Removal of methylene blue by Advanced Oxidation using Fenton's reagent and Microfiltration

Dissertation Report Submitted
in partial fulfillment of the requirement for
the award of degree of

MASTER OF TECHNOLOGY

IN

CHEMICAL ENGINEERING

Submitted by
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June 2015

CERTIFICATE

This is to certify that the thesis entitled, **"Removal of methylene blue by Advanced Oxidation using Fenton's reagent and Microfiltration"** submitted by **Ms. Karishma Jasrotia** (Roll no. 601311003) in partial fulfillment of the requirements for the award of the degree of **Master of Technology** in **Chemical Engineering** at **Thapar University, Patiala** is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied in this thesis has not been submitted to any other university/institute for award of any degree or diploma.

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I, the undersigned, hereby declare that the research work presented in the M.Tech project entitled "**Removal of methylene blue by Advanced Oxidation using Fenton's reagent and Microfiltration**" has been carried out by me under the supervision and guidance of **Dr. Raj Kumar Gupta, Associate Professor and Head, (Department of Chemical Engineering) and Dr. Manoj Kumar, Assistant Professor, (Department of Chemical Engineering), Thapar University, Patiala.**

Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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ACKNOWLEDGMENT

I would like to express my deepest gratitude to Dr. Raj Kumar Gupta, Associate professor and Head, Department of Chemical Engineering, Thapar University, Patiala, under whose guidance I had the privilege to complete the thesis. I wish to express my deep gratitude towards him for providing individual guidance and support throughout the thesis work.

I convey my sincere thanks to my co-guide Dr. Manoj Kumar, Assistant Professor, Department of Chemical Engineering, Thapar University, Patiala for the encouragement and cooperation.

I express my gratitude to my parents for being a continuous source of encouragement. Special thanks to Dr. Vijaya Kumar Bulasara, Assistant Professor, Department of Chemical Engineering, for his support.

Last but not the least my heartfelt gratitude to Harjot Kaur, Ronjish Chugh and Arghya Dutta for helping me in completing my work in time.

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ABSTRACT

In recent years, hybrid processes are being studied for waste water treatment. In the present work, advanced oxidation process (AOP) with Fenton's reagent followed by microfiltration (MF) is studied for the removal of methylene blue dye from the wastewater to save time, energy and cost. Fenton's reagent was responsible for the complete degradation of the dye. The optimal composition of the Fenton's reagent for the degradation of 100 mg/L methylene blue dye was 20 mg/L H_2O_2 and 500 mg/L $FeSO_4.7H_2O$. The pH was maintained 3 during the treatment. A microfiltration membrane with an average pore size of 0.60 μm was used to remove the oxidation products at transmembrane pressures of 30, 40 and 50 psi. After the hybrid treatment, no dye or dispersed particles were found in the permeate solution. Thus 100% removal of the dye was achieved.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

AOP	Advanced Oxidation Process
BOD	Biological Oxygen Demand
CCD	Central composite design
COD	Chemical Oxygen Demand
DOC	Dissolved organic carbon
DRS	Diffuse reflectance spectra
ecb	Electron conduction band
eV	Electron volt
FO−MD	Forward Osmosis−Membrane Distillation
IR	Infrared
MF	Microfiltration
MWCO	Molecular Weight Cutoff
NF	Nanofiltration
nm	Nanometer
PAA-Na	Poly(acrylic acid) sodium
ppb	Parts per billion
ppm	Parts per million
RO	Reverse Osmosis
SEM	Scanning electron Microscope
SS	Suspended solids
TDS	Total dissolved solids
TEM	Transmission electron microscopy
TMP	Transmembrane Pressure

UF	Ultrafiltration
UV	Ultraviolet
XRD	X-ray diffraction
zPc	zero point charge

CHAPTER 1

INTRODUCTION

1.1 Motivation

Water is a naturally available molecule that has a tendency to renew on its own by the process of sedimentation. It easily separates out the pollutants by either breaking them down or diluting the harmful contents to a level that they become less harmful to the human beings. The only problem with this process is that it takes time, and is unproductive when large amount of dangerous contaminants are added to the water.

Water pollution is harmful for the aquatic life to a great extent. Its effectiveness is not limited to an individual or a population only but can cause serious harms to a wide biological community as well. Various organic compounds available in industrial and municipal waste water can even cause life threatening effects.

In the today's era, the most difficult problem for human beings is the lack of natural water supplies available on earth. The growing population demands higher production of goods which leads to more industrialization and therefore more utilization of water for industrial processes. The most evident uses of water for people include bathing, washing, drinking, cleaning, and cooking. Water is even needed to make food and preserve the natural environment. The fundamental usage of water is for domestic purpose but it accounts for a very small part of total. Worldwide, it is just the half of the industrial use which includes cooling for the purpose of electricity production. This usage and it discharge further cause severe environmental problems.

Water pollution occurs when the pollutants are discharged either directly or indirectly into water systems without plenty pre-treatment for the removal of dangerous compounds. One of the biggest water polluters of the world is the textile industry. The World Bank estimates that around 20% of the industrial water pollution is due to the dyeing of the textiles and their treatment. Globally, agriculture industry is the topmost polluter of the clean water. The textile industry is

ranked second in the list. Approximately 72 toxic chemicals which cannot be filtered or removed reach the water systems from textile dying. These untreated dyes cause serious threat to the aquatic life by causing chemical and biological changes in various plant and fish species. The existence of these compounds in water beyond a particular permissible limit makes its use practically unsafe. Textile industry requires a huge amount of process water and therefore generates large amount of waste water as well. The naturally occurring compounds and the synthetic organic chemicals are equally hazardous and cause rigorous problems in the biological treatment systems due to their resistance towards bio-degradation. Various technique that have been used for the removal of these textile dyes from waste-water include biological treatments, ultra-filtration, oxidation, coagulation, ozonation, nano-filtration, adsorption on various kinds of activated carbon, and Advanced Oxidation Processes (AOP).

1.2 Textile industry and wastewater generation

Textile industry is basically classified on the usage of raw materials into three categories:

- Cotton
- Synthetic
- Woolen fibers

The textile dyeing industry uses huge quantities of water and produces large volumes of wastewater from various steps in the dyeing and finishing processes. The textile wastewater is basically characterized by high content of dyestuff, salts, high COD derived from additives, suspended solid (SS), alkalinity, heat, color, acidity and fluctuating pH. Wastewater which is discharged by the textile finishing and dye manufacturing industries has become a major environmental concern. The main environmental concern of textile wastewater lies in the dissolved organic dye compounds as some of them are aromatics and considered to be carcinogenic.

The wastewater treatment techniques like coagulation/flocculation, adsorption, ion exchange, precipitation have various disadvantages which include formation of large amounts of sludge, or generation of toxic by-products when the degradation is incomplete.

Biological degradation whereas, is a technique that does not produce any sludge or any toxic by-product but is highly selective in nature (Tan et al., 2006).

Besides these methods, membrane technology is also one of the prominent techniques used in decoloration of the dyes. Nanofiltration and ultrafiltration are the commonly used techniques due to the small pore size. Zaghbani et al., (2006) reported that more than 97% rejection of methylene blue dye can be done using ultrafiltration technique. However, the decline in the flux and membrane fouling are some of the major drawbacks of these membrane based separations (Chakraborty et al., 2005).

Thus, to overcome the drawbacks of one another, hybrid techniques are used. Basar et al., (2006) proposed that hybrid incorporated membrane techniques can provide some advantages like higher removal efficiency, lower fouling resulting into lesser backwashing and therefore high quantity waste water treatment over the common traditional techniques.

Lee et al. (2005) used microfiltration with coagulation and adsorption for the removal of reactive dyes. Although the combined coagulation–adsorption–membrane process gave better dye removal efficiency but one of the techniques i.e. coagulation is highly dependent on the dye concentration.

Aouni et al. (2008) suggested the treatment of textile wastewater by a hybrid electrocoagulation and nanofiltration process. The two techniques helped in enriching the quality of the treated textile wastewater effluent but due to the extensive use of electricity, the process proved to be cost inefficient.

Another study of the hybrid process was on the combination of polyelectrolyte promoted forward osmosis and membrane distillation for the treatment of dyes in wastewater (Ge et al., 2012). The treatment was highly temperature dependent making it energy and cost inefficient.

Neyens and Baeyens (2003) proposed the removal of dye using AOP with Fenton's reagent in which iron hydroxide is precipitated out and then decanted. However, the major problem related

with this process was the time estimation for the settlement of the colloidal particles. Thus, an alternative for the removal of suspended particles was the use of low cost ceramic microfiltration membranes.

