

**FENTON-LIKE OXIDATION OF ACID AND REACTIVE DYES USING
NATURAL-MATERIALS SUPPORTED CATALYSTS**

by

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LIST OF SYMBOLS

		Unit
λ	Wavelength	nm
Φ	Quantum yield	–
C_0	Initial concentration of dye	mg L ⁻¹
C_t	Concentration of dye at reaction time	mg L ⁻¹
t	Reaction time	min
T	Reaction absolute temperature	K
wt. %	Percent by weight	–

LIST OF ABBREVIATIONS

AOPs	Advanced Oxidation Processes
$\cdot\text{OH}$	Hydroxyl radical
H_2O_2	Hydrogen Peroxide
$\cdot\text{OOH}$	Hydroperoxyl radical
Fe–MK10	Fe–contained Montmorillonite K10
Fe–RHA	Fe–contained rice husk ash
AR1	Acid Red 1
RB5	Reactive Black 5
C.I.	Colour Index
UV	Ultra violet
CO_2	Carbon Dioxide
TiO_2	Titanium Dioxide
ZnO	Zink Oxide
O_3	Ozone
Fe(III)	Ferric ion (Fe^{3+})
Fe(II)	Ferrous ion (Fe^{2+})
$\text{R}\cdot$	Organic radical
Hg	Mercury
L	Organic ligand
COD	Chemical oxygen demand
OII	Orange II
HNO_3	Nitric acid
FTIR	Fourier Transform Infrared

KBr	Potassium Bromide
BJH	Barrett–Joyner–Halenda model
XRD	X–Ray diffraction
SEM	Scanning electron microscope
EDX	Energy Disperse X–Ray
rpm	Rotation per minute
M	Molar
H ₂ SO ₄	Sulphuric acid
NaOH	Sodium hydroxide
AAS	Atomic Absorption Spectrometric
N ₂	Nitrogen
IUPAC	International Union of Pure and Applied Chemistry
BDDT	Brunauer, Deming, Deming and Teller classification
BET	The Brunauer–Emmett–Teller
TOC	Total organic carbon

PENGOKSIDAAN JENIS FENTON BAGI ASID DAN PENCELUP REAKTIF MENGUNAKAN MANGKIN YANG DISOKONG OLEH BAHAN SEMULAJADI

ABSTRAK

Tujuan kajian ini dijalankan adalah untuk mengkaji sistem penggunaan mangkin berlainan fasa untuk rawatan penyahwarnaan bagi dua jenis pencelup sebagai model air sisa daripada industri tekstil iaitu Acid Red 1 (AR1) dan Reactive Black 5 (RB5). Mangkin ini dihasilkan daripada bahan yang berkos rendah dan juga bahan sisa daripada pertanian yang senang didapati di Malaysia iaitu Montmorillonite K10, granite, kaolin dan juga abu daripada sekam padi dengan menggunakan teknik peranakan. Penjerapan/penyahjerapan Nitrogen (N_2), Penyerakan Tenaga X-ray (EDX), mikroskop elektron imbasan (SEM), Spektroskop pramerah jelmaan Fourier (FTIR) dan spektroskop pembelauan serbuk X-ray (XRD) digunakan untuk pencirian mangkin. Kecekapan sistem/proses ini dipengaruhi oleh parameter seperti kesan muatan Fe(III) oksida di atas penyokong, dos mangkin, pH, kepekatan hidrogen peroksida, kepekatan awal pencelup yang digunakan dan suhu bagi tindak balas. Keadaan optimum bagi tindak balas yang diperolehi daripada proses penyahwarnaan bagi kedua-dua jenis pencelup ialah 0.070–0.14 wt.% bagi sokongan yang mengandungi Fe, 3.50–5.0 g L⁻¹ bagi dos mangkin, pH 2.0–2.50 dan 8–20 mM kepekatan awal hidrogen peroksida dengan menggunakan 50 mg L⁻¹ kepekatan awal pencelup pada suhu 30 °C tindak balas. Dibawah keadaan optimum, 96–99 % kecekapan penyahwarnaan dicapai bagi AR1 dan RB5 dicapai dalam masa 150 min dan 240 min bagi Fe-kaolin untuk penyahwarnaan AR1. Perubahan spektrum UV-Vis bagi sampel AR1 dan RB5 dalam larutan berair semasa perawatan

jenis Fenton dikaji. Ikatan kumpulan azo ($-N=N-$) lebih senang untuk dimusnahkan dibandingkan dengan kumpulan cincin aromatik bagi kedua-dua jenis pencelup dengan menggunakan proses pengoksidaan jenis Fenton. Kajian bagi kestabilan jangka panjang bagi semua jenis mangkin (Fe-MK10, Fe-RHA, Fe-granite dan Fe-kaolin) menunjukkan terdapat penyusutan aktiviti selepas empat kali kitaran penggunaan. Ini adalah disebabkan oleh kehilangan jisim mangkin dan juga pengurangan tapak aktif mangkin semasa kajian dijalankan. Ujian pelunturan mengesan Fe yang hilang daripada mangkin adalah kurang daripada 5 mg L^{-1} didapati masih mematuhi peraturan Peraturan Kualiti (sisa-sisa dan bahan buangan industri) Persekitaran 1979 yang dilaksanakan di Malaysia. Keputusan bagi kajian yang dijalankan ini menambahkan ilmu pengetahuan asas bagi perawatan air sisa yang mengandungi AR1 dan RB5 dan juga jenis-jenis pencelup azo yang lain dengan menggunakan proses pengoksidaan jenis Fenton ini.

