Degradation of methyl orange present in industrial waste water using fenton process

THESIS

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Under the guidance and supervision of

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in partial fulfillment for the award of the degree of

MASTER OF ENGINEERING IN CHEMICAL ENGINEERING

Department of Chemical Engineering

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Declaration of Originality and Compliance of Academic Ethics

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his ***Master of Engineering in Chemical Engineering*** studies**.**

All information in this document have been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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CERTIFICATE OF RECOMMENDATION

This is to certify that **Ms. Mousumi Sinha**, final year student of Master of Engineering in Chemical Engineering, Jadavpur University, has completed the Project work titled ―Degradation of methyl orange present in industrial waste water using fenton process under the guidance of **Prof. Dr. Siddhartha Dutta and Prof. Dr. Avijit Bhowal** during her Masters Curriculum. This work has not been reported earlier anywhere and can be approved for submission in partial fulfillment of the course work.

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Approval

The following thesis is hereby approved as a credible study of a Engineering subject and presented in a manner satisfactory to warrant its acceptance as a perquisite to the degree for which it has been submitted. It is to be understood that by this approval, the undersigned do not necessarily endorse or approve any statement made, opinion expressed or conclusion drawn there in, but approve the thesis only for thr purpose for which it has been submitted.

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ACKNOWLEDGEMENT

Though the following project is an individual work, I could never have reached the heights or explored the depths without the help, support, guidance and efforts of a lot of people. Firstly, I would like to thank my Project Guide, Prof. Dr. Siddhartha Dutta & Prof. Dr. Avijit Bhowal (Chemical Engineering) for instilling in me the qualities of being a good researcher. Their infectious enthusiasm and unlimited zeal have been major driving forces through my post graduate career at the Jadavpur University, Kolkata. I would also like to thank my laboratory co researcher Sudhanya Karmakar for her support during the project work. I would like to take this opportunity to thank Mr. Jayant Modak , for his constant encouragement and helpful advice. My very special thanks to my parents whom I owe everything I am today, my father Mr. Som Nath Sinha and my mother Mrs. Pushpita Sinha. Their unwavering faith and confidence in my abilities and in me is what has shaped me to be the person I am today. Thank you for everything. Finally, I would like to take the opportunity to thank all my teachers and support staff of the Chemical Engineering Department, Jadavpur University,
Kolkata.

Mousumi Sinha

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Chapter - I

Introduction

Industrial waste water treatment traverse the techniques and processes used to treat waste water that is produced as a by - product of industrial or commercial activities. After treatment, the treated wastewater may be reused or released to a sanitary sewer or to a surface water in the environment. Complex organic chemicals are manufactured or used by a range of industries. These include pesticides, pharmaceuticals, paints and dyes, petrochemicals, detergents, plastics, etc. Furthermore fossil fuel power stations particularly plants running on coal , are a major source of industrial wastewater. Many of these plants discharge wastewater with noteworthy levels of metals such as lead, mercury, cadmium and chromium as well as compounds of arsenic, selenium and nitrogen .

Figure 1.1 : industrial waste water containing methyl orange

After agriculture, the textile industry is second as the biggest polluter of water globally . Dye are used primarily in the production of consumer products including paints, textiles, printing inks, paper and plastics.. Natural dyes were later altered by chemical dyes that bond with the fabric, providing and retaining richer color throughout washing and exposure. Dyeing, rinsing and treatment of textiles use large amount of clean water. Around 72 toxic chemicals reach our water supply from textile dyeing. Untreated dyes cause chemical and biological changes in our aquatic system, which threaten species of fish and aquatic plants . The presence of these compounds also make practical water use unhealthy or dangerous.

1.1 **Classification Of Dyes**

Dyes are classified according to solubility and chemical properties .[1.1]

a. ***Direct Dyes***

Direct dyes are the most widely used and most economical of all classes. Some of the pastels and light shades possess good wash and light fastness but medium and heavy colors, particularly the latter, are not usually used. The application of Direct dyes is the least complicated; chemically they are salts of complex sulfonic acids. They are soluble in water and have an affinity for a wide variety of fibers.

b. ***Developed Dyes***

The wash fastness properties of Developed dyes are better than Directs, particularly in the medium and heavy ranges of colors. Developed colors have a tendency to be dull. They are not recommended where light fastness is a requisite. Developed dyeings are actually selected Direct dyeings treated in a cold bath with nitrous-acid and coupled with a developer to make a larger molecule of the original Direct dye, while on the other hand, the Direct dyes are physically held onto the fiber.

c. ***Sulfur Dyes***

Sulfur dyes are relatively inexpensive; they are insoluble in water and have no affinity for the fiber until reduced with alkaline sulfide compounds. They are applied to the fiber in a reduced state and oxidized within the fiber to an insoluble dye again. Shades in Sulfur dyes are dull, therefore these dyes are used chiefly for black. They possess good wash and light fastness and are satisfactory for *dry* crocking. They should be classed as poor for wet crocking and chlorine fastness.

d. ***Reactive Dyes***

Very bright shades of pink, green, blue and turquoise can be produced with Reactive dyes. Fastness properties are generally good except to chlorine. These dyes are soluble in water and are salted out of solution onto the fiber where they are make to react chemically within the fibers.

e. ***Mordant Dyes***

Mordant dyes require a mordant, which improves the fastness of the dye against water , light and perspiration . most natural dyes are mordant dyes and there is therefore a large literature base describing dye techniques. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool. the mordant, potassium dichromate, is applied as an after-treatment.

f. ***Vat Dyes***

Vat dyes are essentially insoluble in water and incapable of dyeing fibres directly. However, reduction in alkaline liquor produces the water-soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fibre. Subsequent oxidation reforms the original insoluble dye. The color of denim is due to indigo, the original vat dye.

g**.** ***Disperse Dyes***

Disperse dyes were originally developed for the dyeing of cellulose acetate, and are water-insoluble. The dyes are finely ground in the presence of a dispersing agent and sold as a paste, or spray-dried and sold as a powder. Their main use is to dye polyester, but they can also be used to dye nylon, cellulose triacetate, and acrylic fibers. In some cases, a dyeing temperature of 130 °C (266 °F) is required, and a pressurized dyebath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fiber. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

h. ***Azo Dyes***

Azo dye**,** any of a large class of synthetic organic dyes that contain nitrogen as the azo group −N=N− as part of their molecular structures; more than half the commercial dyes belong to this class. Depending on other chemical features, these dyes fall into several categories defined by the fibres for which they have affinity or by the methods by which they are applied.

1.2 **Methyl Orange**

Methyl orange is an intensively coloured compound used in dyeing and printing textiles. It is also known as C.I. Acid orange 52, C.I. 13025, helianthine B, Orange 3, Gold orange and Tropaeolin D. Chemists use methyl orange as an indicator in the titration of weak bases with strong acids. It changes from red (at pH 3.1) to orange-yellow (at pH 4.4). pH related colour changes results from changes in the way electrons are confined in a molecule when hydrogen ions are attached or detached. Here is the structure of methyl orange. :

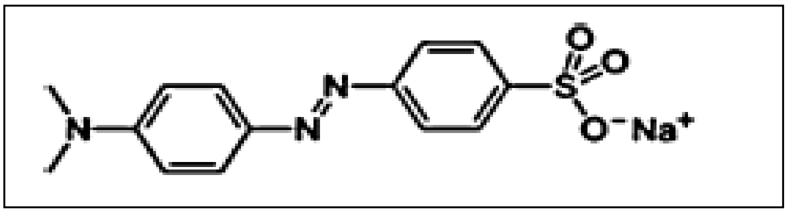
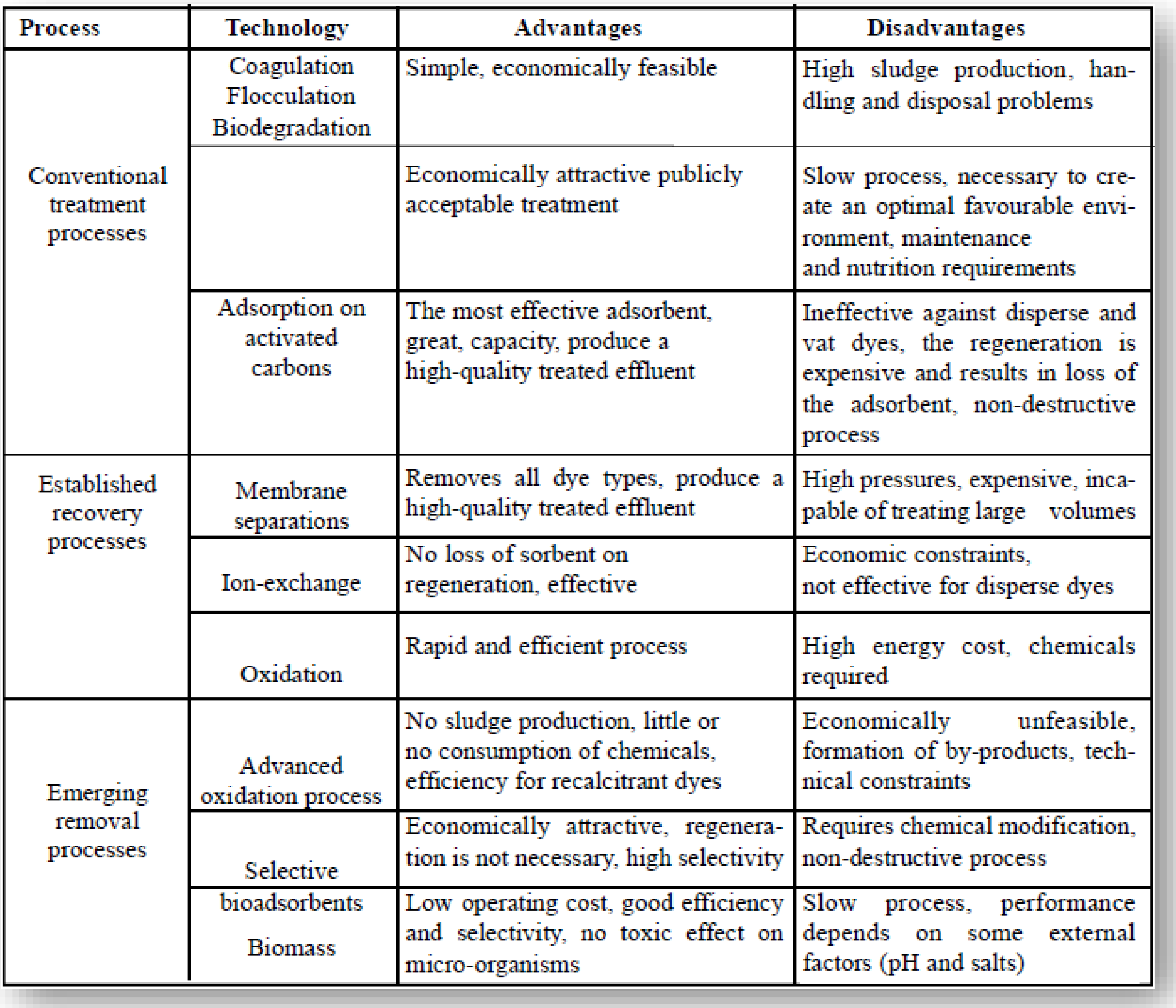


Figure 1.2 : structure of methyl orange

Methyl orange is a type of azo dye, azo compounds are compounds bearing the functional group R-N=N-R' , in which R and R' can be either aryl ar alkyl. The N=N group is called an azo group. Hence the name 'azo' dye . Methyl orange has some potential health effects. It may cause eye irritation & cause skin irritation if absorbed through the skin . Methyl orange is mutagenic i.e. in genetics, a mutagen is a physical or chemical agent that make changes in the genetic material , usually DNA, of an organism and thusincreases the frequency of mutations above natural background level . so it is severely toxic to the body at very low dosages, toxic to reproduction and possibly carcinogenic.

1.3 **Removal Techniques**

Recent quite a lot advances has been made to improve the treatability methods, the different technologies incooperated for dye removal is shown as under :



Process	Technology	Advantages	Disadvantages
Conventional treatment processes	Coagulation Flocculation Biodegradation	Simple, economically feasible	High sludge production, handling and disposal problems
		Economically attractive publicly acceptable treatment	Slow process, necessary to create an optimal favourable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	bioadsorbents Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on micro-organisms	Slow process, performance depends on some external factors (pH and salts)

Table 1 : different technologies for dye removal [1.2]

advanced wastewater treatments have become an area of global focus as to strive for ways to keep essential resources available and suitable for use .

1.3.1 **Advanced Oxidation Processes**

One such available alternative waste water treatment process is ***Advanced Oxidation Processess (AOPs)***. AOPs, as the name suggests are a set of chemical treatment procedures designed to remove organic, sometimes inorganic materials present in waste water by oxidation through reactions with hydroxyl radicals (.OH) [1.3]. AOPs rely on in-situ production of highly reactive hydroxyl radicals.

These reactive species are the strongest oxidants and can perfectly oxidize any compound present in the water matrix. Hydroxyl radicals are produced from one or many primary oxidants like hydrogen peroxide, ozone, oxygen and/or from energy sources like ultraviolet light or catalysts like titanium dioxide. AOPs have the capability to reduce the concentration of contaminants from several hundred ppm to less than a few ppm and significantly bring the COD and TOC down [1.4].

Generally, chemistry in AOPs could be essentially divided into three parts:

1) Formation of • OH.
2) Initial attacks on targets molecules by • OH and their breakdown to fragments.
3) Subsequent attacks by • OH until ultimate mineralization.