1.3 Advanced oxidation processes

Advanced Oxidation Processes refers to a set of chemical treatment procedures enhanced by Ultra sound and UV activation, designed to remove organic and inorganic materials in waste water. Contaminants are oxidized by four different reagents: ozone, hydrogen peroxide, oxygen, and air. These procedures may or may not be combined with Ultra Sound reactors, UV irradiation and specific catalysts. This results in the development of hydroxyl radicals. The AOP procedure is particularly useful for cleaning biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in waste water. The contaminant materials are converted to a large extent into stable inorganic compounds such as water, carbon dioxide and salts, i.e. they undergo mineralization. A goal of the waste water purification by means of AOP procedures is the reduction of the chemical contaminants and the toxicity to such an extent that the cleaned waste water may be recycled or, at least, dumped into a conventional sewage treatment. Many methods are classified under the broad definition of AOPs. Advanced oxidation methods (ozonation, photo-fenton, UV etc.) are the most commonly applied advanced oxidation methods used prior to biological treatment to enhance biodegradability and remove color in textile wastewaters. Membrane filtration and advanced oxidation processes appear to be the essential alternatives for the tertiary treatment of the effluent from biological treatment. Table 1.1 shows some of the most common AOPs.

Table 1.1: Examples of methods classified as AOPs (Source: Stasinakis, 2008)

Dark AOP	**Light driven AOP**
Ozone (O_3)	Photolysis (UV + H_2O_2)
Fenton (Fe^{2+} + H_2O_2)	Photocatalysis (light + catalyst)
Electrolysis (electrodes + current)	Photo-Fenton (solar light + Fenton)
Sonolysis (Ultrasounds)	

Advanced oxidation methods (ozonation, photo-fenton, UV etc.) are the most commonly applied methods used prior to biological treatment to enhance biodegradability and remove color in textile wastewaters. Membrane filtration and advanced oxidation processes appear to be the indispensable alternatives for the tertiary treatment of the effluent from biological treatment.

AOP's have already been used for the treatment of waste water containing recalcitrant organic compounds such as pesticides, surfactants, coloring matters, pharmaceuticals and endocrine disrupting chemicals. Moreover, they have been successfully used as pretreatment methods in order to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes. The important operating parameters, which affect the overall destruction efficiency of the oxidation process, can be given as follows:

1. Initial concentration of the reactant: For highly concentrated effluents, entirely no destruction may be observed and hence dilution becomes essential in this case. Thus the Langmuir–Hinshelwood type of models can be used to relate the observed rates with the initial concentration of the pollutant.

2. Temperature: Usually catalytic systems are operated at room temperature, but with the release of energy in the destruction process due to recombination of electron-hole pairs, temperature might increase. At temperatures above 80 ^{0}C, the exothermic adsorption of pollutant becomes unfavorable and tends to be the rate limiting step, leading to a decreased activity and hence reduction in the reaction rates in the range of 20–80 ^{0}C, usually weak dependence of the degradation rates on temperature has been observed.

3. Medium pH: Medium pH has a complex effect on the rates of catalytic oxidation and the observed effect is generally dependent on the type of the pollutant as well as the zero point charge (zPc) of the semiconductor used in the oxidation process, i.e. more specifically on the electrostatic interaction between the catalyst surface and the pollutant. For some of the pollutants, which are weakly acidic, rate of catalytic oxidation increases at lower pH due to an increase in the extent of adsorption under acidic conditions.

4. Aeration: Presence of electron acceptors is recommended so as to prevent the recombination reaction between the generated positive holes and electrons. Generally

aeration is used for this purpose as it also provides uniform mixing, suspension of the catalyst in the case of slurry reactors and economical source of oxygen.

1.3.1 AOP mechanism

Advanced oxidation involves several steps as follows:

1. Formation of hydroxyl radicals (strong oxidants).
2. Reaction of the radicals with organic compounds in water producing biodegradable intermediates.
3. Mineralization i.e. the reaction of these biodegradable intermediates with oxidants

1.4 Membrane Separation Processes

Membrane separations represent a different type of unit operation. The membrane is basically a semipermeable barrier by which the separation occurs between either two liquid phases, or two gas phases, or a liquid and a gas phase. The cell membrane was discovered by Swiss botanist Carl Naegeli and C. Cramer in 1855. Later in 1960s, the synthetic asymmetric membranes were developed at the University of California, Los Angeles, by Loeb and Sourirajan in 1962 which was used for the separation of salt from seawater. This had lead to a significant development of the membrane technology. Membrane separation processes work without heating and therefore are energy efficient than the conventional thermal separation processes like distillation, or crystallization. The membrane separation process involves two fractions: permeate and retentate. In waste water treatment, membrane technology is becoming more and more significant.

The importance of membrane technology is growing in the field of environmental protection. The application areas mainly focus on the beverage and food industry, pharmaceutical industry, and textile industry. Along with these, major focus was given on the waste water treatment for the reuse and recycle of drinking water. Due to the increasing population and therefore increasing demand of fresh water for the purpose of bathing, cleaning etc. the popularity of the membrane technology is at peak.

The common driving forces are pressure and concentration according to which the membrane processes can be classified as:

Pressure driven:

- Microfiltration
- Ultrafiltration
- Nanofiltration
- Reverse osmosis

Concentration driven:

- dialysis
- pervaporation
- forward osmosis

Table 1.2: Membrane processes operated at various pressures and their pore size

Process	pore size	Operating Pressure (bar)
Microfiltration (MF)	0.1-10	0.5-5
Ultrafiltration (UF)	0.01-0.1	2-10
Nanofiltration (NF)	0.001-0.01	5-20
Reverse Osmosis (RO)	0.0001-0.001	10-80

1.4.1 Membrane operation

Membrane processes can be operated in four different ways:

1. Dead-end filtration
2. Cross-flow filtration
3. Hybrid flow filtration
4. Submerged filtration

In this process, the feed solution flows tangentially to the membrane surface.

Dead-end filtration: This is the most basic form of filtration. The entire fluid flow is forced through the membrane under pressure and is accumulated on the surface of the membrane.

Most pressure-driven membrane processes are operated in the cross-flow filtration mode. In *cross-flow filtration* the feed solution is circulated across the surface of the filter. At the membrane surface, the permeating component moves perpendicularly to the membrane surface.

As the name suggests, *Hybrid flow filtration* is a combination of the above two techniques i.e. dead end filtration and cross-flow filtration. The filtration process has two phases- the production phase and the flushing phase. During the production phase, the tubes are closed on one side which resembles a dead-end filtration. During the flushing phase, the tube is open on both sides and just like in cross flow filtration , the fraction that did not pass through the membranes is removed to clean the membrane surface.

The *submerged filtration* is performed from the outside to the inside of the membrane. In this, the membranes are submerged in the liquid that has to be filtered.

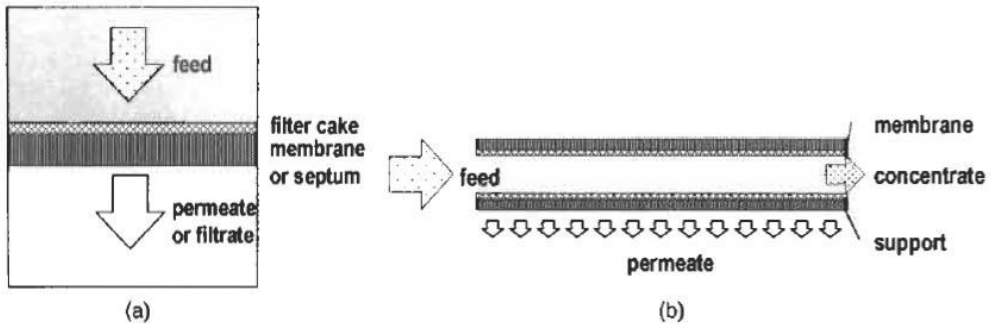


Fig. 1.1**:** Schematic representation of (a) dead-end; and (b) cross-flow filtration mode (Baker, 2004)

Transmembrane pressure (TMP) is the driving force for the pressure-driven membrane processes that is needed to press water through the membrane.

$$TMP = \frac{P_i + P_o}{2} - P_p \quad (15)$$

P_i: inlet pressure

P_o: outlet pressure

P_p: permeate pressure

1.4.2 Pressure-driven membrane separation processes

Membranes are generally classified in broad categories on the basis of the driving force that is used to remove or separate the particles or ions of various sizes: Microfiltration, Ultrafiltration, Nanofiltration, Reverse osmosis.

- Microfiltration (MF): Micro filtration is the process of removing particles or ions in the 0.025 to 10.0 microns range from fluids by passing through a microporous medium such as a membrane filter. Materials that are removed by MF include sand, algae, silt, clays, and some bacterial species. MF is not an utter barrier to viruses. However, when combined with disinfection, MF can control these microorganisms in water as well.

- Ultrafiltration (UF): Ultrafiltration (UF) is the process of separating enormously minute particles and dissolved molecules from fluids. It has a pore size of approximately 0.002 to 0.1 microns. UF can remove all microbiological species removed by MF as well as some viruses.

- Nanofiltration (NF): Nanofiltration membranes have a nominal pore size of approximately 0.001 microns. These membranes can remove practically all viruses, cysts, bacteria, and humic materials.

- Reverse osmosis (RO): Reverse osmosis (RO) separates salts and small molecules from low molecular weight solutes. RO is mostly effective when used in series with multiple units like disinfection to ensure the safety of water.