FENTON-LIKE OXIDATION OF ACID AND REACTIVE DYES USING NATURAL-MATERIALS SUPPORTED CATALYSTS

ABSTRACT

The primary aim of this study was to prepare Fe-based catalysts for the decolorization of two types of dye as a model of real textile wastewater, Acid Red 1 (AR1) and Reactive Black 5 (RB5). The catalysts were prepared from low-cost materials and agricultural by-product abundantly available in Malaysia, namely Montmorillonite K10, granite, kaolin and rice husk ash by impregnation method. Nitrogen adsorption/desorption, Energy Disperse X-ray (EDX), Scanning Electron Microscope (SEM), Fourier Transform Infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD) were used to characterize the catalysts. The efficiency of the reaction system was explored as a function of the experimental parameters such as effect of iron (III) oxide loading on the supports, catalyst dosage, pH, hydrogen peroxide concentration, initial dye concentration and reaction temperature. The optimum conditions obtained for decolorization process for both dyes were 0.070–0.14 wt.% of Fe-contained supports, 3.50–5.0 g L⁻¹ of catalyst dosage, 2.0–2.50 pH and 8.0–20 mM of initial concentration of hydrogen peroxide with 50 mg L⁻¹ of initial dye concentration at 30 °C reaction temperature. Under the optimal condition, 96–99 % decolorization efficiency of AR1 and RB5 were achieved within 150 min of reaction and 240 min of time reaction was needed for Fe-Kaolin to decolorize AR1. The UV-Vis spectral changes of AR1 and RB5 in aqueous solution during Fenton-like treatment were studied. It was easier to destruct the azo linkage (-N=N-) group than to destruct the aromatic rings of both dyes by Fenton-like oxidation. The study of long-term stability revealed that Fe-MK10, Fe-RHA, Fe-

granite and Fe-kaolin showed some activity decay after reuse for four consecutive cycles. This is due to the loss of catalysts (Fe-MK10, Fe-RHA, Fe-granite and Fe-kaolin) and active phase leaching during the experiments. Leaching test indicated that the leached iron from the catalyst was less than 5 mg L^{-1} which is within the Malaysian regulation of Environmental quality Act (Sewage and Industrial Effluents) 1979. The results can provide fundamental knowledge for the treatment of wastewater containing AR1 and RB5 and other azo dyes by Fenton-like oxidation process.

CHAPTER ONE

INTRODUCTION

1.0 Research Overview

Water pollution is a major problem in the global context. It has been suggested that it is the leading worldwide cause of deaths and diseases and that it accounts for the deaths of more than 14,000 people daily (Timofeeva et al., 2005; Berberidou et al., 2007). Chemical process industries, such as oil refineries, petrochemical units, dye and dye intermediate manufacturing industries, textile units, among others, are typical industries that dump toxic organic compounds to the nearer water courses, thus making the water polluted (Kabita et al., 2001). Amongst them, the dye and dye intermediate manufacturing and textile industries stands out as it produces a large amount of effluents which can cause serious environmental problems as they contain colored compounds resulting from dyes unfixed to fibers during the dyeing process (Zhou et al., 2007).

At present time, it is estimated that more than 10,000 dyes are consumed in textile processing industries and their concentrations in range from 10 to 10,000 mgL^{-1} (Meric et al., 2004), depending on the process. It is estimated 10–20 % of dyes are lost in industrial effluents (Song et al., 2007). Color is one of the most hated pollutants, because of several reasons; it is visible and even small quantities of dyes ($\geq 0.005 \text{ mgL}^{-1}$) are not allowed (Song et al., 2007), color also can interfere with transmission of sunlight into natural streams and many of the dyes and their intermediate products, such as aromatic amines, are toxic to aquatic life,

carcinogenic and mutagenic to humans (Lucas and Perez, 2006). Consequently, dyes have to be removed from textile wastewater before discharged.

Over the past two decades, environmental regulatory requirements have become more stringent because of increased awareness of the human health and ecological risks associated with environmental contaminants. Therefore, various treatment technologies have been developed over the last 10 to 15 years in order to cost-effectively meet these requirements. Actually, the removal of dyes from wastewater is a challenge to the related industries, because the synthetic dyes used are stable compounds, difficult to destroy by common treatments. Physical, chemical, and biological methods are presently available for the treatment of wastewater discharged from various industries. However, physical methods such as liquid-liquid extraction, ion-exchange, adsorption, air or steam stripping, etc., are ineffective on pollutants which are not readily adsorbable or volatile, and have further disadvantages because they simply transfer the pollutants to another phase rather than destroying them (Duta et al., 2001).