However, specifically, AOPs have been defined as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification”.

1.3.1.1 **Advantages Of AOPs**

AOPs hold several advantages that are unparalleled in the field of water treatment:

- They can effective eliminate organic compounds in aqueous phase, rather than collecting or transferring pollutants into another phase.
- Due to the remarkable reactivity of • OH, it virtually reacts with almost every aqueous pollutant without discriminating . AOPs are therefore applicable in many, if not all, scenarios where many organic contaminants must be removed at the same time .
- Some heavy metals can also be removed in the form of precipitated M(OH)x.
- In some AOPs designs, disinfection can be achieved, which makes these AOPs an integrated solution to some water quality problems.
- Since the complete reduction product of • OH is H_2O, AOPs theoretically do not introduce any new hazardous substances into the water.

1.3.1.2 **Fenton Process**

Fenton processes are one of the oldest and widely used AOPs which enable degradation of organics in water into environmentally friendly products like CO_2, H_2O and/or inorganic salts via generation of hydroxyl radicals. Fenton reagent is the solution of hydrogen peroxide with ferrous ion as a catalyst that is used to oxidise contaminants or waste waters. Fenton’s reagent can be used to destroy organic compounds such as trichloroethylene (TCE) and tetrachloroetylene. It was developed in the 1890s by Henry John Horstman Fenton as an analytical reagent.[1.5]

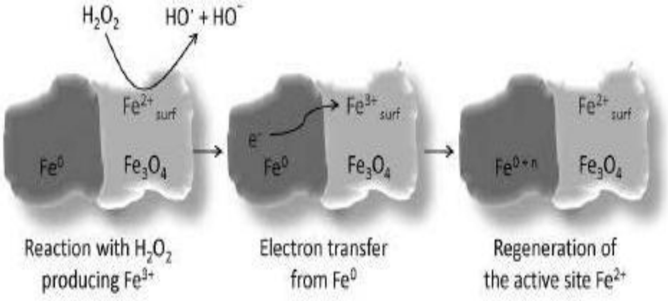


Figure 1.3 : schematic representation of electron transfer from Fe^0 to Fe^{3+} to regenerate Fe^{2+}

Figure 1.4 : degradation capability of fenton process

In Fenton process, $\bullet OH$ radicals are generated through the following reaction :

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH, \qquad (1)$$

Eq. (1) is recognized as Fenton reaction and implies the oxidation of ferrous to ferric ions to decompose H_2O_2 into hydroxyl radicals. It is usually considered as the core of the Fenton chemistry. The generated ferric ions are reduced to ferrous ions by reaction with excessive H_2O_2 and more radicals as shown in Eq (2), also known as fenton – like reaction.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^\bullet O_2H + H^+, \qquad (2$$

In Fenton like reaction, apart from ferrous ion regeneration, hydroperoxyl radicals (•O2H) are produced. The hydroperoxyl radicals may also attack organic contaminants, but they are less sensitive than hydroxyl radicals. It should be noted that, the iron added in small amount acts as a catalyst while H_2O_2 is continuously consumed to produce hydroxyl radicals. [2.5]

The following reactions are involved in Fenton chemistry :

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

This equation shows the scavenging effect of ferrous ions .

$$Fe^{2+} + {}^{\bullet}O_2H \rightarrow Fe^{3+} + HO_2^{-}, \qquad (4)$$

$$Fe^{3+} + {}^{\bullet}O_2H \rightarrow Fe^{2+} + O_2 + H^{+}, \qquad (5)$$

Eqs. (2) –(5) are the rate limiting steps in the Fenton chemistry since hydrogen peroxide is consumed and ferrous iron is regenerated from ferric ion through these reactions shown above.

$$HO^{\bullet} + H_2O_2 \rightarrow HOO^{\bullet} + H_2O \qquad (6)$$

This equation demonstrates the scavenging effect of hydrogen peroxide just like eq(3). , which indicates that it can clearly act as both, radical generator and scavenger.

$$RH + OH^{\bullet} \rightarrow H_2O + R^{\bullet} \qquad (7)$$

Hydroxyl radicals can oxidise organics (RH) by abstraction of protons producing organic radicals (R•) which are highly reactive and can be further oxidised as shown in eq (8).

$$R^{\bullet} + Fe^{2+} \rightarrow R^{-} + Fe^{3+} \qquad (8)$$

The Fenton and related reactions are considered as potentially convenient and economical ways to generate oxidizing species for treating chemical waste. Both Fenton's reagents i.e. hydrogen peroxide and iron possess advantageous properties. Compared to the other bulk oxidants, hydrogen peroxide is relatively safe, and does not make environmental threat since it readily decomposes to water and oxygen. Likewise, iron is comparatively inexpensive, safe, and environmentally friendly and is highly abundant .

Fenton process can be carried out at room temperature and atmospheric pressure. Apart from primitive fenton reagents, a combination of many other techniques such as electrochemistry, ultrasound, UV along with the classical fenton reagent is tested so as to enhance the production of hydroxyl radicals respectively known as electro-fenton(EF), sono-electro–fenton(SEF) and photo-electro-fenton(PEF) processes as the increased production of *OH radicals results in better decolourisation and degradation efficiency.

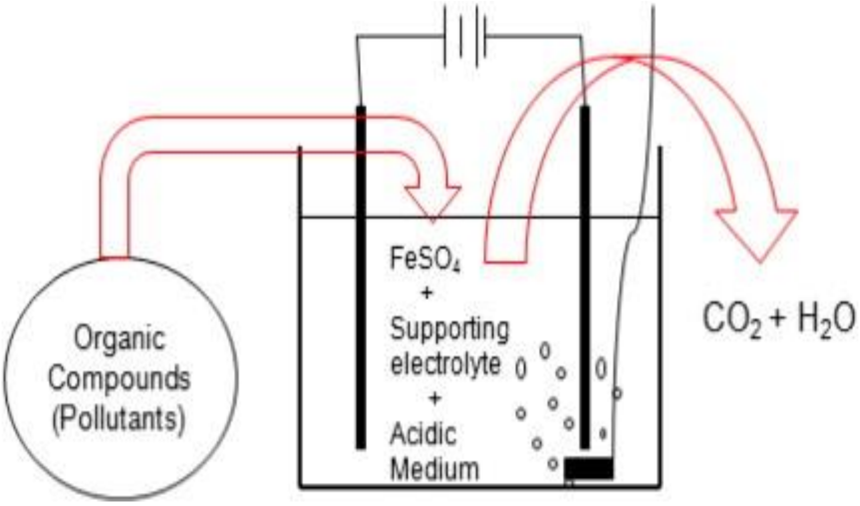


Figure 1.5 : schematic diagram for electro fenton process

There is a greater interest in the development of effective electrochemical treatments for the destruction of toxic and biorefractory organics. Anodic oxidation and indirect electro- oxidation are the most usual techniques utilized to achieve the mineralization of such pollutants. In anodic oxidation, pollutants are mineralized by direct electron transfer reactions or action of radical species (hydroxyl radicals) formed on the electrode surface as shown in Eq (9):

$$H_2O \rightarrow {}^{\bullet}OH_{ads} + H^+ + e^- \qquad (9)$$

This radical, is a powerful oxidizing agent, with an ability to react with organics giving dehydrogenated or hydroxylated derivatives.

In electro-Fenton (EF) process, pollutants are destroyed by the action of Fenton’s reagent in the bulk together with anodic oxidation at the anode surface. Electro-Fenton process is classified into four categories depending on Fenton’s reagent addition or formation. In type 1, hydrogen peroxide and ferrous ion are electro-generated using a sacrificial anode and an oxygen sparging cathode respectively . In type 2, hydrogen peroxide is externally added while ferrous ion is produced from sacrificial anode.

combination of hydrogen peroxide and UV radiation with Fe^{2+} or Fe^{3+} oxalate ion (photo-Fenton (PF) process) produces more hydroxyl radicals compared to conventional Fenton method or photolysis and in turn increases the rate of degradation of organic pollutants . Fenton reaction accumulates Fe^{3+} ions in the system and the reaction does not proceed once all Fe^{2+} ions are consumed. The photochemical regeneration of ferrous ions (Fe^{2+}) by photo-reduction (Eq. 10) of ferric ions (Fe^{3+}) occurs in photo- Fenton reaction . The newly generated ferrous ions react with H_2O_2 and generate hydroxyl radical and ferric ion, and the cycle continues :

$$\mathrm{Fe(OH)^{2+}} + h\nu \rightarrow \mathrm{Fe^{2+}} + {}^{\bullet}\mathrm{OH} \qquad (10)$$

Direct photolysis of H_2O_2 (Eq. 11) produces hydroxyl radicals which can be used for the degradation of organic compounds. However, in the presence of iron complexes, which strongly absorb radiation, this reaction will contribute only to a lesser extent for the photo-degradation of organic contaminants.

$$\mathrm{H_2O_2} + h\nu \rightarrow 2{}^{\bullet}\mathrm{OH} \qquad (11)$$

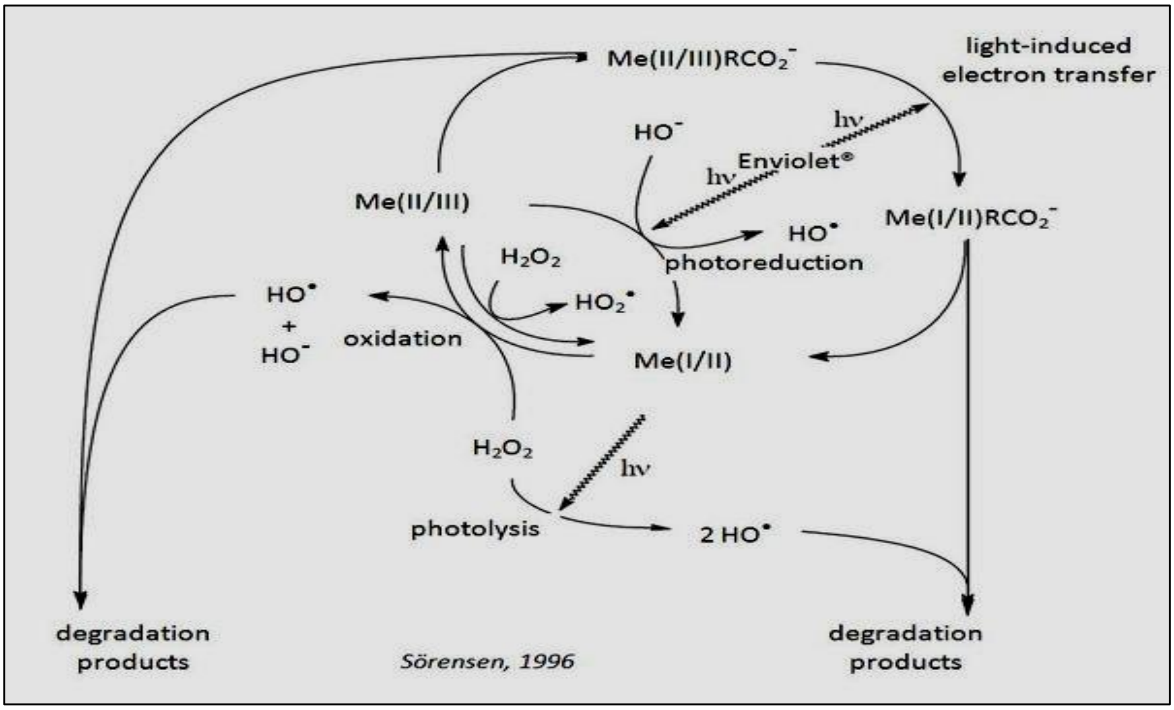


Figure 1.6 : mechanism for photo fenton process

The classical fenton process involves reaction in a homogenous phase known precisely as ***homogenous fenton process,*** where all the Fenton reagents are present in the dissolved phase. The main reagents or factors which can participate in a homogeneous Fenton reaction are H_2O_2, Fe(II), Fe(III), light (UV), and organic or inorganic ligands [1.6].

Reaction between dissolved Fe(II) and H_2O_2 in acidic aqueous solution leads to oxidation of Fe(II) to Fe(III) and consequently highly reactive hydroxyl radicals (•OH) are formed. The reaction is spontaneous and can occur without any external aid.

If the homogeneous Fenton reaction is initiated by Fe(III) & H_2O_2, the reaction rate would be slower than for Fe(II)& H_2O_2, because, in the former case, Fe(III) must be reduced to Fe(II) before hydroxyl radicals are produced. Such reaction is usually termed as "Fenton-like" process [1.7].

However, some major drawbacks were identified. The first is related to the wastage of oxidants due to the radical scavenging effect of hydrogen peroxide and its self decomposition. The second refers to the continuous loss of iron ions and the formation of solid sludge. Several economic and environmental drawbacks have been reported to occur with Fenton sludge . Also the range limit of pH has to be maintained between 2-5. Also an attempt has to be made for the recovery of iron ions and their subsequent recycle and reuse.

As mentioned above, a major disadvantage of using homogenous fenton process is the formation of iron sludge and its removal from the water prior to the end of the process. ***Heterogenous fenton processes*** comes as a scope of particular interest as the iron used here remains in the solid phase and can be easily removed after the process is completed. Furthermore reusability is also an important advantage of this process with the reactions occurring just the same as the classical fenton process. Heterogenous fenton reaction occurs at the mineral catalyst surface and the rate of production of hydroxyl radicals depend on the hydrogen peroxide concentration and the surface area of the iron oxide . Also it has been suggested that the mechanism of the heterogenous fenton reaction only starts at the surface and then continues mainly in the bulk of the aqueous solution with participation of dissolved iron species, just like the conventional homogenous fenton reaction.