Table 1.3: Membrane Processes based on their driving forces (Reynolds et al., 2002)

Membrane Processes	**Driving force**
MF/ UF/ NF/ RO	Pressure difference
Pervaporation	Concentration difference
Dialysis	
Liquid membranes	
Gas separation	
Membrane distillation	Temperature difference
Thermo-osmosis	
Electro-osmosis	Electrical potential difference
Electrodialysis	

1.4.3 Ceramic Membranes:

Generally, membranes are manufactured from a synthetic polymer, but nowadays ceramic and metallic membranes are also available. The membranes which are manufactured for the purpose of drinking water are made of polymeric material, as they are considerably cost efficient than the membranes constructed of other materials.

Membranes which are constructed of polymers often react with oxidants used in drinking water treatment and hence they should not be used with chlorinated water. The most important consideration while constructing a membrane is of mechanical strength, because a membrane having greater strength can withstand larger trans-membrane pressure (TMP), leading to better operational flexibility and the use of higher pressures.

The bi-directional strength membranes may allow cleaning operations or integrity testing to be performed from either the filtrate side or the feed side of the membrane. Certain membranes

carry a particular surface charge that can easily remove the particulate or biological/microbial contaminants of the opposite charge due to the phenomenon of electrostatic interaction. Hydrophilicity (water attracting/loving) and hydrophobicity (water repelling) are the two properties of few membranes which allow them to easily get wet and thereby resist fouling to certain extent.

Every material used for the manufacturation of various membranes carry a unique property like surface charge, pH, extent of hydrophilicity/hydrophobicity, oxidant tolerance, flexibility and strength. These materials include polyvinylidene fluoride, cellulose acetate, polypropylene, polyacrylonitrile, polysulfone, or some other polymers.

Common materials used for the manufacture of RO and NF membranes are cellulose acetate or ployamide materials. Cellulose membranes are prone to biodegradation and therefore they must be operated within a narrow pH range of 4 to 8. Polyamide membranes are not subjected to biodegradation so they can be used under a wide range of pH but they have a very minute and limited tolerance for the strong oxidants. These membranes need appreciably low pressure to operate and therefore have become the mostly used membrane material for the applications of NF or RO.

In the present work, the low cost AOP and microfiltration (using low cost ceramic membranes) were combined to remove one of the most common dyes in textile effluents, methylene blue. The AOP process will degrade the dye and the membrane separation removes the oxidation products. Thus, the two techniques were combined.

CHAPTER 2

LITERATURE REVIEW

With the boost in the industrialization, there is an essential need for the removal of minute amounts of toxic pollutants in the ppm or ppb level from the wastewater and contaminated groundwater. Human health and the environment has a serious impact of these colored wastewater streams. Hence, there is a prior need to treat or decolorize these effluents before discharge. Among various dyes, methylene blue is a basic aniline dye that has been used as temporary hair colorants, and in leather, cotton, wool, and paper industry. It is not particularly hazardous, but can cause some harmful effects (Hamdaoui, 2006).

There are various techniques available for the removal of dyes such as adsorption (Ramakrishna et al., 1998), membrane separation (Wu et al., 2007), coagulation/flocculation (Shi et al., 2006) and biological treatment (McMullan et al., 2001) and Advanced Oxidation Processes. The most commonly used AOP methods are discussed in the following section.

Titanium dioxide/UV light process

Research interest in TiO_2 photocatalysis has grown appreciably since Fujishima and Honda discovered photocatalytic water-splitting on crystalline TiO_2 electrodes for hydrogen production in 1972. It basically has a strong oxidizing power under ultraviolet (UV) light, environmental friendly, biocompatible features and incredible chemical stability. It requires UV light to be activated because of its large band gap of ~3.2 eV (for the crystalline anatase phase). In this process, hydroxyl ions are generated whena titanium peroxide semiconductor absorbs UV light and therefore conduction band electrons (ecb) and valence band holes are initially yielded (Eq. 1). The band electrons interact with molecular oxygen to yield superoxide radical anions (Eq. 2), whereas hydroxyl radicals are produced when band holes interact with water. (Eq. 3) (Crittenden et al., 2005):

$$TiO_2 + h\nu \rightarrow ecb + h^+ \quad (1)$$

$$ecb + O_2 \rightarrow O_2^-\bullet \quad (2)$$

$$h^+ + H_2O \rightarrow H^+ + HO\bullet \quad (3)$$

Oxidative degradation of organic compounds occurs through their reactions with valence band holes, hydroxyl and peroxide radicals as well as reductive cleavage through their reactions with electrons. The main advantages of this process are the lack of mass transfer limitations when nanoparticles are used as photocatalysts, the operation at ambient conditions, and the feasible use of solar irradiation which makes TiO_2/UV light process an extensively used process for wastewater treatment. In TiO_2 the photogenerated holes are capable for oxidation of a wide variety of organic compounds into harmless compounds such as CO_2 and H_2O. The initial organic load, UV irradiation time, amount of catalyst, reactor's design, temperature, pH of the solution, light intensity and presence of ionic species are the major factors affecting TiO_2/UV light process.

The pH of the solution has a complex effect on the rates of photocatalytic oxidation. The reaction rates increase at lower pH (Andreozzi et al., 2000) whereas; pollutants which are hydrolyzed under basic conditions might show an increased reaction rate with the increase of pH (Choi and Hoffmann, 1997). The presence of ionic species could even affect the process of degradation by means of absorption of UV light, adsorption of the pollutants and reaction with hydroxyl radicals (Gogate and Pandit, 2004). The wide use of photocatalytic oxidation is to treat olive-oil mill wastewater (Marques et al., 1996; Vigo and Cagliari, 1999). In a recent study, for the treatment of diluted (1/100) olive mill wastewater, TiO_2 under UV irradiation was used. In the presence of 1 g/L TiO_2 after 24 h, almost 22% and 94% of COD and phenols were removed (El Hajjouji et al. 2008). Again, Chatzisymeon et al., (2008) investigated the application of this process in the treatment of olive wastewater. It was found that with decreasing initial COD and increasing contact time and catalyst concentration, the treatment efficiency was increased.

(Sohrabi and Ghavani., (2008) investigated the photocatalytic degradation of Direct Red 23 dye in UV/TiO_2 system. The determination of optimum conditions for maximum degradation was done. It was found that acidic pH was suitable for the photocatalytic removal of Direct Red 23. The rate of dye decomposition was increased with concentration of TiO_2 up to 4 g/L, and then it decreased with increasing TiO_2 concentration.

UV/TiO_2 photocatalytic degradation is a successful process as it uses the solar light which is easily available and non hazardous. In a study, UV/TiO_2 photodegradation was studied for the removal of estrone, 17β-estradiol (EDCs) (Zhang and Zhou, 2008). It was found that under natural sunlight, with a rate constant of 0.01/h, the degradation of estrone and 17β-estradiol followed a pseudo-first-order kinetics.

Advancement in this process was the doping of a metal ion into the lattice of TiO_2. As the conduction band electrons and the produced holes recombine before they undergo any chemical reactions, the technique of doping was adopted. (Sahoo et al., 2005). In a recent study, Behnajady et al., (2008) reported that undoped TiO_2 was less efficient than silver doped TiO_2 for the photocatalytic degradation of C.I. Acid Red 88 dye. The ability of silver to trap electrons explained the positive effect on dye degradation.

Basically, TiO_2 in the anatase phase is used for the experimental purposes. For the enhanced photocatalytic degradation of dye in the presence of visible light, TiO_2 powder was doped with nitrogen. It shifts the TiO_2 absorption towards the visible region. In order to prepare nitrogen doped TiO_2, it was grinded manually with urea and then annealed for 1 hr at 400C. Then the catalyst properties were studied by diffuse reflectance spectra (DRS), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The comparison of the N-doped TiO_2 nano particles with undoped ones was done to check the enhancement in the photocatalytic degradation of C.I. Basic Red46 (BR46). Furthermore, Central composite design (CCD) was employed not only for developing a model for prediction of color removal efficiency, as a function of the initial amount of N-dopedTiO_2, initial BR46concentration and reaction time, but also for finding individual and interactive effects of the mentioned parameters. The predicted values of photocatalytic decolorization efficiency were found to be quite similar with the experimental values (R^2 =0.916), which showed that the CCD model was perfectly suitable. Moreover, the results showed that the color removal efficiency was clearly affected in diverse operational conditions.

Hydrogen peroxide/UV light process

The fundamental of this process includes injecting H_2O_2 and then mixing it in a reactor that is equipped with UV light (200 to 280 nm). In this process, hydroxyl radicals are generated when the ultraviolet radiations cleave the O-O bond present in hydrogen peroxide. The reactions which describe the UV/ H_2O_2 process are shown below (Buxton et al., 1988):

$$H_2O_2 + h\nu \rightarrow 2\ HO\bullet \quad (4)$$

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O \quad (5)$$

$$H_2O_2 + HO_2\bullet \rightarrow HO\bullet + H_2O + O_2 \quad (6)$$

$$2\ HO\bullet \rightarrow H_2O_2 \quad (7)$$

$$2\ HO_2\bullet \rightarrow H_2O_2 + O_2 \quad (8)$$

$$HO\bullet + HO_2\bullet \rightarrow H_2O + O_2 \quad (9)$$

In the above mentioned equations, reaction in Eq. 4 is considered to be the rate limiting reaction because the rates of the other reactions are much higher than that of Eq. 4. Theoretically, in this process, more the concentration of hydrogen peroxide initially, more will be the production of hydroxyl radical (Eq. 4), which decomposes more target compound. However, an optimal hydrogen peroxide concentration exists because overdosing of hydrogen peroxide would lead to reaction with hydroxyl radical and formation of $HO_2\bullet$ (Eq. 5).