To overcome this, the use of advanced oxidation processes (AOPs) has been widely proposed, as they operate at temperature near ambient and atmospheric pressure (Aleboyah et al., 2003). Heterogeneous catalytic oxidation falls into the category of advanced oxidation processes (AOPs), a giant group of chemical oxidation processes which have been developed and characterized by using different oxidation agents (ozone, hydrogen peroxide, etc.) as primary oxidants to generate hydroxyl radicals ($\cdot\text{OH}$), an extraordinarily reactive species capable of attacking organic molecules with rate constants in the order of 10^6 to $10^9 \text{ M}^{-1}\text{s}^{-1}$

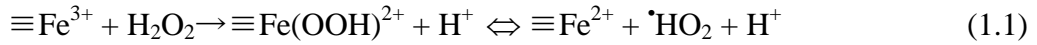
(Rey et al., 2008). Hydroxyl radicals are not only one of the most powerful oxidation agents, but also have higher oxidation potential than other chemicals commonly used in wastewater treatment (Molina et al., 2006). However, this high oxidizing power correlates with a relative lack of selectivity due to the rapid evolution of hydroxyl radicals that tend to attack the molecules in close vicinity (Jones, 1999).

Fenton reaction wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water (Sabhi and Kiwi, 2001). Fenton's reagent was discovered about 100 years ago, but its application as an oxidizing process for destroying toxic organics was not applied until the late 1960s (Ramirez et al., 2007a). The key step in the Fenton type reaction is the formation of hydroxyl radicals (HO^\bullet) from H_2O_2 and Fe (II)/Fe (III). This advantageous system is versatile, can be used very easily and provide very high (even up to the total mineralization) degradation efficiency at relatively low cost (Molina et al., 2006; Klaewkla et al., 2007). The use of Fenton's reagent as an oxidant for wastewater treatment is attractive due to the fact that iron is widely available and nontoxic element, and hydrogen peroxide is easy to handle and the excess decomposes to environmentally safe products (Zazo et al., 2005). Hydrogen peroxide (H_2O_2) has increasingly become an important chemical in manufacturing plants for environmental reasons due to the innocuous nature of its by-product-water (Molina et al., 2006; Han et al., 2008). While this makes it an environmentally appealing choice for many of the industrial applications, the continual decomposition of hydrogen peroxide does have significant disadvantages: in addition to superior oxidizing power, one of the key characteristics of H_2O_2 is its

instability (Jones, 1999). The effectiveness of H_2O_2 is clearly reduced as its concentration decreases, turning a valuable chemical into simple water and oxygen. Furthermore, heat is produced during the decomposition reaction, and this can create a safety hazard in combination with the buildup of oxygen. Despite of this, hydrogen peroxide is often the oxidant of choice for chemical oxidation because of its simplicity of operation (Esplugas et al., 2002). One of the desirable aspects of hydrogen peroxide instability is a tendency to liberate oxygen when in contact with active surfaces, like high surface area substances (e.g. activated carbon, a transition/heavy metal or its oxide, etc.), which tend to transfer electrons to the peroxide molecule (Puzari and Baruah, 2000, Carballo et al., 2008). Thus, coupled with sufficient catalyst, hydrogen peroxide exhibits excellent reactivity and high utilization efficiency (Zazo et al., 2005; Yube et al., 2007). Without any doubt, hydrogen peroxide has made an appreciable contribution as an oxidant to a cleaner chemical industry where it plays an important role especially in selective oxidation (Carballo et al. 2008). Among the advantages of Fenton's process unlike other AOPs techniques are the simplicity of equipment and the mild operation conditions (atmospheric pressure and low temperature). Thus, mainly for these reasons, Fenton's process has been regarded as the most economical alternative for a wide array of applications (Perez et al., 2002). However, although it is known that the systems of Fenton type are responsible for oxidizing of different organic materials, but their using as catalysts induces an additional pollution (Dantas et al., 2006).

To overcome the disadvantages of the homogeneous Fenton or Fenton-like processes (the later one referring to the use of ferric rather than ferrous ions), the

immobilization of the catalyst on inert support surfaces has been tried in order to avoid the catalyst recovering step. Indeed, some attempts have been made to develop heterogeneous catalysts, prepared by incorporating Fe ions or Fe oxides into porous supports, subsequently used in a wide range of applications. Reported data from the literature indicate that H₂O₂ initiates a chain reaction that leads to the formation of [•]OOH, by contact with Fe(III) sites available on the surface of support particles dispersed in aqueous solution. Fe(III) is converted to Fe(II) on the solid surface. New reaction sites are then formed and allow H₂O₂ to generate [•]OH radicals. The Fe(III) sites are recovered via oxidation of Fe(II) in the cyclic mechanism (Guimaraes et al., 2008). The reaction mechanism for generation of hydroxyl radicals on Fe(III) surface is proposed on the basis of the fundamental reactions describing the surface complexation chemistry for iron and generally accepted Haber Weiss mechanism for the interaction of H₂O₂ with the surface sites and other reactive species:



1.1 Problem Statement

The removal of synthetic dyes from wastewater stream to the acceptable limit is necessary in order to protect the environment, aquatic life and human. Azo dyes are among of the primary pollutants which are produced by textile and chemical industries and should be treated cautiously. Fenton process was proposed as the ideal process for wastewater treatment and has been proven as among the most effective method to treat a variety of wastes such as those associated with the textile and chemical industries.