1.4 Hydrogen Peroxide

Hydrogen peroxide (main reagent of the Fenton process) was first recognized by Thenard in 1818 as the product of the reaction of barium peroxide with nitric acid. In industries it finds use as a bleaching agent and disinfectant.

Previously , hydrogen peroxide was prepared industrially by hydrolysis of ammonium peroxydisulfate . today hydrogen peroxide is manufactured almost exclusively by the anthraquinone process , formalized in 1936 and hence patented in 1939. The economics of the process highly depends on effective recycling of quinone.

Owing to its low molecular weight, hydrogen peroxide is a more efficient oxidizing agent than other oxidants, such as nitric acid and sodium hypochlorite, hence very conveniently utilised in fenton process. However, its major disadvantage comes out not only from the side reactions, which require regeneration of the solution and the hydrogenation catalyst, but also from the separation steps involved in the removal of organic impurities from the hydrogen peroxide product; this makes it a costly and non-environmentally friendly process.

Chapter - 2

Literature Survey

Destructive chemistry has become the most demanding task in many plants, since detoxification of hazardous substances is now demanded in parts per million (ppm) and even parts per billion (ppb). Advanced oxidation processes (AOPs) are quite useful in treating wastes because of the generation of hydroxyl radicals, a powerful oxidant. The fenton reagent system is found to be used to treat effectively both laboratory based inorganic and organic substances as well as actual effluents from industries (Bigda, 1996) [2.1].

Murcia et al.,2009 [2.2] compared different oxidation processes for degrading 4 - Chloro phenol. Oxidation experiments were carried out using two 4-chlorophenol concentrations: 100 mg L-1 and 250 mg L-1 and UV generated from a KrCl excilamp with (molar ratio H_2O_2: 4-chlorophenol = 25:1) and without H_2O_2, and, with Fenton process (molar ratio H_2O_2:4- chlorophenol of 25:1 and Fe2+ concentration of 5 mg L-1). The experiment revealed that 4-chlorophenol concentration was totally removed with the three advanced oxidation processes as furnished : KrCl excilamp, KrCl excilamp with hydrogen peroxide and Fenton reagent. But a few intermediate photoproducts were also formed which had to be removed using the second method provided.

Chan & Chu, 2001 [2.3] modelled the reaction kinetics of fenton's process on the removal of atrazine(ATZ). A series of batch tests were conducted to analyse the degradation of ATZ under different conditions of fenton reagent(Fe(II):H_2O_2). The decay rates of ATZ
and the oxidation capacities of Fenton Reagent were found to depend on the concentrations of hydrogen peroxide and ferrous ion. A mathematical model was successfully developed to describe the two-stage reaction kinetics by using two simple but critical parameters: the initial ATZ decay rate and the final oxidation capacity of Fenton's process. In general, higher [Fe(II)] or H_2O_2 concentrations result in faster initial decay rate and higher oxidation capacity.

The removal kinetics of ATZ are initiated by a rapid decay and then followed by a much slower one .The studies revealed that higher concentrations of either of the two results in faster initial decay and oxidation capacity but there is a greater chance of occurrence of some side reactions that hinders in the degradation process. So an accurate evaluation of doses was advisory for a proper performance.

Similarly , Haddad et al., 2013 [2.4] tested the use of fenton reagent as advanced oxidative process for removing textile dyes from aqueous solutions. The paper presented optimum operation parameters for better decolorization efficiency & apart from obvious parameters like dosage of Fe(II), H_2O_2 concentration and pH, reaction time and temperature was also counted into the process. The optimum amounts of Fenton reagent was 25 mg/L of Fe^{2+} and 250 mg/L of H_2O_2 for an initial Reactive Yellow 84 concentration at 60 mg/L.

The ratio of Fe^{2+}/H_2O_2 is found equal to 0.1 to give the best result for the decolorization efficiency. The Fenton process was effective under pH 3 and the decolorization efficiency of Reactive Yellow 84 attained 85% for 20 min reaction time. Kinetics decolorization of RY84 followed pseudo second-order reaction.

Apart from the classical fenton process , fenton can be utilized in many combined fenton reactions to enhance the degradation chemistry . A review on fenton and its improvements for waste water treatment , Babuponnusami et al.,(2014) [2.5] revealed the fundamentals and main applications of methods like Fenton, electro-Fenton, photo-Fenton, sono-Fenton, sono-photo-Fenton, sono-electro-Fenton and photo-electro-Fenton and hence discussed the various possibilities of the typical fenton process developed to decolorize and degrade pollutants. This review also highlighted the application of nano-zero valent iron in treating refractory compounds. To increase the hydroxyl radical concentration in the bulk solution, Fenton and sonolysis can be combined together.

These methods utilize the advantages of ultrasound and Fenton’s reagent, allowing improved degradation of organic pollutants. In electro-Fenton (EF) process, pollutants are destroyed by the action of Fenton’s reagent in the bulk together with anodic oxidation at the anode surface. The study reports showed that the combination of Fenton reaction with conventional radiation zone of the visible and near ultraviolet gives a better degradation of organic pollutants. Pollutants such as 4-chlorophenol nitrobenzene and anisole , herbicides and ethyleneglycol were degraded effectively by photo-Fenton process. Similarly in case of sono- photo- fenton The direct photolysis (l < 400 nm) of H_2O_2 also generates hydroxyl radicals and the process is cyclic one with respect to Fe^{2+} ions.

In a study carried out to determine the applicability of fenton and photo fenton processes to combined industrial and domestic wastewater , Arslan & Öztürk(2009) [2.6] found that colour removal was obtained with oxidation but organic matter removal was achieved by coagulation in fenton treatment whereas as per the case of photo fenton, both colour and COD removal was obtained quite effectively under experimental conditions. The waste water used for the research was the influent of the 42 Elver Combined Wastewater Treatment Plant. The effects of different process variables such as initial Fe^{2+} (c_0 = 8-33 mmol L^{-1}) and H_2O_2 (c_0 = 65-165 mmol L^{-1}) concentrations, pH (3-7.75) and reaction time (*t* = 5-180 min) were evaluated. The Fenton process was investigated which under the operating conditions (pH 3, C_{Fe2+} = 12 mmol L^{-1}, C_{H2O2} = 130 mmol L^{-1}) 100 % color and 44 % total organic carbon (TOC) removal were achieved. However, 71 % TOC removal was achieved at pH 7.75 by coagulation but color was poorly removed (c = 20 mmol L^{-1} Fe^{2+}, c =165 mmol L^{-1} H_2O_2). In the photo-Fenton process, 84 % TOC and 87 % color removal were achieved in 30 min reaction time (pH 3, C_{Fe2+} = 26 mmol $L^{-1,}$$C_{H2O2}$ = 130 mmol L^{-1}).

Waste water can be treated by using both homogeneous and heterogenous fenton processes. Decolourization and mineralization of commercial reactive dyes by using homogenous and heterogenous fenton and UV fenton process, conducted by Papić et al., 2009 [2.7] showed the effect of each of the above mentioned methods on 3 organic dyes : Cibacron yellow, Cibacron blue and Cibacron violet. The conclusions drawn from the study were that system parameters played a quite effective role for the efficient degradation and the additional use of the UV lamp in the fenton processes enhanced the dye degradation . The mineralization and the decolourization rates depended on dye chemical structure and the processes used like the Cibacron violet decolourization was fastest in the UV homogenous fenton process. By using this process, the high levels of mineralization (78–84%) and decolourization (95–100%) were achieved. Pseudo-first-order degradation rate constants were obtained from the batch experimental data.

A review by Bokare et al. [2.8], illustrated the iron-free Fenton-like systems for activating H_2O_2 in advanced oxidation processes . Elements with multiple redox states (like chromium, cerium, copper, cobalt, manganese and ruthenium) all directly decompose H_2O_2 into HO• through conventional Fenton-like pathways. The in situ formation of H_2O_2 and decomposition into HO• can be also achieved using electron transfer mechanism in zero - valent aluminium /O_2system. Although these Fenton systems (except aluminum) work efficiently even at neutral pH, the H_2O_2 activation mechanism is very specific to the nature of the catalyst and critically depends on its composition. However, the experiments revealed that each non-ferrous catalyst has its demerits, which may offset the practical advantages of higher catalyst stability and working at neutral pH range. The cytotoxic nature of soluble species like cerium, chromium and cobalt seriously limits the extent of large-scale applications, with only restricted usage permitted in controlled reaction conditions (as demonstrated in the case of chromium).

Methyl orange being one of the many dyes present in industrial waste water , is carcinogenic and can be treated by heterogenous fenton process using steel industry wastes as carried out by Ali , Gad-allah & Badawy (2013) [2.9] . The iron containing wastes contains 90% iron as detected by atomic absorption spectrometer. To assess the catalytic activity of iron-containing waste as a catalyst for the degradation of MO via heterogeneous Fenton process, experiments were conducted under different reaction conditions; (1) H_2O_2 only, (2) catalyst only, and (3) catalyst and H_2O_2., where 98% decolourisation was obtained in the third condition revealing excellent catalytic activity. Moreover variation of pH was also experimented with , ranging 2 to 5 , where pH 2 gave the best result of complete decolourisation within 60 mins with respect to the batch runs conducted. Effect of catalyst and hydrogen peroxide concentrations were also considered. Decolourisation rate increased on increase of addition of catalyst as well as hydrogen peroxide but to a certain extent. Beyond that , more addition retarded the deolurisation rate. Different kinetic models were investigated to determine the exact rate equation that fits the experimental data.

Apart from primitive batch processes , initiatives were introduced to degrade dyes using continuous processes as treatment of textile effluents in continuous packed bed reactor studied by Duarte et al.(2013) [2.10] . The study was conducted with the treatment of textile effluents by the heterogeneous Fenton-like process in a fixed-bed reactor filled with a catalyst based on activated carbon impregnated with iron (AC/Fe). In a preliminary stage, the dye Alcian Blue-tetrakis (methylpyridinium) was used as model compound. the effect of the main operating conditions was analyzed, and the H_2O_2 dose, pH and temperature were optimized; the best conditions found using C_{AB},feed = 0.01 mM and a contact time of 3.3 g min ml^{-1} were: C_{H2O2},feed = 30.0 mM, pH = 2.5 and T = 50 ℃, with which it was achieved 93.2% of discoloration and 54.1% of total organic carbon (TOC) removal in the steady-state. It was verified that pH had a preponderant effect on the oxidation performance. Finally, the selected catalytic system was applied to the treatment of a real textile effluent used in the cotton dyeing. It was achieved almost total discoloration (96.7%) and a strong abatement of the TOC – 73.6%, as well as of the chemical oxygen demand (COD) – 66.3%, and biochemical oxygen demand (BOD5) – 72.5%. The iron leached reached very low levels in every run, which is a crucial factor for the catalyst long-term use.

Similarly Muqing Qiu et al. (2014) [2.11] experimented on Degradation of organic compounds by fluidized bed fenton process. In this paper, the treatment of the municipal landfill leachate from Shaoxing landfill was evaluated by using gas-liquid fluidized bed with Fenton reagent. The effects of various operating conditions such as treatment time, initial pH value, initial [H_2O_2], initial [Fe^{2+}]. The results revealed that 61% COD removals rate were obtained. It was distinctly proved that the organic compounds from the municipal landfill leachate could be treated effectively using fluidized bed Fenton process.

Chapter - 3

objectives

The objectives of this study is furnished as under :

- Optimization of influential process parameters such as pH, catalyst, feed and oxidant concentration in homogeneous Fenton reaction.
- Study of the above parameters with respect to heterogenous fenton reaction.
- Investigation of the mechanism of heterogeneous Fenton reaction in packed bed.
- Comparision of both heterogenous and homogenous fenton reaction in batch process as well as in continuous packed bed.
- Testification of the effectibility of catalyst used .