UV/ H_2O_2 process is efficient in mineralization of the organic pollutants. A major disadvantage of this process is that it cannot utilize solar light as the source of UV light. This is due to the reason that the UV energy required for the photolysis of the oxidizer is not accessible from the solar spectrum (Niaounakis and Halvadakis, 2006). Moreover, UV being the input source of light for the reactor is wasted when water matrix absorbs a lot of UV light. This is due to the reason that H_2O_2 has poor UV absorption characteristics. This is why special reactors are designed for UV illumination , while residual H_2O_2 should be addressed (Crittenden et al., 2005).

The main factors which affect this process are:

- Initial concentration of the target compound
- H_2O_2 used
- pH of the wastewater

- Presence of bicarbonate
- Reaction time

According to Gogate and Pandit., (2004) there is a prior need for diluting the wastewater at an optimum level because the kinetic rate constant for the degradation process is inversely proportional to the initial concentration of the pollutant. Moreover, H_2O_2 should also be present in a limited quantity because beyond a certain limit its presence shows a negative effect on the degradation reaction due to scavenging action. The entire process works effectively at low pH values (2.5- 3.5), however pH values depend on the pKa of the target compounds. UV/ H_2O_2 process has been widely used for dyes removal. In a recent study investigating C.I Acid Orange 7 dye removal, Daneshvar et al. (2008) reported that in the absence of H_2O_2/UV, the dye removal efficiency became almost negligible.

Rezaee et al. (2008) used this process for decolorization of Reactive blue 19 dye and the effects of initial dye concentration, H_2O_2/UV dosage and pH on decolorization were evaluated. It was found that there was 100 % decolorization of the dye in less than 30 minutes using 2.5 mmol/L H_2O_2 and 55 W UV-C lamps. It was even observed that the decolorization rate increased linearly with UV dosage and nonlinearly with increasing initial H_2O_2 concentration. Fung et al., (1999; 2001) reported that combined use of UV/ H_2O_2 with ultrasonic waves (US) also helps to enhance color removal efficiency during dyeing wastewater treatment. In a recent study, removal of malachite green as a model contaminant from textile industry was studied and the efficiency of UV/ H_2O_2 and US/UV/H H_2O_2 processes on the removal was investigated (Behnajady et al., 2008). It was found that US/UV/ H_2O_2 was the most effective process for the degradation of malachite green as compared to the one where ultrasound waves were not used. This was due to the reason that ultrasound contributes together with photolysis to the scission of H_2O_2. The rate of malachite green removal followed first-order kinetics, whereas the rate of reaction increased with increasing the temperature from 294 K to 307 K, power density from 0.049W/ml to 1.163 W/ml and decreasing the initial concentration from 10 mg/l to 2 mg/l of the target compound. This process has been used for the degradation of the compounds containing phenol present in olive mill wastewater (Benitez et al., 1996; 1998). In a recent study, Ugurlu and Kula (2007) investigated the effect of various operating parameters: H2O2/UV dosage and pH on the

decolorization and removal efficiency of phenols and organic carbon from olive mill wastewater. In samples which were exposed to natural sunlight, removal efficiency was found to be around 90%. For the abovementioned experimental conditions, the removal of lime enhanced phenol and lignin removal was found to be 100% and 40%, respectively. The reduction in the COD of the abovementioned process showed that almost 90% of the COD could be removed where initial COD concentration = 1050 mg/L, COD/H_2O_2 = 1/2, pH = 3, and temperature = 39-43 ^{0}C (Dincer et al., 2008).

Fenton's reactions

Advanced oxidation process with Fenton's reagent is one of the potential processes for the wastewater treatment (Thakare, 2004). The most important benefit of this process is its cost efficiency as compared to the other AOP's, such as UV/H_2O_2 process. Basically, Fenton's reagent is a homogenous solution which consists of hydrogen peroxide (H_2O_2) and Ferrous ions (Fe^{2+}), being the catalyst in an acidic medium. In the reaction, when hydrogen peroxide reacts with ferrous ions, there is a production of hydroxyl radicals [HO•] which have the capability of destroying a wide range of organic pollutants in wastewater (Legrini et al., 1993).

Fenton's reagent is a very powerful oxidant for organic contaminants which consists of ferrous iron (catalyst) and hydrogen peroxide (oxidizing agent).Fenton process follows the below mentioned mechanism (Neyens and Baeyens, 2003; Niaounakis and Halvadakis, 2006):

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet$ (10)

$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^-$ (11)

$HO\bullet + RH \rightarrow H_2O + R\bullet$ (12)

$R\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+}$ (13)

There are basically two types of Fenton reactions: Dark Fenton (without light) and Photo Fenton (with light).

In photo Fenton process (H_2O_2/ Fe_2^+ /UV), HO• formation takes place through the photolysis of hydrogen peroxide (H_2O_2/UV) and Fenton reaction (H_2O_2/ Fe_2^+). The ferric ions (Fe_3^+) which are produced in Equation 10 are converted photocatalytically to ferrous ions (Fe_2^+) in the presence of UV irradiation (Moraes et al., 2004).

$$Fe^{3+} + H_2O \rightarrow Fe^{2+} + H^+ + HO\bullet \quad (14)$$

The hydroxyl radicals which are produced in the above mentioned reaction react with the organic species that leads to their oxidation. As the name suggests, photo Fenton reaction is accelerated by light, it gives faster rates and higher degrees of mineralization as compared to the dark Fenton process (Pignatello et al., 2006). This can also be achieved with the help of solar irradiations because this reaction can be driven by low energy photons easily (Torrades et al., 2004). This fact makes the treatment process cost efficient. Following parameters affect the Fenton process: initial concentration of the pollutant, pH of the solution, amount of ferrous ions, H_2O_2 concentration, and presence of other ions (Gogate and Pandit, 2004). The pH ranging from 2-4 is found to be optimum pH for Fenton's reagent processes. At pH higher than 4, the reaction rate decreases due to the reason that Fe^{2+} ions are unstable and they are easily transformed to Fe_3^+ ions, forming complexes with hydroxyl. At alkaline pH, H_2O_2 loses its oxidative power because it breaks into oxygen and water (Niaounakis and Halvadakis, 2006). Thus, before the treatment of wastewater with Fenton reagent it becomes necessary to adjuct the pH of the wastewater. More the number of ferrous ions and higher the concentration of H_2O_2, more will be the degradation rate (Lin and Lo, 1997).

However,H_2O_2 is highly toxic to certain microbes, therefore usage of excessive amounts of H_2O_2 can possibly affect the overall efficiency of degradation when the Fenton process is further followed by biological oxidation (Gogate and Pandit, 2004). Phosphate, fluoride, sulfate, bromide and chloride ions inhibit the Fenton oxidation of organic compounds. The two possible reasons for the inhibition by these species are: scavenging of HO• due toprecipitation of iron, or formation of less reactive complex due to coordination with dissolved Fe (III) (Pignatello et al., 2006).

Besides these methods, membrane technology is also one of the prominent techniques used in decoloration of the dyes.

MF membranes comprise the largest fraction of total membrane production due to their increasing usage in recent years. MF provides a simple clarification of the effluent by removing suspended solids and colloidal dyes (Bottino et al., 2000). Therefore, its application alone has

been reported to be inadequate for water recycling, making it more generally adopted in pre-treatment for further membrane processes.

Latif et al. (2002) explored the use of microfiltration membrane separation processes to remove the suspended solid (mainly due to dyes in the painting and coloring processes) from wastewater of batik industry. The results showed that the dye concentration, pH of dye, and the operating pressure were found to affect the filtration process.

Nanofiltration and ultrafiltration are the commonly used techniques due to the small pore size. Zaghbani et al., (2006) reported that more than 97% rejection of methylene blue dye can be done using ultrafiltration technique.

Fersi et al. (2009) investigated the parameters that determine the flux decline of textile wastewater by membrane technologies, where MF and UF processes were studied in order to be investigated as pre-treatment for the NF process in the case of textile effluent treatment.

Nigmet et al. (2009) focused on the applicability of microfiltration (MF)/ultrafiltration (UF) as a pretreatment to nanofiltration (NF) for the reclamation of rinsing waters of indigo dyeing process. Two different MF alternatives, single 5 mm MF and sequential 5 mm and/0.45 mm MF, were evaluated as pre filtration to improve the performance of the proceeding UF stage. Single stage 5 mm MF followed by 100 kDa UF was selected as the best pre-filtration train to NF that permits the textile producer to reclaim indigo dyeing wastewater.