Fenton processes have been used as a powerful source of hydroxyl radicals from H_2O_2 in the presence of iron cations and mild reaction conditions to treat these effluents. Common homogeneous Fenton processes involve the application of ferrous or ferric salts and hydrogen peroxide in order to produce hydroxyl radical. Although these systems offer a cost-effective source of hydroxyl radicals, there are some major drawbacks that limit the industrial application of this technology due to the tight range of pH in which the reaction precedes the need for recovering the precipitated catalyst after treatment and deactivation by some ion-complexing agents like phosphate anions. The resulting sludge may also contain organic substances as well as heavy metals and has to be treated further, thus increasing the overall costs (Kasiri et al., 2008).

An alternative method could be the use of heterogeneous solid Fenton-like catalysts to overcome the disadvantages which provide an easy separation and recovery of the catalyst from the treated wastewater. The crucial point of heterogeneous catalytic systems is linked to the resistance of immobilized iron

species to be leached out into the solution under the typically acidic and strong oxidizing conditions in which Fenton-like reactions occur. The goal of this study was to investigate the applicability of Fe-based catalysts (Fe-MK10, Fe-RHA, Fe-granite and Fe-kaolin) as heterogeneous Fenton catalysts for decolorization of two types of dye as a model of real textile wastewater, Acid Red 1 (AR1) and Reactive Black 5 (RB5). The effects of different parameters such as different loading of iron (III) oxide on different supported catalysts, catalyst dosage, initial concentration of dye and H₂O₂ and initial pH and temperature on the decolorization efficiency of the process were studied. Leaching and reusability test for prepared heterogeneous catalysts also studied in this research. In this way, research efforts are currently addressed to design new catalysts with high reactivity and allowing an efficient use of the hydrogen peroxide due to its relative high cost.

1.2 Research Objectives

The main objectives of this research are to:

- a) To prepare Fe-Montmorillonite K10 (Fe-MK10), Fe-rice husk ash (Fe-RHA), Fe-granite and Fe-kaolin as heterogeneous catalysts for decolorization of Acid Red 1 (AR1) and Reactive Black 5 (RB5) dye solutions.
- b) To evaluate the effectiveness of prepared catalysts for decolorization of model textile dyes in batch process.
- c) To characterize the prepared catalysts for their physical and chemical properties.
- d) To study the influence of reaction conditions (initial dye concentration, H₂O₂ dose, catalyst dose, iron (III) oxide loading on the supported catalyst, solution

pH and temperature) on the catalytic decolorization activity of prepared catalysts.

- e) To study the leaching and reusability of the prepared catalysts.

1.3 Organization of the Thesis

This thesis consists of five chapters, which is every chapter represent a concrete and valuable information about the project's study. In chapter one, we have briefing the current scenario on water pollution and the types of dye removal techniques. The problem statement and also research objectives of this study was also represented.

In chapter two, we represent the types of advanced oxidation process (AOPs), types of Fenton process and also previous study on that type of processes. Briefing explanation about dyes and also supported catalysts that were used in this study was also has been focused. Information about parameters that affected the reaction process was discussed in detail.

In chapter three, we listed the chemicals and materials that were used in this study. This chapter also explains the experimental procedure and describes the parameters that affected on the reaction catalytic process. Description of the analysis techniques performed for characterization of prepared catalysts also included.

Chapter four represents the experimental results and detail discussion of the results obtained. The first section discussed about the characterization properties of the prepared catalysts followed by parameters that affected the reaction that are

effect of iron (III) oxide loading on supported catalysts, catalyst dosage, pH, H₂O₂ dosage, initial concentration of dye and also reaction temperature. This study was also focused on leaching and reusability study on catalysts for reaction process.

Chapter five concludes the overall conclusions obtained from this study and also give the list recommendations for future study.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

Saving water to save the planet and to make the future of mankind safe is what we need now. With the growth of mankind, society, science and technology, our world is reaching to new high horizons but the cost which we are paying or will pay in near future is surely going to be too high. Among the consequences of this rapid growth is environmental disorder with a big pollution problem. Besides other needs the demand for water (“Water for People, Water for Life” United Nations World Water Development Report UNESCO) has increased tremendously with agricultural, industrial and domestic sectors consuming 70, 22 and 8 % of the available fresh water, respectively and this has resulted in the generation of large amounts of wastewater containing a number of ‘pollutants’ (Ikehata and El-Din, 2006).

Chemical process industries, such as oil refineries, petrochemical units, dye and dye intermediate manufacturing industries, textile units, among others, are typical industries that dump toxic organic compounds to the nearer water courses, thus making the water polluted (Kabita et al., 2001). Amongst them, the dye and dye intermediate manufacturing and textile industries stands out as it produces a large amount of effluents which can cause serious environmental problems as they contain colored compounds resulting from dyes unfixed to fibers during the dyeing process (Colphini et al., 2008) and once they enter the water it is no longer good and sometimes difficult to treat as the dyes have a synthetic origin and a complex

molecular structure which makes them more stable and difficult to be biodegraded (Forgacs et al., 2004; Rai et al., 2005).