Chapter - 4

Experimental section

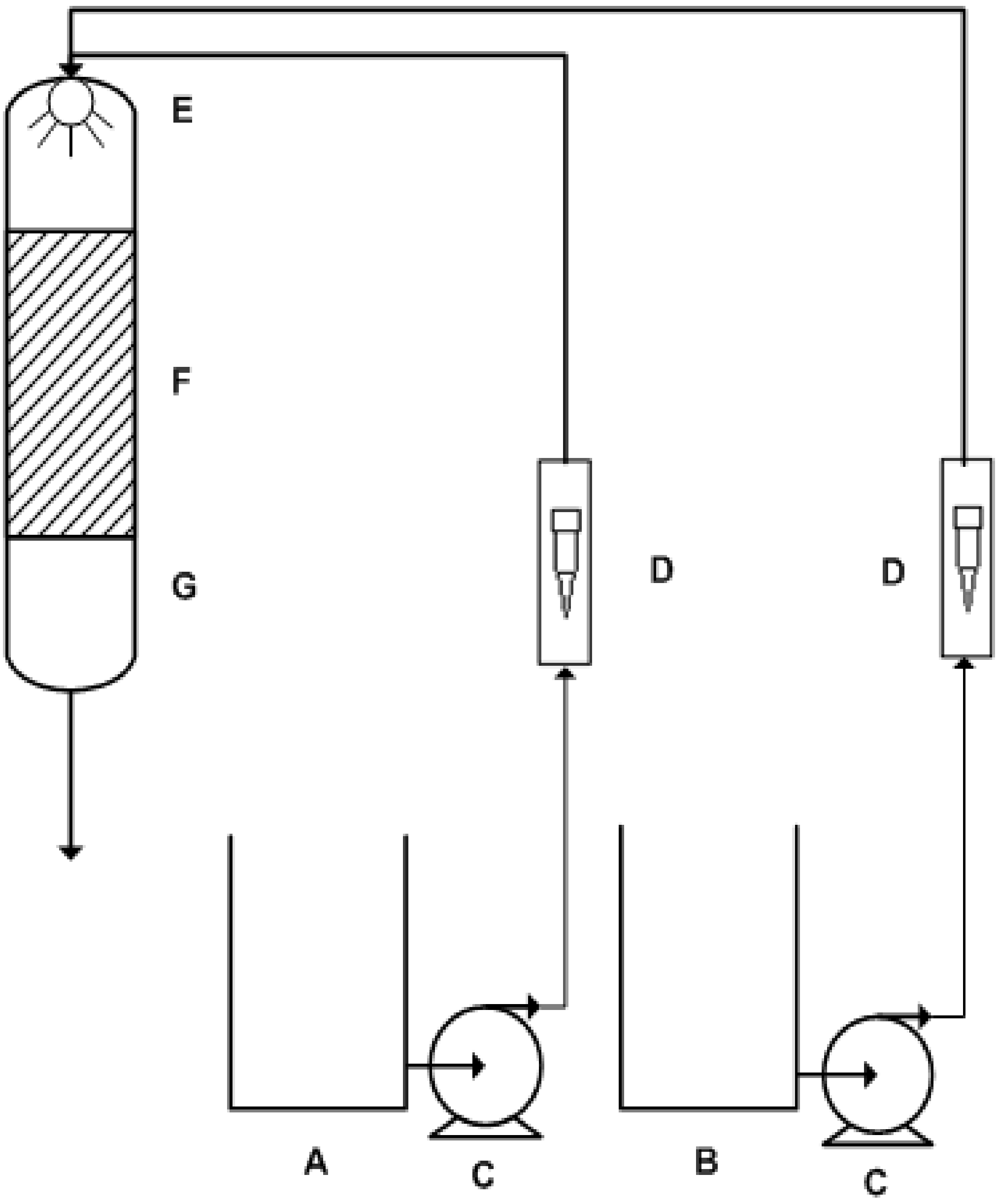
4.1 ***Materials :***

Methyl orange ($C_{16}H_{18}ClN_3SCl$) was obtained from Merck and its aqueous solution was prepared using distilled water. Iron(II) sulfate heptahydrate [$Fe(II)SO_4.7H_2O$] was used as the source of Fe^{2+} ions whereas hydrogen peroxide (30% H_2O_2) was used as an oxidizing agent. Sulfuric acid was used to adjust the pH and NaOH solution was used to stop the reaction. All the chemicals were used as received. Glass beads of average 4 mm diameter and discarded iron screws were used as packing material in homogeneous and heterogeneous Fenton process respectively.

4.2 ***Experimental setup :***

Fig. shows the schematic diagram of the experimental setup of the reactors used to study homogeneous Fenton process. A glass vessel equipped with an agitator Fig. was used for carrying out homogeneous Fenton process in batch mode . Packed bed studies were carried out in a tubular glass column of 3.5 cm diameter with a distributor mounted at the top . The bed was packed with glass beads placed on a support.

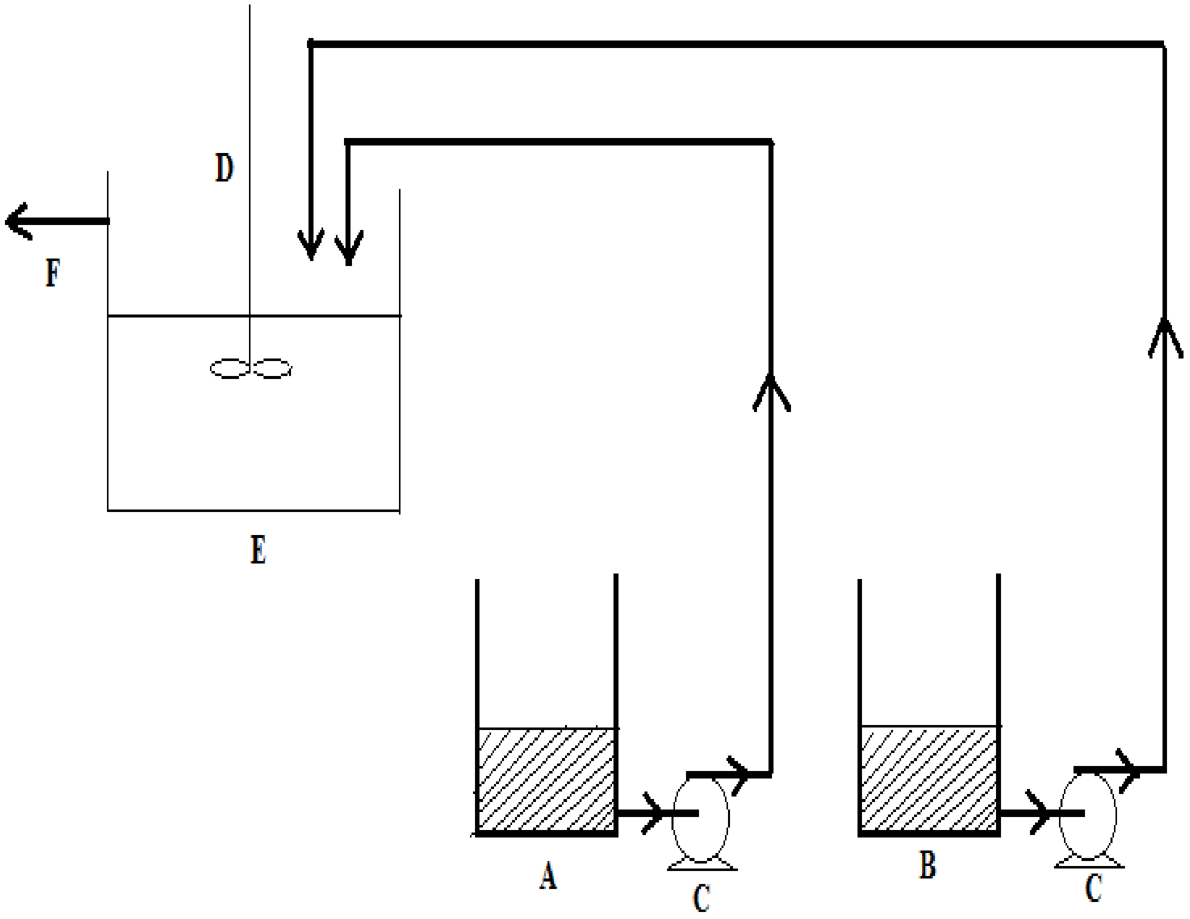
The schematic diagram and the original experimental setup for the packed bed is shown below :



A – Storage tank for dye solution containing catalyst, B – Storage tank for hydrogen peroxide, C – Pump, D – Rotameter, E - Distributor, F – Glass bead packed bed, G – Glass column

Figure 4.1 : Schematic for homogeneous Fenton process in fixed bed.

Figure 4.2: experimental setup for the packed bed study



A – Storage tank for dye solution containing catalyst, B – Storage tank for hydrogen peroxide, C – Pump, D –agitator, E –batch reactor, F – outlet

Figure 4.3: schematic for homogeneous Fenton process in batch reactor.

Figure 4.4 : labaratory experimental setup for batch study

Experimental setup of packed bed and batch reactor for heterogeneous Fenton process was same as that used for homogeneous Fenton. Discarded Iron screws that were used to serve the purpose of catalyst instead of Iron(II) sulfate solution , were used as the packing material.

4.3 ***Experimental Procedure :***

In homogeneous Fenton experiments, an aqueous solution of Methyl orange (MO) containing desired amount of catalyst concentration was kept in a storage vessel. The pH of dye solution was adjusted by concentrated sulfuric acid. Hydrogen peroxide solution was stored in a separate reservoir. Both the streams were fed separately into the packed bed and were allowed to fall down along the bed packed with glass beads. The exiting stream was then collected at different time intervals .

Homogeneous degradation reaction was also studied in batch reactor. In this equipment, samples drawn at a given experimental time were collected at different locations in the solution and averaged.

Heterogeneous Fenton process was carried out by feeding a solution of dye and hydrogen peroxide over the bed of iron screws. Process parameter optimization for heterogeneous Fenton process was carried out in batch experimentation and reaction mechanism was investigated in packed bed column.

4.4 ***Method of analysis :***

One drop of 0.5 N NaOH solution was added to the sample to stop the reaction. The residual concentration of dye was analyzed using UV-Visible spectrophotometer (Thermo Scientific Genesys 10S UV-Vis) at a wavelength of 465 nm. The experiments were performed at room temperature (~ 25 ^{o}C).

Iron content in effluent was measured by standard redox titration. Concentration of hydrogen peroxide in effluent was determined spectrophotometrically using potassium titanium oxalate reagent. Titanium reagent was prepared by mixing 272 mL of concentrated sulfuric acid with about 300 mL of distilled water and dissolving in this mixture 35.4 g of potassium titanium oxalate followed by making up the total volume to 1 L. 5 mL of sample was mixed with 5 mL prepared reagent and the volume was made upto 25 mL. the absorbance of solution was then measured at 400 nm wavelength using UV-Vis spectrophotometer. The concentration of hydrogen peroxide was measured by the formula :

$$[H_2O_2] = \frac{(A_t - A_b)}{37.4 \times V \times L} \tag{12}$$

where, A_t and A_b are the absorbance of the test and blank solutions (without H_2O_2) respectively, V is the volume of sample (mL) and L is the path length of the spectrophotometer cell (cm).

4.5 Mathematical modelling :

At steady state, the rate of change in dye concentration, $\left[MO\right]$ due to reaction within packed bed of volume, dV assuming plug flow can be written as

$$Qd\left[MO\right] = -R_n \phi dV_c \qquad (13)$$

where, Q is the liquid flow rate and ϕ is the average liquid holdup. The above equation takes the following form assuming pseudo first order reaction kinetics i.e.

$$R_n = k_1\left[MO\right] \qquad (14)$$

$$\frac{d\left[MO\right]}{\left[MO\right]} = -\frac{k_1}{Q}\phi dV_c \qquad (15)$$

where, k_1 is the pseudo first order constant. Integration between the inlet and outlet of the contactor yields

$$\ln\frac{\left[MO\right]_e}{\left[MO\right]_i} = -\frac{k_1\phi V_c}{Q} \qquad (16)$$

where, $\left[MO\right]_i$ and $\left[MO\right]_e$ represents the inlet and outlet concentration of methyl orange from the contactor, and V_c is the reactor volume.

Chapter - 5

Results and Discussion

Results are displayed for homogenous and heterogenous fenton processes in both batch and continuous mode (packed bed) . All the parameters effecting the degradation of the dye is taken into consideration.

5.1 ***Homogenous fenton process :***

Homogenous fenton process for the degradation of dye is studied primarily in batch mode and then the optimum results obtained for different parameters is applied in the continuous mode (packed bed).

pH : The effect of variation of pH on % discoloration can be viewed in fig. 5.1 . it clearly shows that there's a decrease in % degradation from 98.74% to 94.20% when the pH was increased from 2.25 to 2.75. Furthermore when the pH was elevated to 3.25 there's a sharp decline in % degradation to 64.09% which precisely indicates that high value of pH hinders the degradation efficiency. The reason for the above mentioned phenomena can be estimated to be the formation of inactive iron oxohydroxides which in turn causes low production of hydroxyl radicals hence decreasing their oxidation potential [2.5]. On the contrary the higher production of Fe^{2+} ions at lower pH results in an increased formation of ·OH radicals thus causing better degradation [5.1].

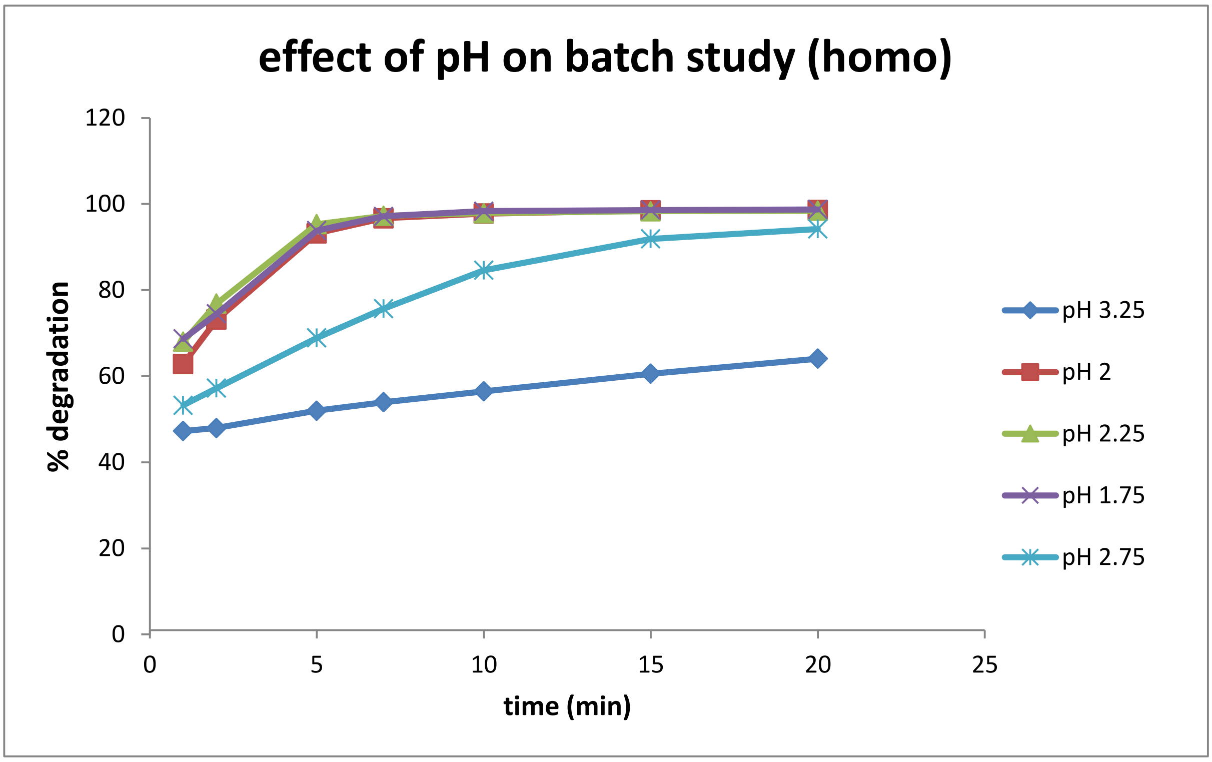


Figure 5.1: Effect of pH of initial solution on dye degradation.