A. Alkhudhiri et al. (2012) studied on Membrane distillation: A comprehensive review. Membrane Distillation (MD) is a thermally-driven separation process, in which only vapor molecules transfer through a microporous hydrophobic membrane. The driving force in the MD process is the vapor pressure difference induced by the temperature difference across the hydrophobic membrane. The study of different types of membrane distillation process and this process has various applications, such as desalination, wastewater treatment and in the food industry. This review addresses membrane characteristics, membrane-related heat and mass transfer concepts, fouling and the effects of operating condition.

However, the decline in the flux and membrane fouling are some of the major drawbacks of these membrane based separations (Chakraborty et al., 2005). Thus, to overcome the drawbacks

of one another, hybrid techniques are used. The following literature works involve the use of hybrid techniques:

Basar et al. (2006) proposed that hybrid integrated membrane techniques can provide some advantages like higher removal efficiency, lower fouling therefore lesser backwashing and high quantity waste water treatment over the common traditional techniques.

Nowak and Winnicki (1986) studied the efficiency of organic dye removal from aqueous solutions and actual textile effluents using a tubular membrane module. It was found and reported that 90–100% removal of organic dye with a polysulfone ultrafiltration membrane was achieved.

Lee et al. (2005) used microfiltration with coagulation and adsorption for the removal of reactive dyes (Orange 16 and Black 5). As the presence of very low concentrations of dyes (1 mg/L) in the effluent is even highly visible and is considered aesthetically undesirable so the study focuses on the removal of the dye from wastewater completely. They studied and evaluated the performance of adsorption using three kinds of powdered activated carbons, coagulation and membrane processes and compared these with the hybrid process with combined coagulation–adsorption–membrane treatment system. It was found that adsorption capacity and kinetics of Orange 16 were much higher and faster than those of Black 5. The combined coagulation–adsorption–membrane process gave better dye removal efficiency.

Aouni et al. (2008) suggested the treatment of textile wastewater by a hybrid electrocoagulation and nanofiltration process. They examined the use of electrocoagulation treatment process followed by nanofiltration process of a textile effluent sample. In this, the electrocoagulation process was studied under several conditions such as various current densities and effect of experimental tense. Efficiencies of COD and turbidity reductions and color removal were studied for each experiment. The electrochemical treatment was indented primarily to remove color and COD of wastewater while nanofiltration was used to further improve the removal efficiency of the color, COD, conductivity, alkalinity and total dissolved solids (TDS). The experimental results, throughout the present study, indicated that electrocoagulation treatment followed by nanofiltration processes were very effective and were capable of elevating quality of the treated

textile wastewater effluent but due to the extensive use of electricity, the process proved to be cost inefficient.

Yu et al. (2010) studied the impacts of membrane properties on the reactive dye removal from dye/salt mixtures by nanofiltration membranes. Two types of nanofiltration membranes of similar pore size, namely asymmetric cellulose acetate membrane and thin-film composite polyamide membrane were fabricated, and their key physical, chemical and performance properties were characterized which were employed to perform dye removal experiments with aqueous solutions of reactive black 5 and NaCl under different operational parameters. It was found that there were significant differences between the dye removal performances of the two membranes, and that the membrane properties played an important role in dye removal rate, stable permeate flux and their change behaviors under operational conditions. Over 99% removal of reactive dyes from dye/salt mixtures was achieved by asymmetric cellulose acetate and composite polyamide nanofiltration membranes.

Another study of the hybrid process was on the combination of polyelectrolyte promoted forward osmosis and membrane distillation for the treatment of dyes in wastewater (Ge et al., 2012). In this work, the concept of a polyelectrolyte-promoted forward osmosis−membrane distillation (FO−MD) hybrid system was demonstrated and applied to recycle the wastewater containing an acid dye. A poly(acrylic acid) sodium (PAA-Na) salt was used as the draw solute of the FO to dehydrate the wastewater, while the MD was employed to re-concentrate the PAA-Na draw solution. With the integration of these two processes, a continuous wastewater treatment process was established. Almost a complete rejection of PAA-Na solute was observed by both FO and MD membranes. The practicality of PAA-Na-promoted FO−MD hybrid technology demonstrates not only its suitability in wastewater reclamation, but also its potential in other membrane-based separations, such as protein or pharmaceutical product enrichment. The treatment was highly temperature dependent making it energy and cost inefficient.

2.1 Objectives of the present study

In the present work, the low cost AOP and microfiltration using low cost ceramic membranes were combined to remove one of the most common dyes in textile effluents, methylene blue. The

AOP process will degrade the dye and the membrane separation removes the suspended particles. Thus, the two techniques were combined.

Overall objective of the study was to investigate the effectiveness of combined process (AOP and Microfiltration) for dye treatment.

- Optimization of initial concentration of methylene blue dye.
- Optimization of Fenton's reagent dose.
- Preparation of low-cost ceramic microfiltration membranes.
- Ceramic membrane characterization for porosity and pore size.
- Treatment of the treated dye by dead-end microfiltration process.

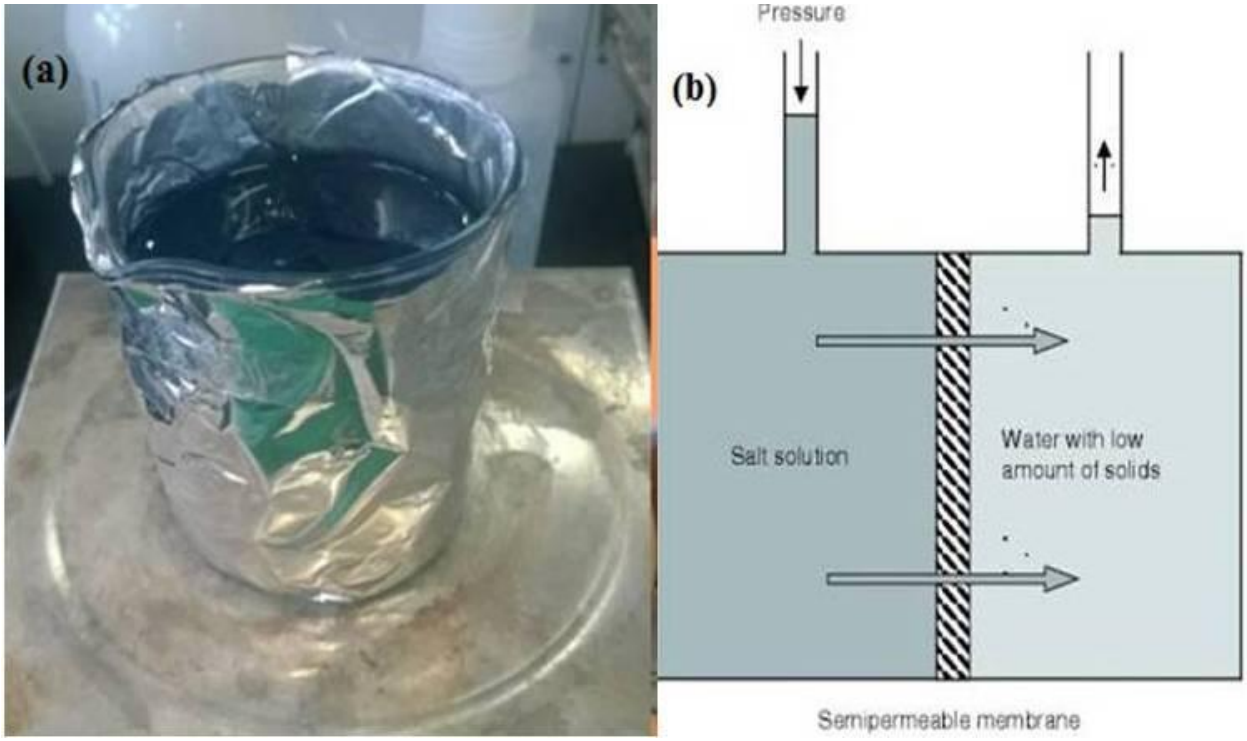


Fig 2.1: Schematic representation of (a) Fenton's process (b) Microfiltration

CHAPTER 3

METHODOLOGY

3.1 Raw materials

All the chemicals namely kaolin, sodium carbonate, calcium carbonate, sodium metasilicate and boric acid, graded with at least 99.5% purity were procured from CDH India Ltd. and were used without any pre-treatment. These five different constituents impart different properties to the ceramic supports. Kaolin is a cheap raw material which provides low plasticity and better refractory characteristics. Boric acid brings homogeneity to the membrane structure and increases the mechanical strength. Sodium metasilicate is used as a binder which forms silicate bonds among the particles and induces high mechanical strength to the membranes. Porous texture to the membranes is due to the presence of calcium carbonate and sodium carbonate.

Methylene blue was received from Rankem, India, 30% hydrogen peroxide solution and ferrous sulfate heptahydrate was received from Merck Specialties Private Limited and SD-fine Chem Limited respectively.