2.1 Dyes

Mankind has used dyes for thousands of years and the earliest known use of a colorant is believed to be by Neanderthal man about 180,000 years ago (Christie, 2007). However, the first known use of an organic colorant was much later, being nearly 4000 years ago, when the blue dye indigo was found in the wrappings of mummies in Egyptian tombs. Till the late nineteenth century, all the dyes/colorants were more or less natural with main sources like plants, insects and mollusks, and were generally prepared on small scale. It was only after 1856 that with Perkin's historic discovery of the first synthetic dye, mauveine, that dyes were manufactured synthetically and on a large scale (Hunger, 2003).

Dye molecules comprise of two key components: the chromophores, responsible for producing the color, and the auxochromes, which can not only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity (to attach) toward the fibers. Dyes exhibit considerable structural diversity and are classified in several ways. These can be classified both by their chemical structure and their application to the fiber type (Hunger, 2003). Dyes may also be classified on the basis of their solubility: soluble dyes which include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes. Besides this, either a major azo linkage or an anthraquinone unit also characterizes dyes chemically. It is worthwhile noting that the azo dyes are the one most widely used and accounts 65–70 % of the total

dyes produced. Though, the classification of dyes on basis of structure is an appropriate system and has many advantages, like it readily identifies dyes as belonging to a group and having characteristic properties, e.g., azo dyes (strong, good all-round properties, cost-effective) and anthraquinone dyes (weak, expensive), there are a manageable number of chemical groups (about a dozen) (Acero et al., 2002).

Besides these, both the synthetic dye chemist and the dye technologist use this classification most widely. However, the classification based on application is advantageous before considering chemical structures in detail because of the complexities of the dye nomenclature from this type of system. It is also worth to point that classification by application is the principal system adopted by the Colour Index (C.I.). This system includes the name of the dye class, its hue, and a number. A five digit C.I. number is assigned to a dye when its chemical structure has been disclosed by the manufacturer. It is also worth to note here that though a dye has a C.I. number, the purity and precise chemical constitution may vary depending upon the name (Alfano et al., 2001).

Reactive dyes have been identified as the most environmental problematic compounds in textile dye effluents. They are structurally similar to acid dyes with the important difference in containing of Cl or O-SO₃Na which can be easily detached as a leaving group, enabling the dyes to form covalent bonds with fibres (primarily cellulose). Among C.I. reactive dyes, nearly half have mono- or di-chlorotrazines reactive systems; and the rest is equally divided between trichloropyrimidines and vinyl sulfones. According to chromogens, nearly all the yellow, orange, red, violet,

brown and black dyes are azo, but the blues consist of almost equal numbers of azo, anthraquinone and phthalocyanine derivatives; the greens are mainly anthraquinones and phthalocyanines but there are a few browns and blacks and most of the reactive dyes for wool are Cr or Co complexes (Garcia–Montana et al., 2006).

Research on textile effluent decolourization has often focused on reactive dyes for three reasons. First, reactive dyes represent an increasing market share, currently about 20–30 % of the total market for dyes, because they are used to dye cotton which makes up about half of the world's fiber consumption. Second, a large fraction, usually around 30 %, of the applied reactive dyes is wasted because of dye hydrolysis in the alkaline dye bath. As a result, dye house effluents typically contain 0.60–0.80 g L⁻¹ of dye. Third, conventional wastewater treatment plants, which rely on adsorption and aerobic biodegradation, have low removal efficiency for reactive and other anionic soluble dyes (Sanja et al., 2009). Acid Dyes were known from the past as synthetic dyes and were used for nylon, wool, silk, modified acrylics, and also to some extent for paper, leather, ink–jet printing, food, and cosmetics. They are generally water soluble. The principal chemical classes of these dyes are azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso (Gupta and Suhas, 2009).

Overall at present there are more than 100,000 commercial dyes with a rough estimated production of 7×10^5 – 1×10^6 tons per year (Qiuqiang et al., 2009). Of such a huge production the exact data on the quantity of dyes discharged in environment is not available. However, it is reported that 10–15 % of the used dyes enter the environment through wastes (Husain, 2006; Hai et al., 2007). The big consumers of

dyes are textile, dyeing, paper and pulp, tannery and paint industries, and hence the effluents of these industries as well as those from plants manufacturing dyes tend to contain dyes in sufficient quantities. Dyes are considered an objectionable type of pollutant because they are toxic generally due to oral ingestion and inhalation, skin and eye irritation, and skin sensitization leading to problems like skin irritation and skin sensitization and also due to carcinogenicity (Rai et al., 2005; Christie, 2007). They impart color to water which is visible to human eye and therefore, highly objectionable on aesthetic grounds. Not only this, they also interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic communities present in ecosystem. Further, the dyes have a tendency to sequester metal and may cause micro toxicity to fish and other organisms. As such it is important to treat colored effluents for the removal of dyes (Gupta and Suhas, 2009).

2.2 Wastewater Treatment Technology

Few decades earlier, the dyes selection, application and use were not given a major consideration with respect to their environmental impact. With the growing concern on health mainly on aesthetic grounds, it was more from 80s that people started paying much attention to the dye wastes too. In the last few years, however, more information on the environmental consequences of dyestuff usage has become available and the dye manufacturers, users and government themselves are taking substantial measures to treat the dye containing wastewaters (Gupta and Suhas, 2009).