<u>Catalyst concentration :</u> the presence Fe^{2+} ions plays a crucial role in MO degradation. The effect of variation of catalyst concentration is shown in fig.5.2. the notable increase in the the degradation of MO can be visualised with the increase of initial catalyst concentration from 0.5 L to 0.075 L . the regeneration of ferrous ions with excess H_2O_2 can be shown by the following reaction :

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\bullet} + H^{+}$$

The slower rate of regeneration as compared to the higher rate of formation might conceivably tend the reaction to depend solely on the initial catalyst concentration. The high concentration of Fe^{2+} ions tend to increase in the production of ·OH radicals which results in the improvement of the degradation efficiency. The minute change visible when the $FeSO_4$ concentration was increased to 0.1 L may be because of excess ferrous ions act as a hydroxyl ion scavenger [5.2] as shown in the following reaction:

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

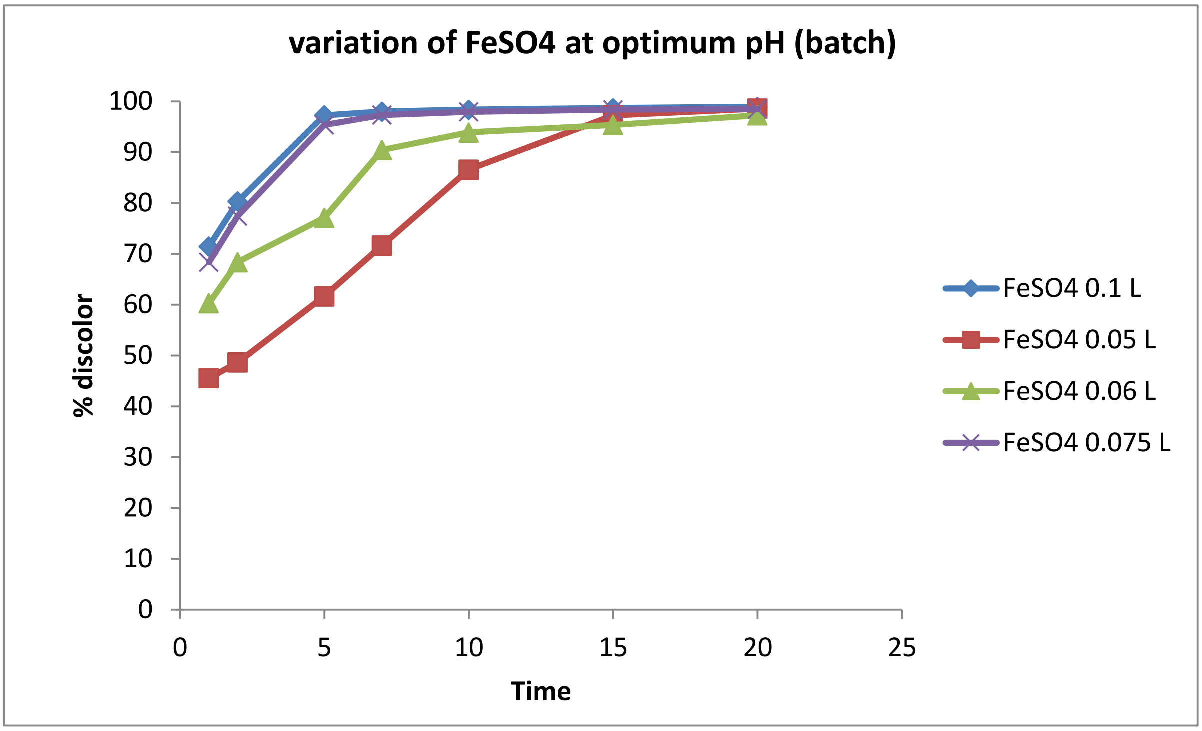


Figure 5.2 : Effect of catalyst concentration on dye degradation

H2O2 Concentration : fig 5.3 shows the increase in % degradation when the H_2O_2 concentration was elevated from 0.025 L to 0.045 L , due to higher amount of •OH radicals generated. The degradation percentage decreased to 93.45% when the H_2O_2 concentration was further raised to

0.075 L. This decrease of percentage may be due to the scavenging effect of H_2O_2 and its self – decomposition [5.3] as shown in the following reactions:

$$HO^{\bullet} + H_2O_2 \rightarrow HOO^{\bullet} + H_2O$$

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

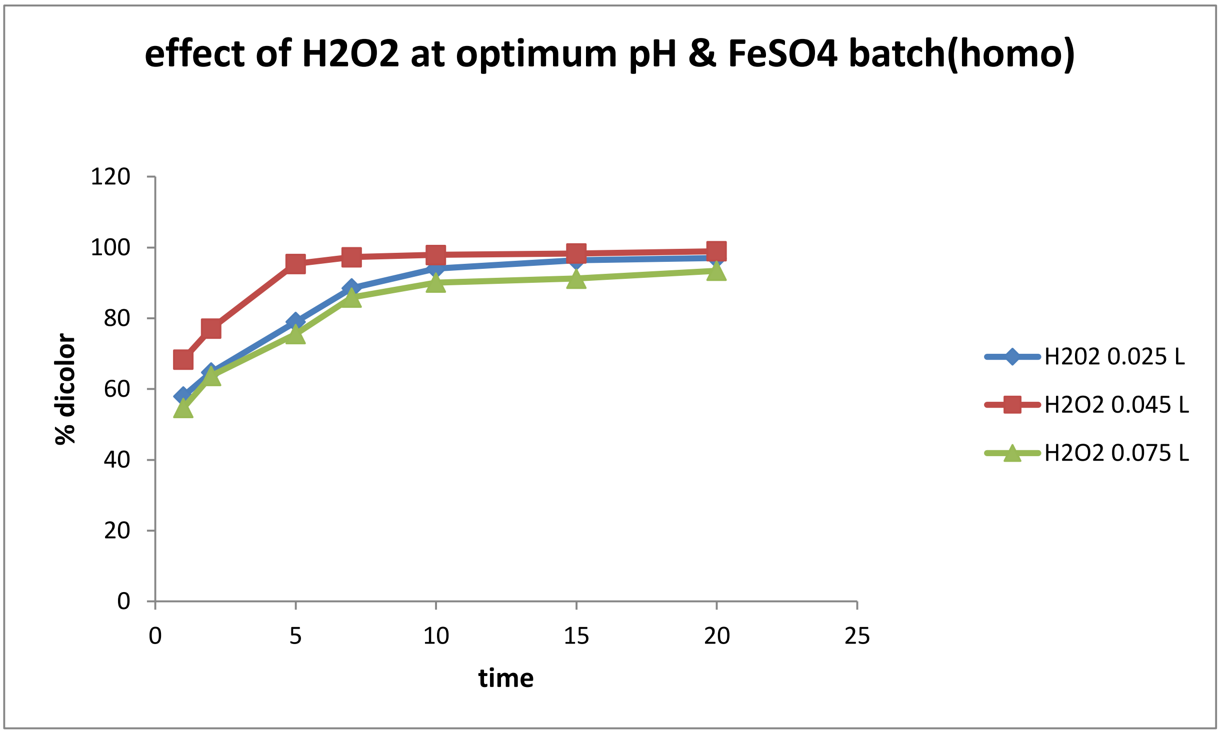


Figure 5.3: Effect of oxidant concentration on dye degradation

<u>Effect of agitator speed :</u> agitator speed was varied ranging from 250 to 4000 rpm. It is visible that with the increasing agitator speed, the % degradation increases. This observation might occur as micromixing is noted to increase with rotational speed [5.4]. This effect of rotational speed can be

incooperated in case of many continuous reactors as increase of speed leads to higher degradation though it should also be noted that dye degradation extent within the reactor is also a function of time. As in continuous mode the available reaction time would decrease with the increase in rotational speed.

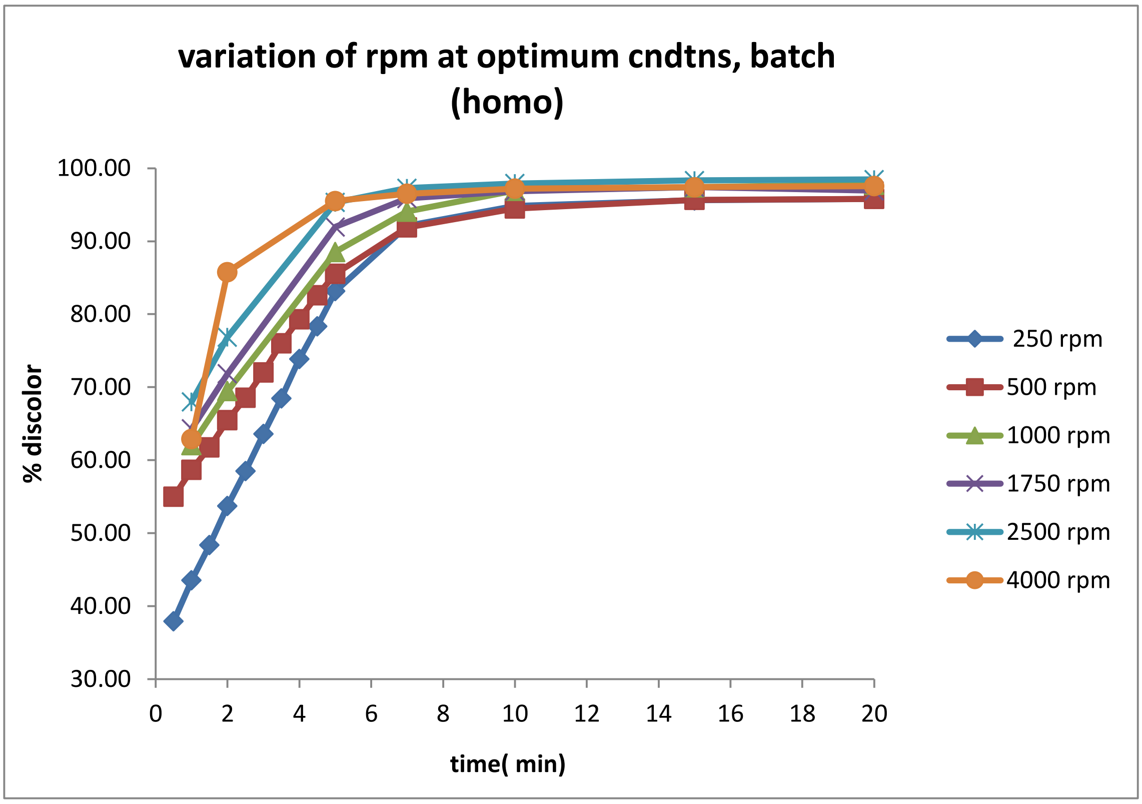


Figure 5.4 : Effect of agitator speed on dye degradation.

Assuming that degradation of MO can be represented by pseudo first order kinetics i.e. Eq 13, the change in MO concentration with time can be represented by :

$$\ln \frac{[MO]}{[MO]_i} = -k_1 t \tag{14}$$

The plot of $\ln \frac{[MO]}{[MO]_i}$ versus time for some of the experimental conditions is given in Fig 5.5 .

The value of R^2 in all cases was ~ 0.98. The figure also indicates that the constant k_1 is dependent on experimental parameters.