3.2 Membrane preparation and characterization

The raw materials (kaolin, calcium carbonate, sodium carbonate, sodium metasilicate and boric acid) were crushed and grinded in ball mill to get a narrow size particle distribution. The raw materials were mixed with distilled water so as to make a thick and uniform paste. Round disc shaped moulds of 50 mm diameter and 5 mm thickness were used to caste the membranes by a basic paste casting technique (Singh et al., 2015). The membrane composition is given in Table 3.1. The prepared ceramic supports were kept under heavy weight for 12 hours to avoid any bend followed by drying before they were subjected to sintering. The supports were placed in a muffle furnace for sintering and the temperature of the furnace was increased slowly to 250°C at a heating rate of 50^{o}C/h and increased from 250^{o}C to 900^{o}C at a rate of 100^{o}C/h. Temperature was maintained at 900^{o}C for 4 hours to complete the sintering process. The sintered ceramic supports were then taken out of the muffle furnace and polished with C-100 and C-220 SiC abrasive papers and cleaned in ultrasonic bath to remove the loose particles that were formed during

polishing. The pore size and porosity of the membrane were determined by air and water permeability and pycnometric methods.

Porosity

The pycnometric method was used for determining the porosity of the membrane (Nandi et al., 2008). The average dimensions (diameter and thickness) of the membrane were obtained to calculate its volume. The difference between wet and dry weights of a membrane gives its pore volume. Distilled water was used as the wetting medium. The following equation was used for the calculation of porosity.

$$\text{Porosity (\%)} = \frac{\text{volume of pores}}{\text{Total volume}} \times 100 \quad (15)$$

The surface average pore size ($d_{p,s}$) was calculated by area averaging of all pores as follows:

$$d_{p,s} = \left[\frac{\sum n_i d_i^2}{\sum n_i}\right]^{0.5} \quad (16)$$

where, d_i is the diameter of i^{th} pore and n_i is the number of pores of size d_i.

Water permeation

The water permeation test was used to determine mean pore size of the membranes. A batch permeation cell with effective volume 28.2 cm^2 was used for permeation studies. The permeation cell was filled with water and pressurized with compressed air and the membrane was compacted till the steady flux of water is obtained at a pressure of 50 psi. The permeate flux was measured at upstream pressures between 0 to50 psi and downstream atmospheric pressure. The average pore radius (r_l) of the membrane can be estimated using the equation (reference):

$$J = \frac{n\pi r^4 \Delta P}{8\mu l} = L_h \Delta P \quad (17)$$

Using Eq. (17), the J versus ΔP graphs were plotted and the slopes of those graphs yielded the values of hydraulic permeability of various membranes. The average pore radius (r_l) of the membranes was then evaluated by assuming presence of cylindrical pores in the membrane matrix using the following equation deduced from Eq. (17) as

$$r_l = \left[\frac{8\mu l L_h}{\varepsilon} \right]^{0.5} \quad (18)$$

Air Permeation

Air permeation was done for calculation of average pore size (r_g) and effective porosity ($\frac{\varepsilon}{q^2}$) are related as follows:

$$K = 2.133 \frac{r_g v}{l} \frac{\varepsilon}{q^2} + 1.6 \frac{r_g^2}{l\eta} \frac{\varepsilon}{q^2} \bar{P} \quad (19)$$

where, K is evaluated as

$$K = \frac{QP_2}{S\Delta P} \quad (20)$$

From equation (19) can be plotted as a straight line to obtain the first term of the equation from its intercept, which corresponds to Knudsen diffusion, and the constant in the second term from the slope, which corresponds to viscous diffusion. The average pore size value that was obtained from water permeation was greater than that for gas permeation. This is due to the reason that gas can easily permeate through the nanopores whereas water cannot permeate at low pressures (up to 50 psi).

Table 3.1: Membrane composition (weight %)

Components	**Composition**
Kaolin	60
Calcium carbonate	25
Sodium carbonate	10
Sodium metasilicate	2.5
Boric acid	2.5

3.3 Advanced Oxidation Process

AOPs, advanced oxidation processes is for chemical treatment in which hydroxyl radicals [HO•] formation takes place. These highly reactive radicals cause chemical decomposition reactions and also react with organic or inorganic substances that cannot be degraded biologically. Degradation of dye using Fenton's reagent yields highly reactive organic radicals [R•] which are oxidized by Fe^{3+} ions. These oxidation reactions cause the precipitation of iron hydroxides.

Reaction rates with Fenton's Reagent are generally limited by the rate of HO• generation which depends on the concentration of iron catalyst. So to find the optimal composition of Fenton's reagent, different concentration of ferrous sulphate heptahydrate and hydrogen peroxide were selected for the decoloration of 100 ppm methylene blue dye solution. The dye solution was mixed with Fenton's reagent and kept in beakers under continuous stirring, the color removal was observed visually.

After the visual observations, the dye degradation profiles with respect to time were obtained for various concentrations of methylene blue, ferrous sulphate heptahydrate and hydrogen peroxide. The experimental conditions are shown in Table 3.2. After maintaining the pH of the solution as 3, all the experiments were conducted at room temperature (~25 °C), in the absence of direct sunlight. During the degradation experiments, absorbance readings were taken after every 5-10 minutes at λ_{max}=664 nm (Zhang et al., 2002) using Perkin Elmer lambda 35 UV-Vis spectrophotometer.

3.4 Microfiltration experiments

Before microfiltration experiments, the treated dye solution was kept undisturbed for 1 hour for the settlement of the dispersed solids. The solution was decanted and subjected to microfiltration for the removal of any suspended solids and the oxidation products. A dead end membrane cell was used for the microfiltration experiments at different pressures. The membrane was back-flushed and cleaned properly after each run. The permeate was tested to check the dye concentration using spectrophotometer. Methylene blue and the oxidation products which were passed through the membrane were investigated by IR Prestige21 FTIR Spectrometer (Shimadzu).

Table 3.2: Experimental conditions for advanced oxidation with Fenton's reagent

	Methylene blue (mg/L)	**Ferrous sulphate heptahydrate (mg/L)**	**Hydrogen peroxide, H_2O_2 (mg/L)**
Methylene blue	100	500	20
	150		
	200		
$FeSO_4.7H_2O$	100	1000	20
		500	
		250	
H_2O_2	100	500	30
			20
			10

4.1 Calibration curve for methylene blue

For obtaining the spectra 100 ppm (1.4 ml in 500 ml D.I. water) of the dye solution (0.354 % in solution) was used to obtain the curve shown in Fig. 4.1. Two peaks obtained at 293 nm and 664 nm corresponds to degradation and decolorization respectively.

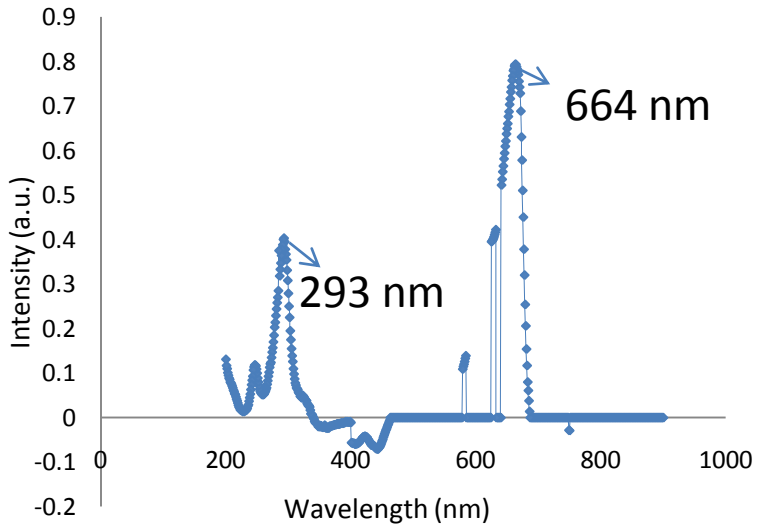


Fig. 4.1: Spectra of methylene blue dye

Calibration curve

The calibration curve for methylene blue (Fig 4.2) was prepared by using 100 ppm solution as a stock solution. Different concentrations of the solution were prepared and absorbance measured at 664 nm and 293 nm respectively for decolorization and degradation.