The traditional treatment technologies applied in dye wastewater treatment, such as coagulation/flocculation, membrane separation or activated carbon adsorption, only do a phase transfer of the pollutant, and biological treatment is not a suitable solution to the problem due to biological resistance of some dyes (Lucas and Peres, 2006). Therefore, it is necessary to find an effective treatment technology that leads to complete destruction of the dye molecules, in terms of limited water resources management and the need for nature preservation. Among these treatments, advanced oxidation processes (AOPs) are powerful alternative to conventional treatment methods for such wastewater decontamination (Munter, 2001). For this reason, this process has attracted considerable attention, and numerous studies on their ability to degrade colored compounds in wastewater are reported in the literature (Vajnhandl et al., 2007; Bandala et al., 2008).

2.2.1 Advanced Oxidation Process (AOP)

Advanced oxidation processes (AOPs) are the processes involving simultaneous use of more than one oxidation processes, since sometimes a single oxidation system is not sufficient for the total decomposition of dyes. These reactions, all of which involve the accelerated production of the hydroxyl free radical, which is very reactive, are termed advanced oxidation processes (AOPs) and include techniques as Fenton's reagent oxidation, ultra violet (UV) photolysis and sonolysis. They are capable of degrading dyes at ambient temperature and pressure and may also have an advantage over biological treatment for waste streams containing toxic or bioinhibitory contaminants. The central attraction of advanced oxidation processes is that organic contaminants are commonly oxidized to CO₂ (Allison, 2007).

A wide variety of advanced oxidation processes are available like chemical and catalytic processes, photochemical and photocatalytic processes, electrical processes and also mechanical processes. Chemical processes involve the application of ozone and/or hydrogen peroxide, while a subcategory of this type of AOPs can be named catalytic processes that involve usage of some powerful catalyst (e.g. iron or copper ions) in combination with hydrogen peroxide to produce $\cdot\text{OH}$ radicals, so-called Fenton type processes. Photochemical and photocatalytic processes involve application of UV or solar irradiation in combination with some powerful either oxidant (ozone and/or hydrogen peroxide) or photocatalyst (e.g. TiO_2 , ZnO , etc). $\cdot\text{OH}$ radical can be also produce under influence of mechanical (e.g. ultrasound process, radiolysis) or electrical (e.g. electrohydraulic discharge and non-thermal plasma processes energy) (Allison, 2007). Figure 2.1 shows the schematic of advanced oxidation processes classification. Among these AOPs, Fenton's reagent is particularly attractive because of the low costs, the lack of toxicity of the reagents (i.e., Fe (II) and H_2O_2), the absence of mass transfer limitation due to its homogeneous catalytic nature, high efficiency, simplicity in destroying the contaminants (eventually leaving no residues), stability to treat a wide range of substances and the simplicity of the technology (non-necessity of special equipment) (Ramirez et al., 2007b).

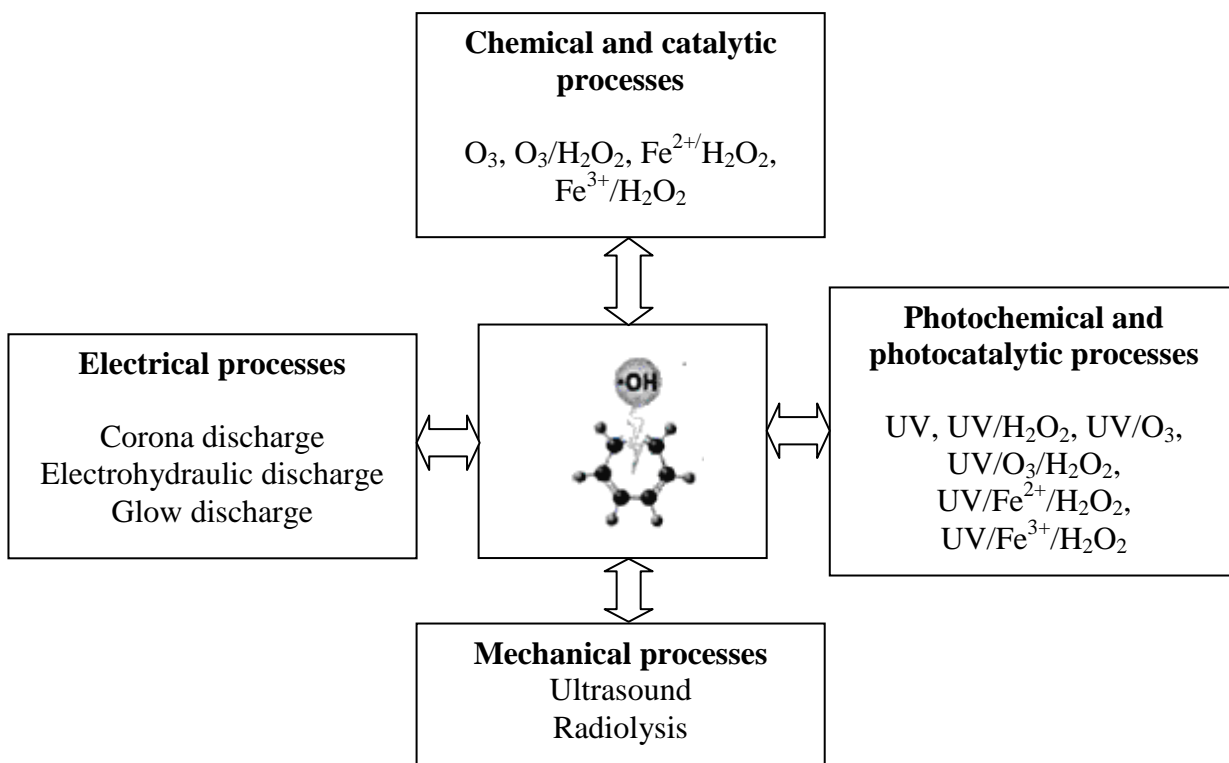


Figure 2.1 Schematic of advanced oxidation processes classification (Allisson, 2007).

