOD removal, Odour and color removal, biodegradability improvement. Reduction in COD should be a critical measure of the success of this method.

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