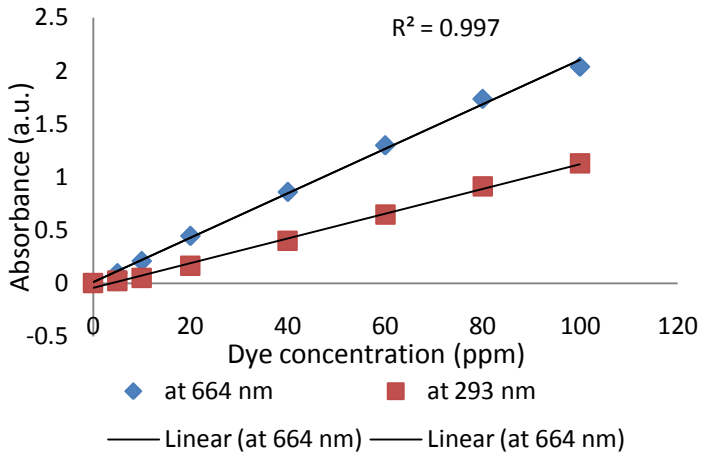


Fig. 4.2: Calibration curve for methylene blue

4.2 Optimal ratio of reactants for advanced oxidation

Prior to the experimental runs some exploratory runs were done for deciding the dose of Fenton's reagent. Some works available in literature (Jana et al., 2010; Dutta et al., 2001) were consulted for selecting the initial dose of the chemicals. High concentrations of $FeSO_4.7H_2O$ (1000 mg/L) and H_2O_2 (50 mg/L) makes the 100mg/L dye solution colorless instantaneously. As the concentration of $FeSO_4.7H_2O$and H_2O_2 was lowered to 10 mg/L and 250 mg/L respectively, the solution did not become clear even after a long time showing that below a critical concentration range, 100% removal does not take place. The observations and the experimental conditions are shown in Table 4.1. It is clear from this table that high concentrations of $FeSO_4.7H_2O$ (1000 mg/L) and H_2O_2 (50 mg/L) makes the 100 mg/L dye solution colorless instantaneously. Whereas, the low dose of $FeSO_4.7H_2O$ (250 mg/L) and H_2O_2 (10 mg/L) could not remove the color even after a long time; indicating that below a critical concentration range, 100% removal of the dye does not take place.

Table 4.1: Evaluation of optimal conditions to decolorize 100 mg/L methylene blue

Methylene blue (mg/L)	**$FeSO_4.7H_2O$ (mg/L)**	**H_2O_2 (mg/L)**	**Observations**
100	1000	50	Colorless in 20 minutes
100	500	50	Colorless in 30 minutes
100	250	50	Not colorless even after 2 hours
100	500	40	Colorless in 40 minutes
100	500	30	Colorless in 45 minutes
100	**500**	**20**	**Colorless in 60 minutes**
100	500	10	Not colorless even after 2 hours

Hydrogen peroxide

The main chemical cost in the Fenton's reagent is the cost of hydrogen peroxide, so in order to make the process cost efficient it was necessary to optimize the amount of hydrogen peroxide in the Fenton's oxidation process. At higher H_2O_2 concentration, the rate of dye degradation was higher (Fig. 4.3) due to the increased concentration of hydroxyl radicals. To make the technique cost efficient, minimum amount of hydrogen peroxide was determined. For each run100 mg/L of the dye solution was treated with 20 mg/L H_2O_2 and 500 mg/L $FeSO_4.7H_2O$ and varying amount of H_2O_2.Initial pH was adjusted at 3 and the solution was stirred for 2 hours. The absorbance readings were taken initially after every 5 minutes and then after 10 minutes. Fig. 4.3 shows that initially the degradation rate was very fast and then decreased gradually. This was due to the presence of large amount of Fe^{2+} ions in the beginning which were later converted into Fe^{3+} ions. The regeneration of the Fe^{2+} ions is the slowest and rate determining step in the reaction (Jaafar et al., 2014). At higher H_2O_2 concentration, the rate of dye degradation was higher (Fig. 4.3) due to the increased concentration of hydroxyl radicals which promoted degradation. 30 mg/L H_2O_2 gave complete removal in 45 minutes, whereas, with 10 mg/L H_2O_2 dose the complete removal could not be achieved. A dose of 20 mg/L was found to be appropriate as 99% removal was obtained in 1 hour.

Ferrous sulphate and methylene blue

Fig. 4.4 shows the effect of $FeSO_4.7H_2O$ dose on the dye removal. The rate of degradation increased with increasing the amount of $FeSO_4.7H_2O$ as Fe is the catalyst in the degradation reaction. 500 mg/L dose $FeSO_4.7H_2O$ was found sufficient for the dye removal. The effect of initial dye concentration on the removal is given in Fig. 4.5. With increasing the concentration of the dye the rate of degradation increased, however, the higher concentration took more time for removal.

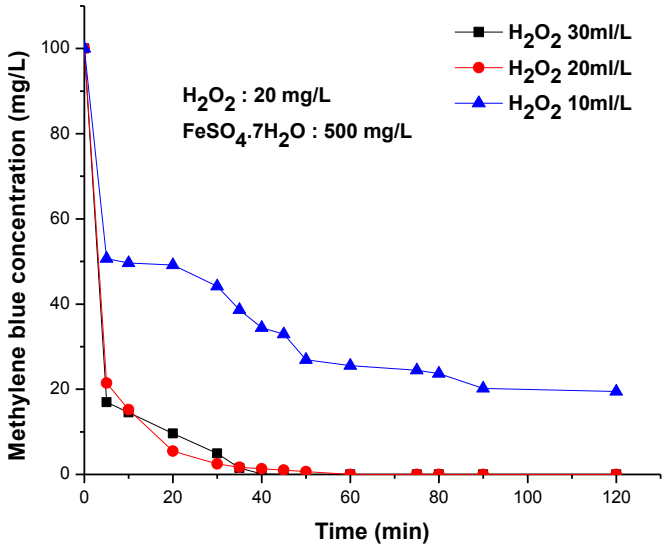


Fig. 4.3: Dye degradation as a function of hydrogen peroxide concentration

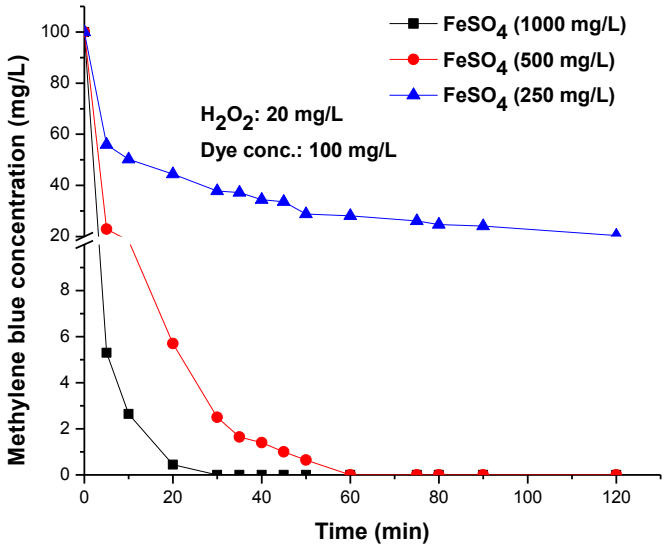


Fig. 4.4: Dye degradation as a function of ferrous sulphate concentration

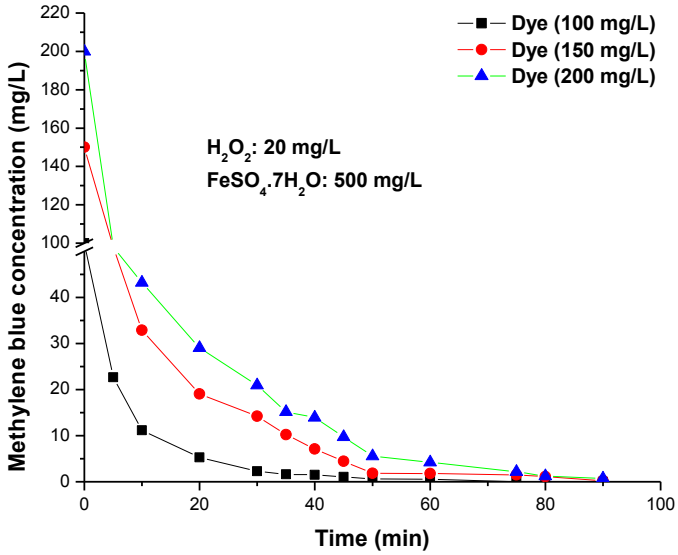


Fig. 4.5: Dye degradation as a function of dye concentration

4.3 Membrane properties

The average pore size of the membrane was calculated to be 0.60 μm, which confirmed that the membrane was in microfiltration range. The porosity of the membrane was 0.44. SEM images were used to determine the pore density, surface morphology and the surface pore size distribution of the membranes. Fig. 4.6 shows the SEM (Microscope S-3400N, Hitachi Make) image of the membrane surface.