2.2.1.1 Fenton Type Processes

There are a few varieties of Fenton process including Fenton-like, photo-Fenton, electro-Fenton, photoelectro-Fenton, peroxi-coagulation, and chelating agent assisted Fenton-type processes (Table 2.1) (Oppenlander, 2003). The fundamental aspects of these various Fenton and $\text{H}_2\text{O}_2/\text{UV}$ processes are briefly described below.

Table 2.1 Type of Fenton processes (Oppenlander, 2003)

Process	Oxidant(s)	Chemical(s)	Energy source	Remark
Fenton	Hydrogen peroxide (H ₂ O ₂)	Ferrous ion (Fe ²⁺)	None	pH < 3
Fenton-like				
<ul style="list-style-type: none"> • Usage of ferric salt • Usage of heterogeneous Fenton type catalyst • Usage of other metal ion e.g. Cu, Mn etc. 	H ₂ O ₂	Ferric ion (Fe ³⁺)	None	pH < 3
Photo assisted Fenton (Photo Fenton)	H ₂ O ₂	Fe ²⁺ or Fe ³⁺	Ultraviolet radiation and visible light (UV/Vis) or solar radiation	λ < 400 nm for FeIII(OH) ²⁺
Photo ferrioxalate/H ₂ O ₂ (Photo Fe ³⁺ chelate/H ₂ O ₂)	H ₂ O ₂	Fe ³⁺ , oxalate (chelating agent)	UV/Vis or solar radiation	λ < 550 nm for [FeIII(C ₂ O ₄) ₃] ³⁻
Anodic Fenton	H ₂ O ₂	Sacrificial iron electrode	Electrical current	Fenton reactions occur only in the anodic half-cell
Electrochemical Fenton (Electro Fenton)	Electrogenerated H ₂ O ₂	Dioxygen and Fe ²⁺	Electrical current	

Table 2.1 Continued

Process	Oxidant(s)	Chemical(s)	Energy source	Remark
Peroxi-coagulation	Electrogenerated H ₂ O ₂	Dioxygen and sacrificial iron electrode	Electrical current	Coagulation with iron hydroxides
Photoelectro Fenton/ photoperoxi-coagulation	Electrogenerated H ₂ O ₂	Dioxygen and Fe ²⁺ or sacrificial iron electrode	UV/Vis or solar radiation, electrical current	
H ₂ O ₂ /UV	H ₂ O ₂	None	UV radiation	$\lambda = 250\text{--}254$ nm for H ₂ O ₂

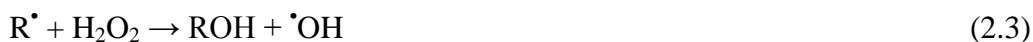
2.2.1.1(a) Classic Fenton and Fenton-like Processes

Fenton process was first demonstrated by Fenton (1894) utilizing a mixture of hydrogen peroxide and ferrous salts (i.e., Fenton's reagent) to oxidize tartaric acid to dihydroxy maleic acid. Haber and Weiss (1934) later suggested the formation of hydroxyl radicals upon the iron-catalyzed decomposition of hydrogen peroxide. In addition to the ferrous ion (Fe^{2+}), a number of other metal ions, including Cu^+ , Ti^{3+} , Cr^+ , Co^{2+} , were found to have the oxidative features of Fenton's reagent in the presence of hydrogen peroxide. The generation and subsequent reaction of hydroxyl radicals in Fenton process involves complex chain reactions (Neyens and Baeyens, 2003). The first step is the chain initiation and rate limiting;



$$k = 70 \text{ M}^{-1}\text{s}^{-1}$$

This reaction requires a proton to initiate; thus the Fenton process generally needs to be employed under acidic conditions. Radical chain reactions propagate further through the reactions shown in equations (2.2) to (2.4).



Hydroxyl radicals may also react with ferrous ion to terminate the chain reactions (equation (2.5)). The values for the rate constants shown in equations (2.5) to (2.9) are taken from Neyens and Baeyens (2003).



$$k = 3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

The ferric ion may react with hydrogen peroxide in the following manner:



$$k = 0.001\text{--}0.01 \text{ M}^{-1} \cdot \text{s}^{-1}$$

The iron (II) hydroperoxyl ion (Fe-OOH^{2+}) decomposes into hydroperoxyl radical and ferrous ion.



The reaction of hydrogen peroxide with ferric ion (equations (2.6) and (2.9)) is often referred to as a “Fenton-like” reaction. Hydroperoxyl radicals may react with ferric or ferrous ions.