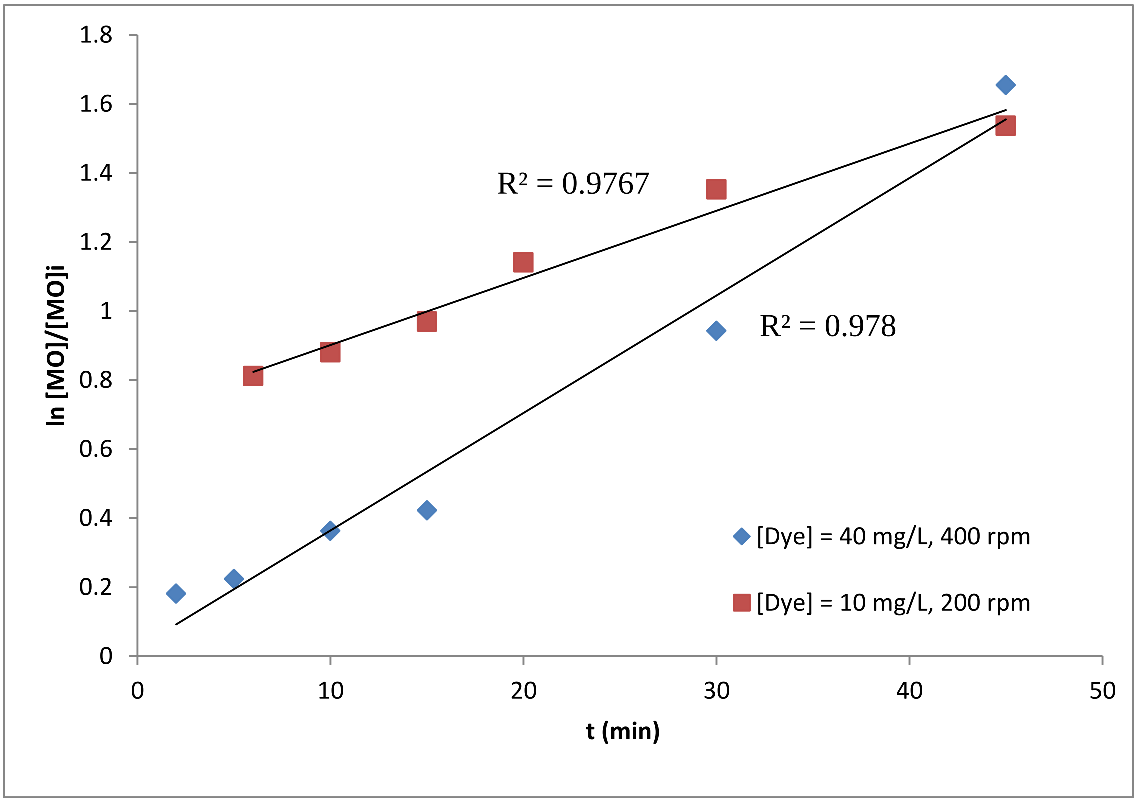


Figure 5.5: Pseudo first order rate constant in batch process.

pH	1.75 – 2.25
Catalyst Concentration	0.075 L of 0.2g/L in 0.5 L of dye conc. 20mg/L
H2O2 Concentration	0.045 L of 24mM in 0.5 L of dye conc. 20mg/L
Agitator speed	1750 - 4000 rpm

Table 2 : Values of operating parameters in the study obtained from batch data

As from the optimum parameters set from the batch study, it was clearly understood that fenton reactions is likely to give best results at 1.75-2.25. It is known that fenton reactions give optimum results at a pH of 2-3 [2.5]. Here in the continuous process i.e in the packed bed study the dye concentration was varied along with the H2O2 concentration in the pH study itself so as to confirm that the pH acts as an independent property . from fig 5.6 & fig 5.7.Its distinctly perceptible that in both the cases the degradation efficiency was diminished when the pH was increased from 2.25 to 2.5 & it dropped sharply from 84.43% to 60.07% in fig 5.6 and from 38.21% to 29.71% in fig 5.7 when further the pH was raised to 2.75.

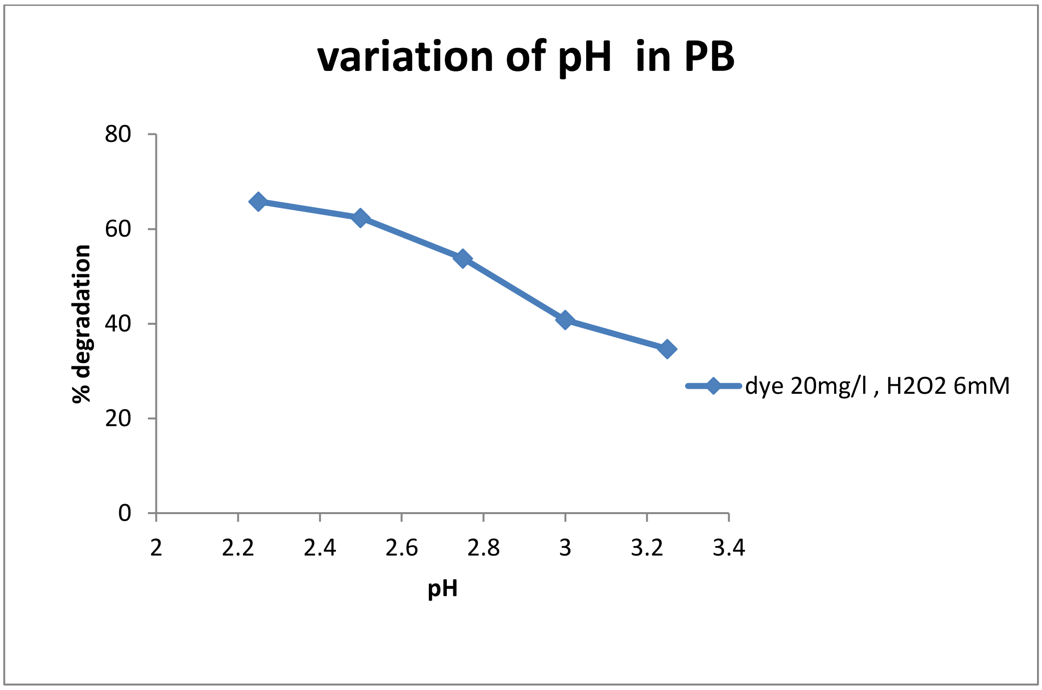


Figure 5.6 : Effect of pH of initial solution on dye degradation in packed bed.

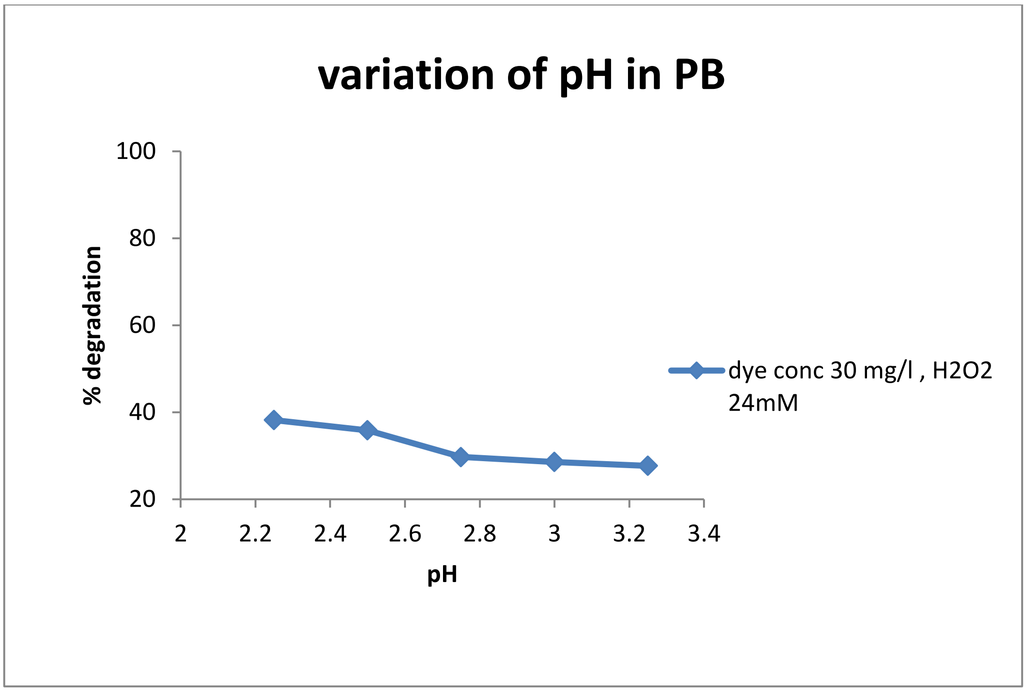


Figure 5.7 : Effect of pH of initial solution on dye degradation in packed bed.

As being a continuous process , flow rate also plays a very crucial role in the dye degradation efficiency .From fig 5.8 it can be concluded that at the lowest flow rate i.e at 250 LPM, degradation efficiency is highest which gradually decreases with the increase of LPM. The reduction continues as the flow rate is increased to 0.5 LPM, O.75 LPM at finally to 0.875 LPM. This may be because at the lower rpm, the reactants are getting more reaction time and a better mixing efficiency is achieved as they slither down through the bed but with increasing flow rate, this ability gets diminished [5.4].

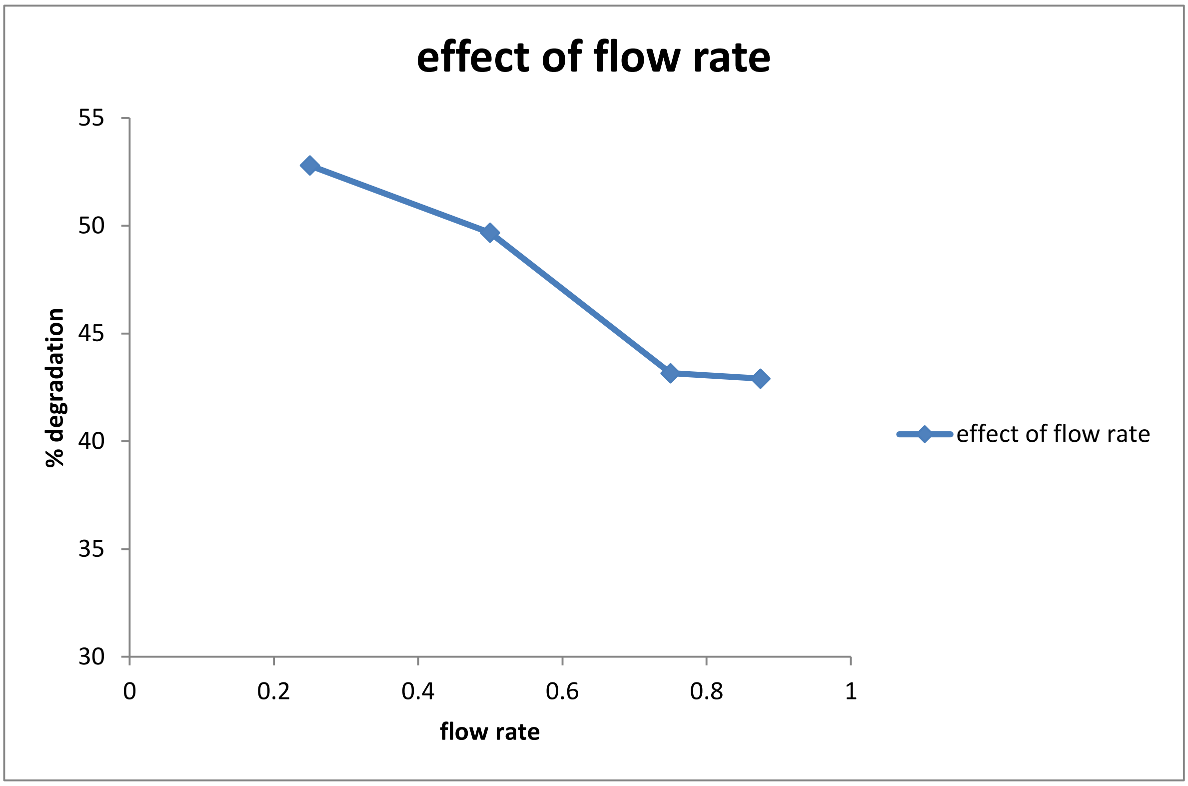


Figure 5.8: Effect of flow rate on dye degradation

The degradation efficiency depends greatly on the concentration of Fe^{2+}. As shown in the batch study , the formation of Fe^{2+} ions is quite high than its regeneration.

The effect of catalyst concentration on % degradation is represented in fig 5.9. The % degradation of Methyl Orange increased significantly from 28.70% to 65.435% when the catalyst concentration was increased from 5 mg/L to 24 mg/L . A marginal increase was also viewed when the Fe^{2+} concentration was further increased to 32 mg/L, the cause may being the scavenging effect of hydroxyl radicals by excess ferrous ions.