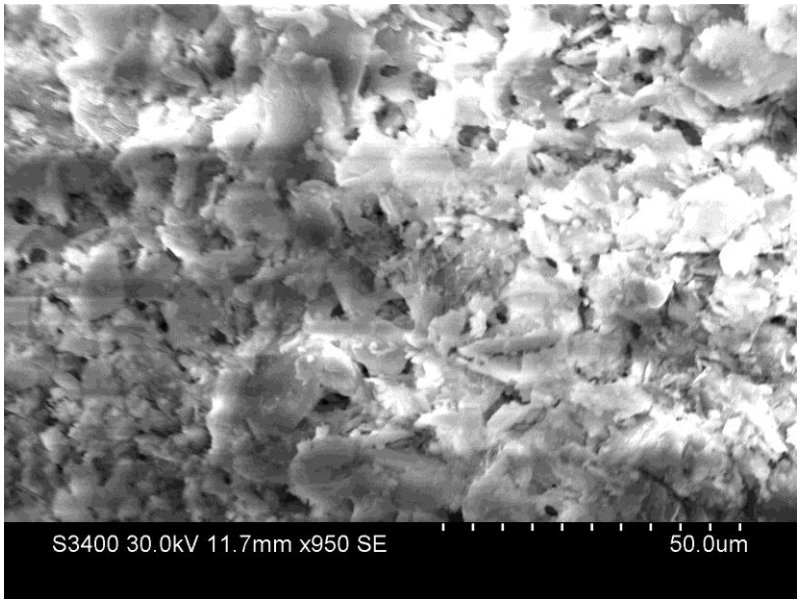


Fig. 4.6: SEM image of ceramic membrane

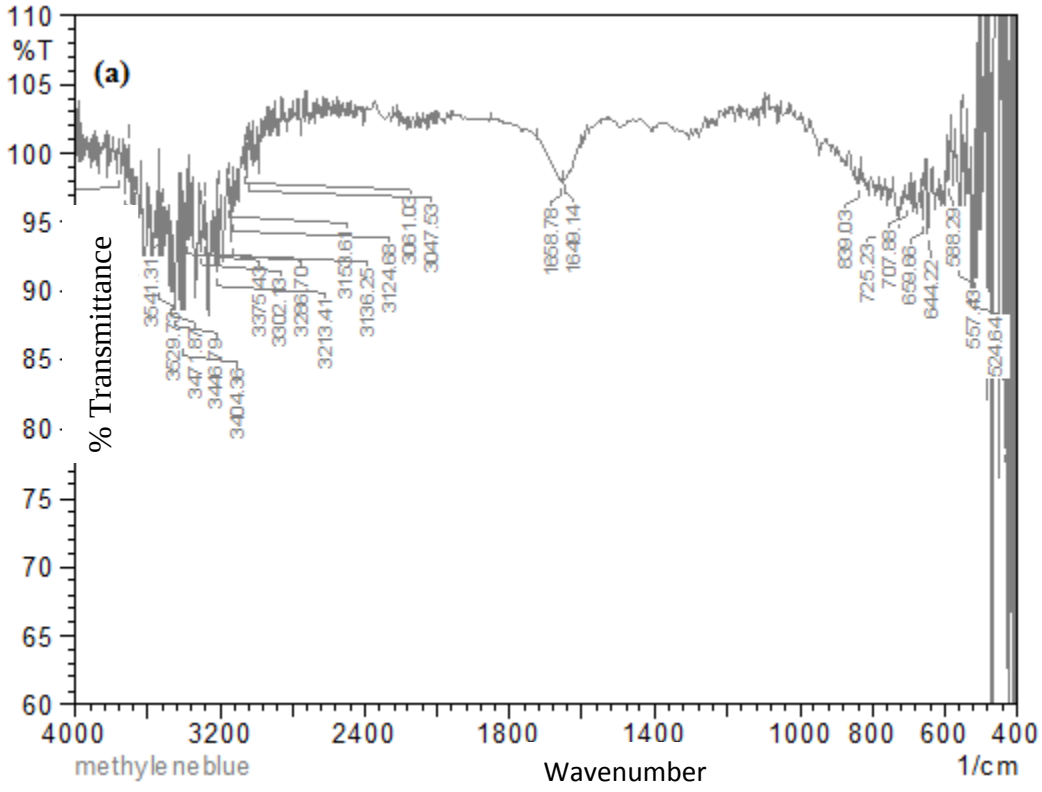
4.4 Analysis of the oxidation products

FT-IR spectra

Fig. 4.7 shows FT-IR spectra of methylene blue and the oxidation products in the treated water sample. The changes in the spectra of the treated sample are visible in Fig. 4.7 (b). Table 4.2 shows the FT-IR bands and the respective groups present in each band. The bands around 1658, 839, 725, and 659 cm^{-1} of methylene blue (Fig. 4.7a) were absent in the oxidation products (Fig. 4.7b). The bands of 839 and 707 cm^{-1} represented the =CH out of plane and the bending modes of CH. The band around 725 cm^{-1} representing chlorine was absent in the oxidation products. The absence of 1658 and 1649 cm^{-1} band in the oxidation products indicates the absence of aromatic substitution pattern on the ring. Thus the chlorine of the dye molecule and the aromatic groups were oxidized.

Table 4.2: FT-IR bands of methylene blue and oxidised products

Band (cm^{-1})	Methylene blue	Oxidation products	
3556	Present	Present	-OH group
3529	Present	Present	-OH group
725	Present	Absent	Chlorine group
1658	Present	Absent	Aromaticity
1649	Present	Absent	Aromaticity
839	Present	Absent	=CH out of plane
707	Present	Present	=CH bending mode



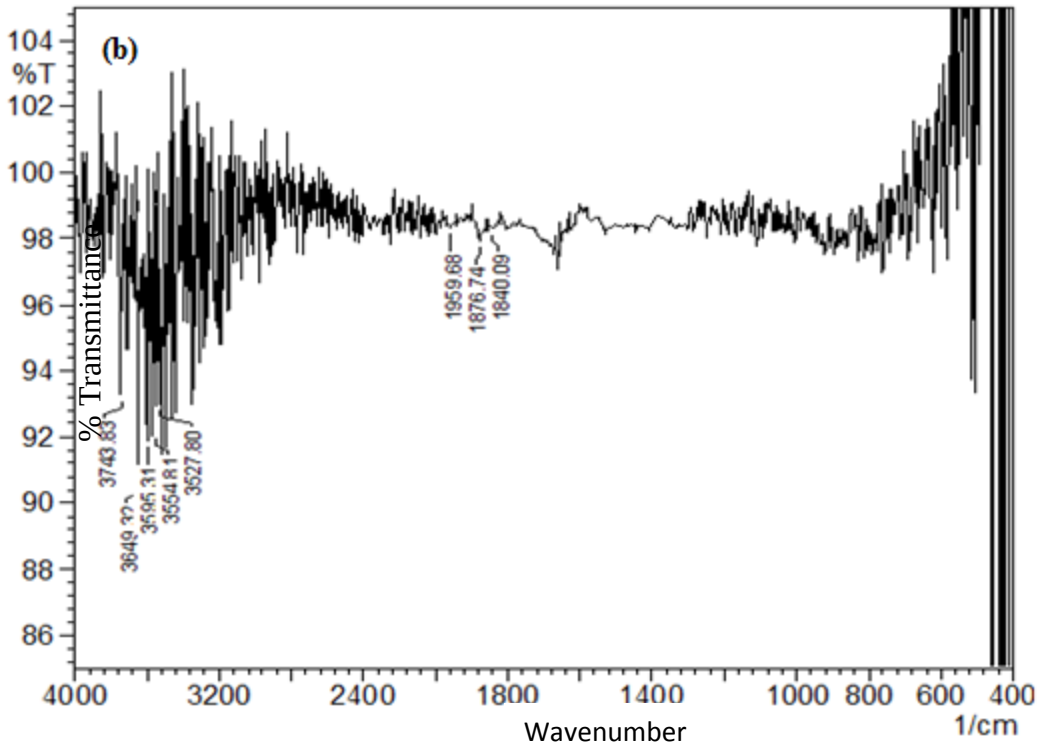


Fig. 4.7: FT-IR spectra of (a) Methylene blue (b) oxidation products

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

Textile dyeing processes are among the most environment unfriendly industrial processes, because they produce coloured wastewaters that are heavily polluted with dyes, textile auxiliaries and chemicals. The wastewaters originating from dyeing processes are generally characterized by the high content of color caused by the dyestuffs, salts, chemical oxygen demand (COD) deriving from additives such as acetic acid, detergents and complexing agents, suspended solids including fibers, high temperature and broadly fluctuating pH. Since textile is one of the major industries and it utilizes a huge volume of water, Hybrid technique consisting of AOP and microfiltration can be used which has high separation efficiency, low energy consumption, easy operation, and low cost.

Methylene blue was removed completely by the hybrid technique comprising of AOP and microfiltration. In order to degrade the dye (100 mg/L) completely, a dose of 20 mg/L H_2O_2 and 500 mg/L $FeSO_4.7H_2O$ was found to be optimum. The treatment time required for the AOP step was found to be 1 hour. To remove the fine suspended particles, low cost microfiltration membrane, with average pore size of 0.6 μm, was fabricated for the complete removal of the suspended particles from the treated water. Thus, the methylene blue dye was completely removed by the combined AOP and low cost filtration. Thus, the combined process seems promising for the decolorization and degradation of wastewater.

In the light of the present study, the following future work is recommended:

- ✓ The proposed tertiary treatment process may be used for the removal of dye from the real effluent.
- ✓ A detailed study regarding the effect of temperature and aeration on Fenton's reaction and pH on the separation performance of the membranes for the recovery of dyeing effluents should be performed. In this way, it should be determined whether the pH is effective on the wastewater or on the membrane characteristics, or both.

- ✓ The composition of the membrane may be optimized to obtain maximum flux.
- ✓ Fouling should be studied in detail to understand the causes of flux decline and to develop new approaches for minimizing the flux declines.

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