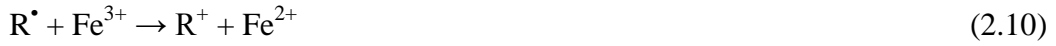


$$k = 1.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \text{ at pH 3}$$

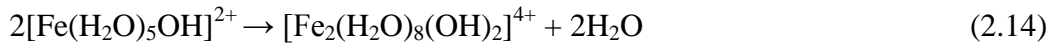
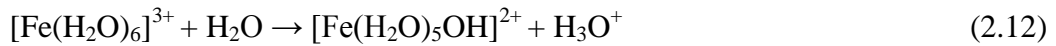


$$k = 1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \text{ at pH 3}$$

In addition, organic radicals $\text{R}\cdot$ generated in equation (2.2) can be oxidized by ferric ion or reduced by ferrous ion.



The reaction in equation (2.10) regenerates ferrous ion and concludes the catalytic cycle of Fenton process. Meanwhile, the ferrous ions generated during Fenton process described above may be hydrated, and subsequently react with hydroxide ions to form ferric hydroxo complexes that precipitate between pH 3 and 7 (Neyens and Baeyens, 2003).



These reactions account for the coagulation capacity of Fenton's reagent. Suspended solids can be captured and precipitated along with the ferric complexes. This feature may be useful for the treatment of wastewaters having high suspended solids content. Besides Fenton process, Fe^{2+}/H_2O_2 , that involves the application of ferrous salts, mostly ferrous sulphates, as a source of iron catalyst for Fenton reaction, there are a number of studies that investigated the application of so-called Fenton "like" processes for the degradation of pollutants in wastewater.

There are three types of Fenton 'like' processes. The first group of processes considers the usage of ferric salts instead of ferrous salts as catalysts for the incitation of Fenton reaction (equations (2.6) and (2.9)). Next group of processes considers the usage of heterogeneous Fenton type catalysts such as iron powder,

iron–oxides, iron ligands, or iron ions doped in supported catalysts such as pillared clays or resins, instead of homogeneous ferrous ions obtained from the dissolution of added ferrous salts. Third group are processes that use other metal ions, e.g. copper, manganese or cobalt, instead of ferrous ions in Fenton reaction. The primary benefits of Fenton type processes are their ability to convert a broad range of pollutants to harmless or biodegradable products and the fact that their relatively cheap reagents are safe to handle and are environmentally benign (Allison, 2007).

2.2.1.1(b) Photo–Fenton process

The rate of organic pollutant degradation following the Fenton process is strongly accelerated by irradiating UV–Vis rays. This modified Fenton process is called photo–assisted Fenton (or photo Fenton) process and involves photolysis of the hydroxyl complex of ferric ion $[\text{Fe}(\text{OH})^{2+}]$ into a hydroxyl radical and a ferrous ion (Oppenländer, 2003).



The hydroxyl complex has a maximum UV absorbance at about 300 nm, and the quantum yields (Φ) of the above photochemical reaction are 0.14 at 313 nm and 0.017 at 360 nm. The regeneration of ferrous ion and additional generation of hydroxyl radical during the photolysis facilitate the degradation of organic compounds. In addition to typical UV lamps, UV–A and visible light sources such as polychromatic Hg lamps, black light bulbs, fluorescent light bulbs, and sunlight can be used as a light source for photo–Fenton process (Malato et al., 2003*b*). In addition to the hydroxyl radical reactions, direct photolysis of organic compounds and

hydroxyl radical generation by hydrogen peroxide decomposition may need to be accounted for pollutant degradation pathways when a light source emitting short wavelength UV-radiation (below 300 nm) is used (Wadley and Walte, 2002).

2.2.1.1(c) Chelating ligand-assisted Fenton/photo-Fenton process

Addition of chelating agents, such as oxalate and citrate, to the photo-Fenton system is known to broaden the range of wavelength applicable to photolysis of ferric complexes to ferrous ions. Chelating ligands facilitate the dissolution of ferric ions at pH ranging from 3 to 8. The Fe^{3+} -chelate photo dissociates by a ligand-to-metal charge transfer excitation (Barbusinski and Filipek, 2001):



where L represents an organic ligand. The photo-reduced iron can react with hydrogen peroxide in the Fenton reaction (equation (2.1)). Unlike the simple photo-Fenton process (equation (2.15)), generation of hydroxyl radicals from the Fe^{3+} -chelate complexes is not likely to occur because the charge transfer to iron from an organic ligand is favored over a hydroxide ligand (Sun and Pignatello, 1993a).

It was also reported that some chelating organic ligands, such as gallic acid and picolinic acid, could enhance hydroxyl radical generation in Fenton and Fenton-like reactions with or without UV irradiation. In addition to hydroxyl radicals, formation of ferryl complexes such as $\text{Fe}^{4+} = \text{O}$ and $[\text{L}^{\bullet+}]\text{Fe}^{4+} = \text{O}$ was suggested as active oxidants involved in this system. Organic ligands are not very stable and can also be degraded by the hydroxyl radicals as the treatment proceeds (Sun and Pignatello, 1992). Thus, the ligand does not act as a catalyst in this type of