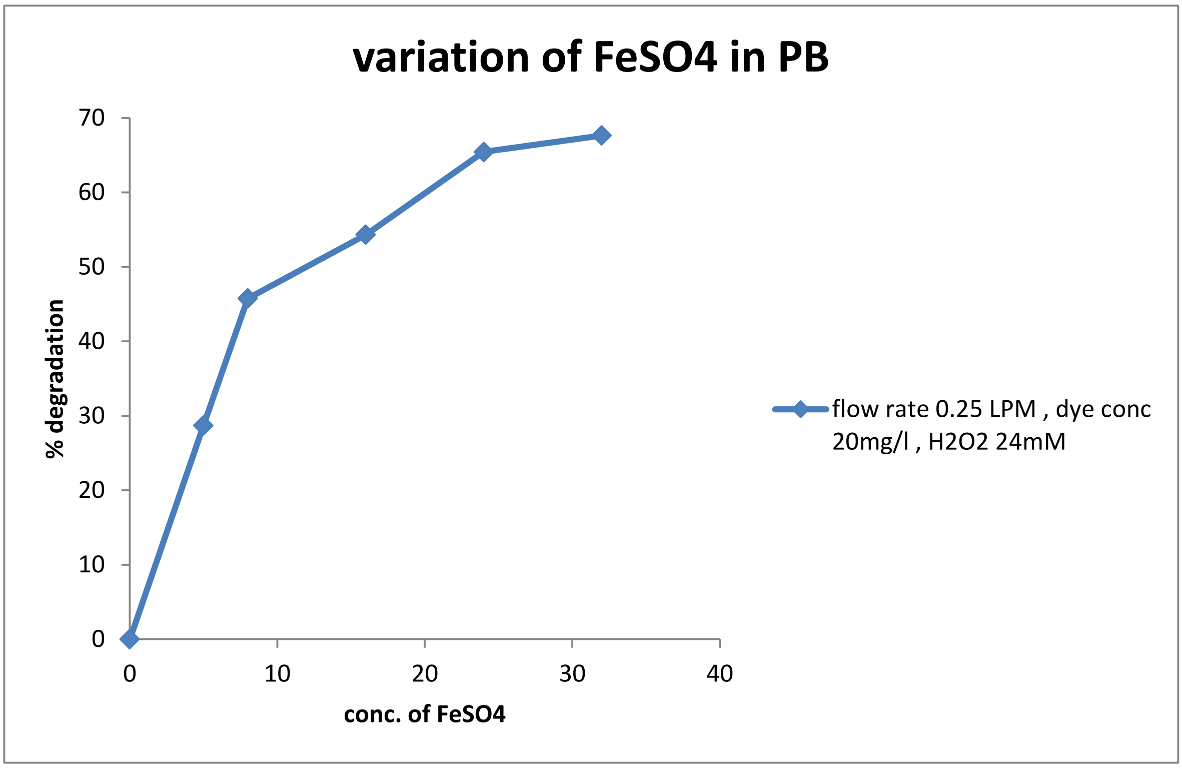


Figure 5.9 : Effect of catalyst concentration on dye degradation in packed bed

Percentage degradation was found to increase when the H_2O_2 concentration was augmented from 1 mM to 6mM. The % degradation increased from 32.56% to 67.45% but subsided to 63.6 % when the H_2O_2 concentration was further increased to 24 mM. Identical optimum values of H_2O_2 concentration have been reported in different studies related to this particular one [5.5].

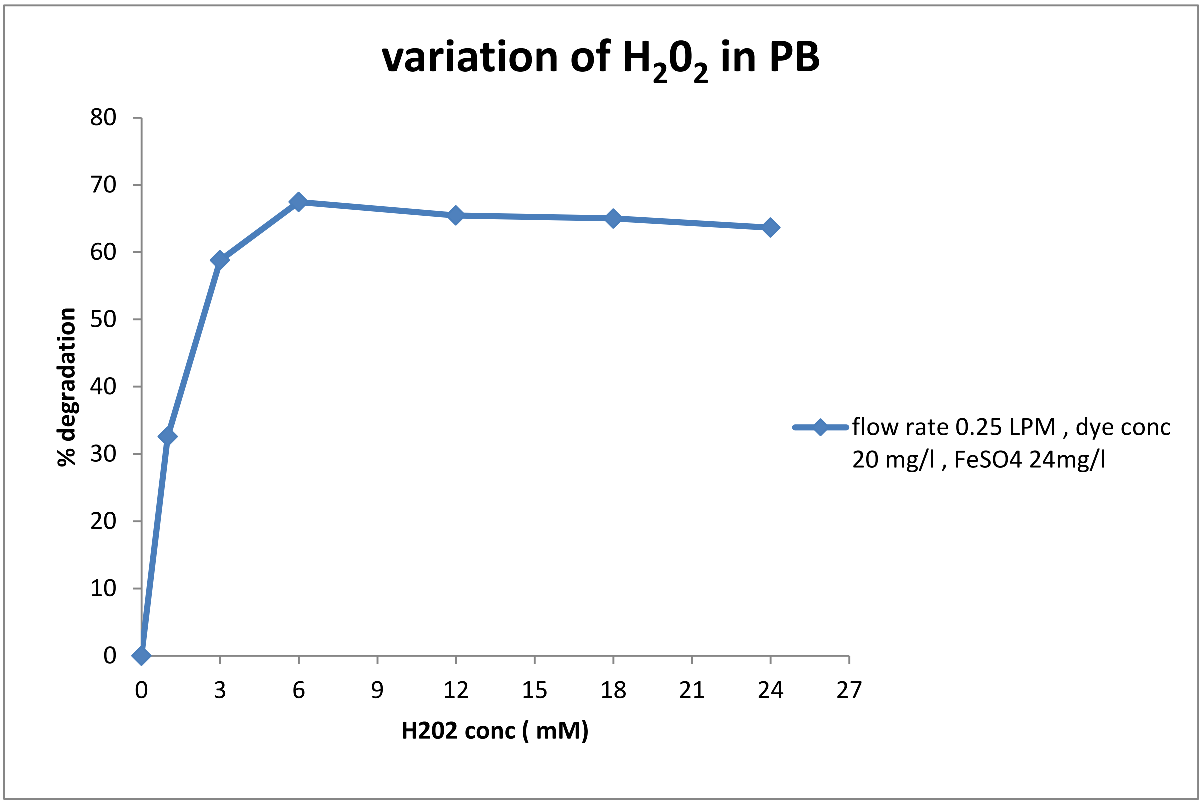


Figure 5.10: Effect of oxidant concentration dye degradation in packed bed

5.2 ***Heterogenous fenton process :***

In case of Heterogeneous Fenton reaction, soluble Fe^{2+} catalyst is replaced by Fe-containing solids. This kind of Fenton reaction has been proved to be also effective in the treatment of industrial wastewater containing non-biodegradable organic pollutants .This process was conducted similar to the homogenous study, i.e in both batch and continuous processes .

pH : Preliminary batch studies were conducted as carried out in case of homogenous fenton. The effect of pH is depicted in fig 5.11. The pH was varied from 2.25 to 4. It was seen that the dye degradation increased by 82% at initial pH 2.25 and by 10% at initial pH 4 after 10 min.

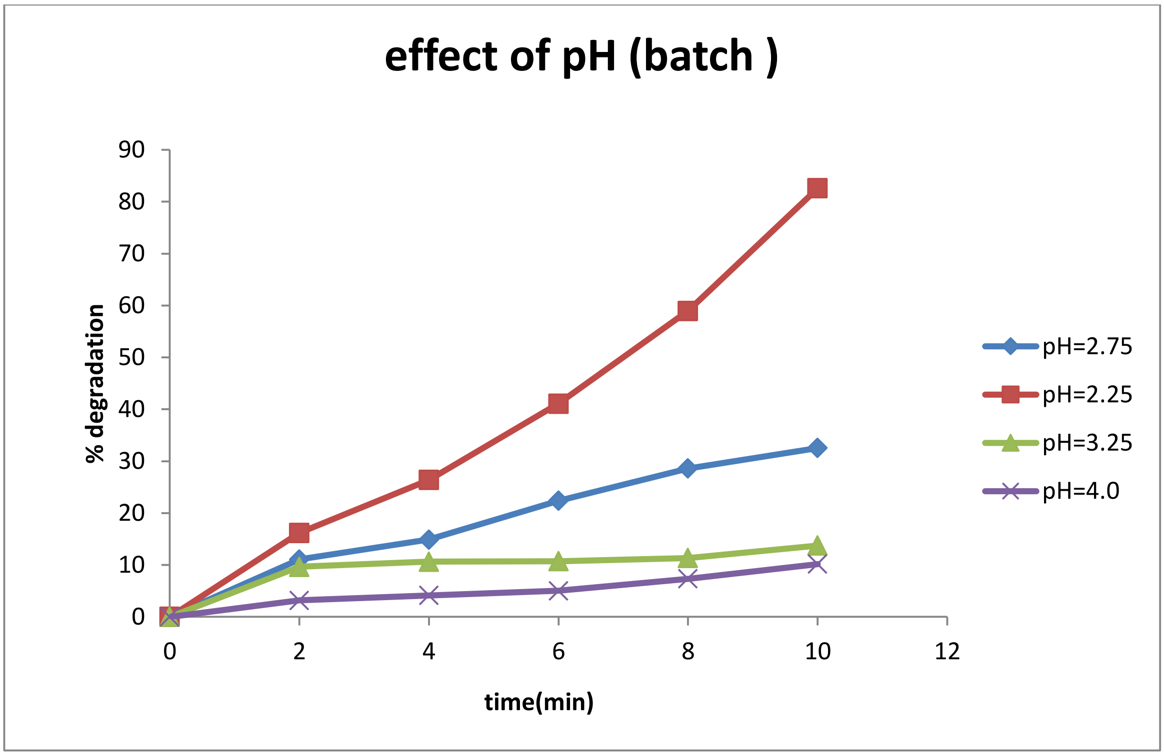


Figure 5.11: Effect of pH on dye degradation efficiency.

H_2O_2 Concentration : The effect of H_2O_2 concentration was demonstrated in fig.5.12. Its clearly visible that the dye degradation increased slightly from 56.4% to 57.6% when H_2O_2 concentration was varied from 15 mM to 30 mM and then decreased on further increase of H_2O_2 to 45 and 60 mM respectively .The occurrence of this phenomena being the same as in the homogenous fenton process.

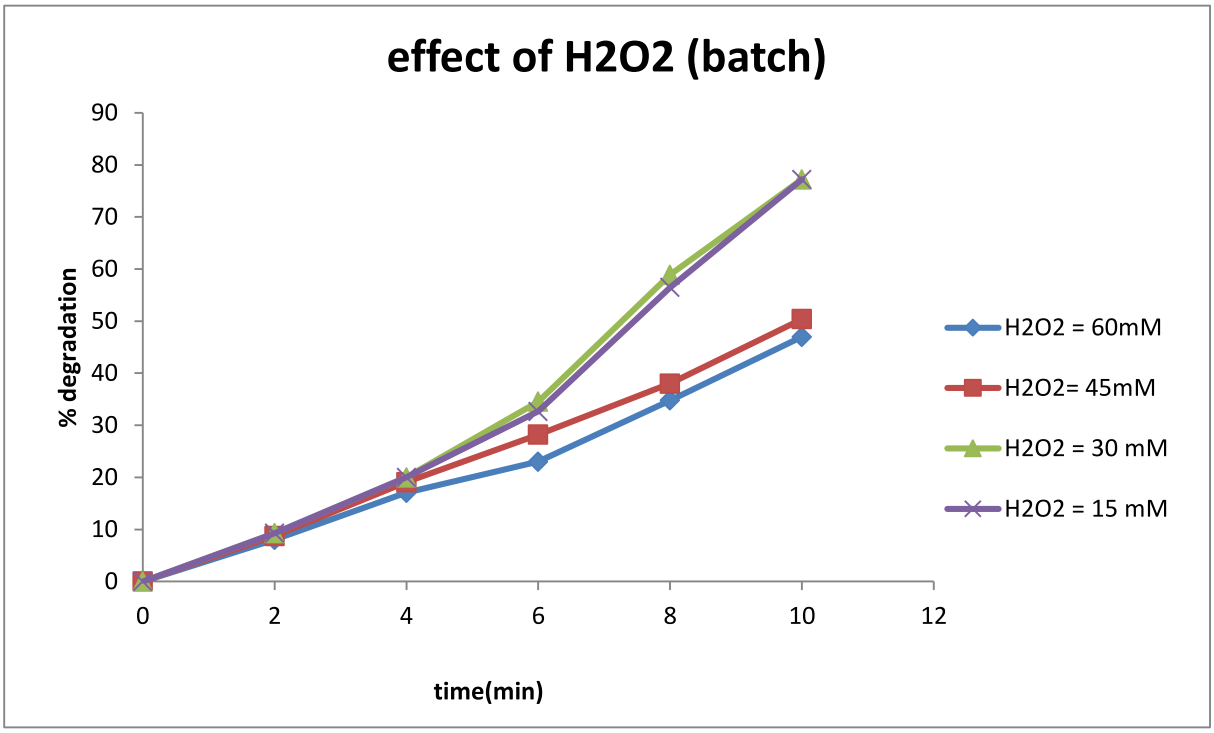


Figure 5.12: Effect of H_2O_2 concentration on dye degradation

In the classical fenton reaction, only catalytic degradation of methyl orange is apparent but in fenton-like reaction i.e heterogenous reaction both adsorption and catalytic degradation occurs. Thus, the removal of dye could be either due to adsorption onto the particle surface or homogeneous Fenton reaction in the solution phase.

Equilibrium adsorption studies were carried out to determine the equilibrium uptake capacity of the particles for methyl orange.

The amount of dye adsorbed at equilibrium q was calculated by the following equation:

$$q = \frac{(\mathrm{C0} \ - \mathrm{Ce})\mathrm{V}}{\mathrm{W}} \qquad (15)$$

&

Percentage (%) removal of dye can be calculated by :

$$p = \frac{(\mathrm{C0} \ - \mathrm{Ce})}{\mathrm{C0}} * 100 \qquad (16)$$

where, Co and Ce are the initial and equilibrium concentration of dye in the liquid phase respectively, V is the volume of the solution and W is the mass of dry adsorbent used.

The adsorption data was fitted into the following isotherms : linear , langmuir , freundlich and temkin so as to examine the relationship between amount of dye adsorbed (qe) and equilibrium dye concentration in aqueous phase (Ce). The results are demonstrated in figures 5.13. ,5.14, 5.15 & 5.16.

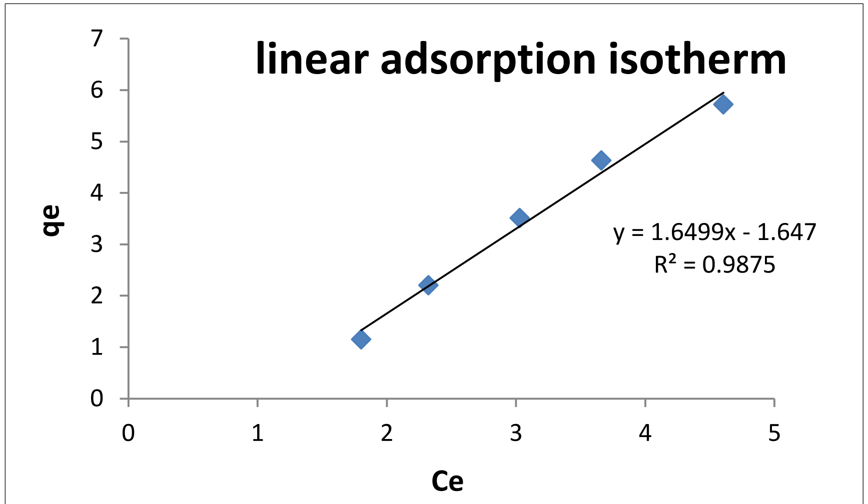


fig 5.13

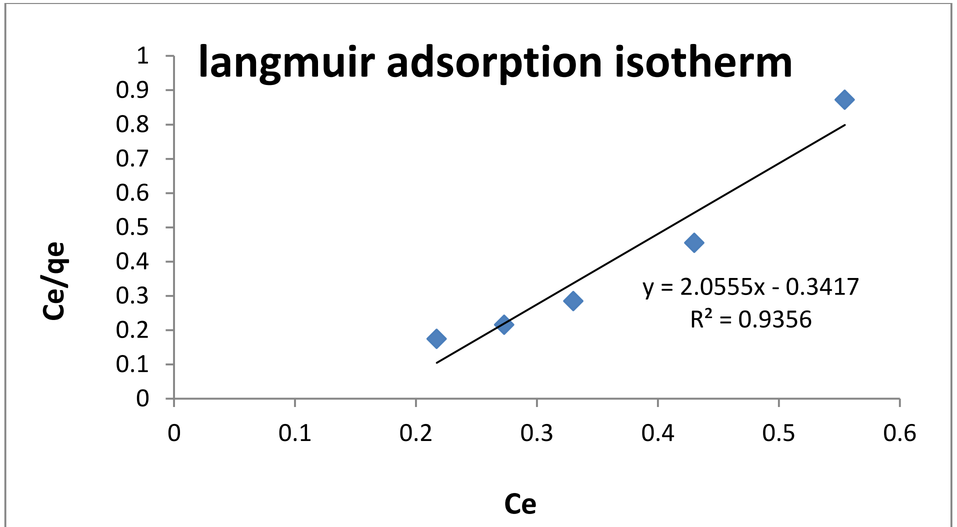


fig 5.14

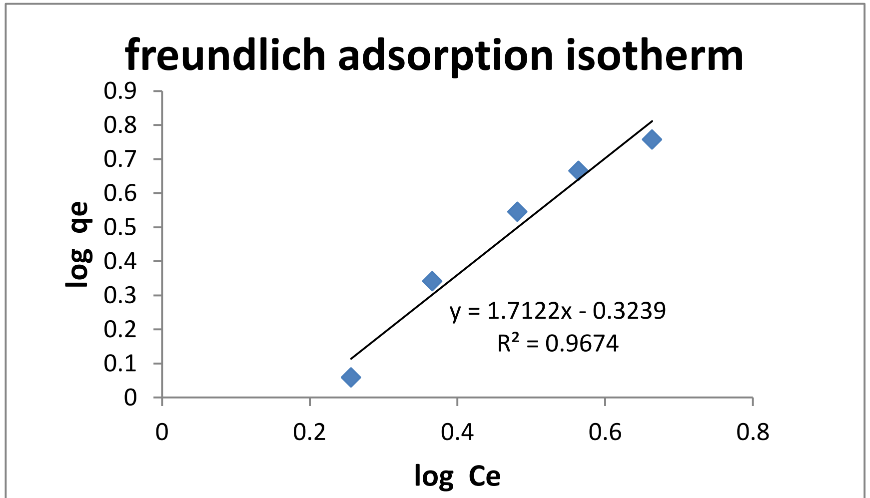


fig 5.15

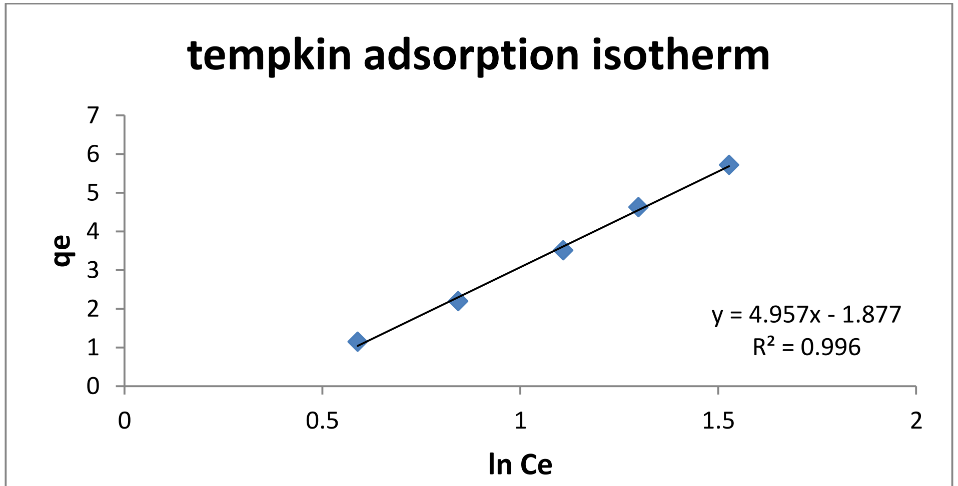


fig 5.16

adsorption isotherms

The packed column was filled up with discarded iron screws and the study was conducted. Because of a massive amount of screws packed up in a narrow and congested area, it was analysed that perhaps apart from just degradation, as already discussed adsorption was also affecting the dye removal and that the dye was being adsorbed by the metallic rough surface of the screw. So pH variations were overseed so as to inspect the effect of adsorption at different pH ranges. From fig 5.17 it is visible that around 47% adsorption occurred at pH 2 whereas the adsorption rate decreased at pH 3 to around 37% and a steep decrease in adsorption was noted when the pH was further raised to 3.5 showing an occurrence of adsorption and an obvious effect of pH on the phenomena.

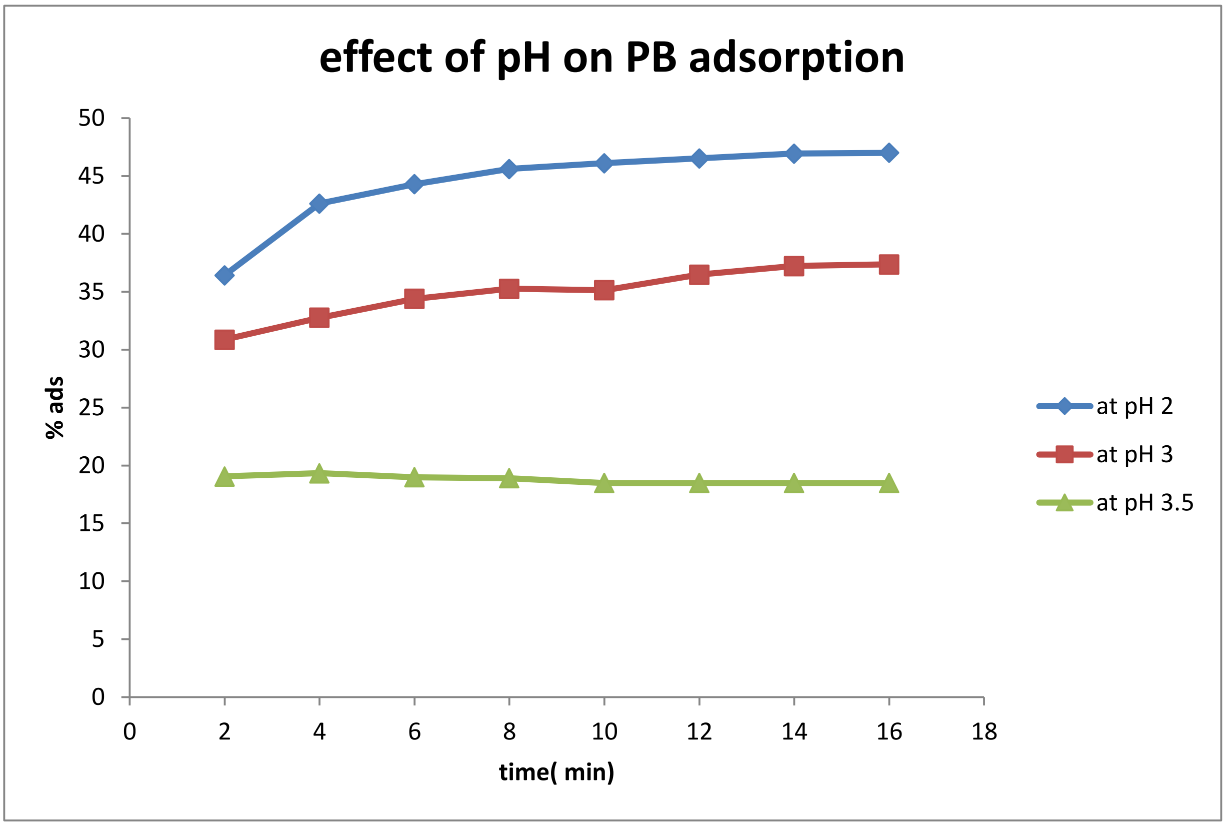


Figure 5.17: Effect of pH on adsorption capacity of iron screw

After the effect of pH was tested on the adsorption study, it was repeated on the study of dye degradation as shown in fig. 5.18, the degradation efficiency increased massively from 41.37% to 77.65% when the pH was lowered to 3 and further raised to 97.4% when reduced to 2 .

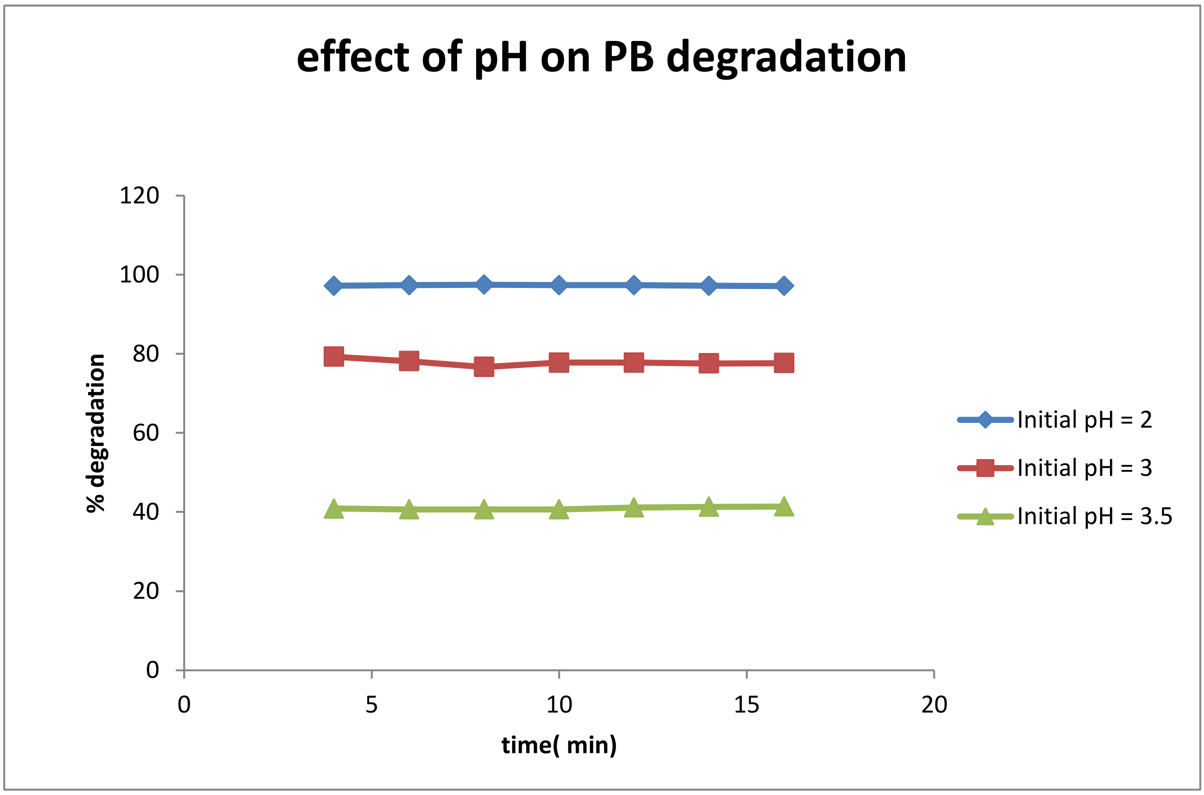


Figure 5.18: Effect of pH on degradation efficiency of iron screw

Effect of bed height of the packed bed was also examined . 4 different bed heights were considered to obtain a precise result. once the bed height was increased from 11.2 cm to 24.7 cm , the % adsorption rose up to 36.23% and then to 47% on further increase of bed height to 30.6 cm.

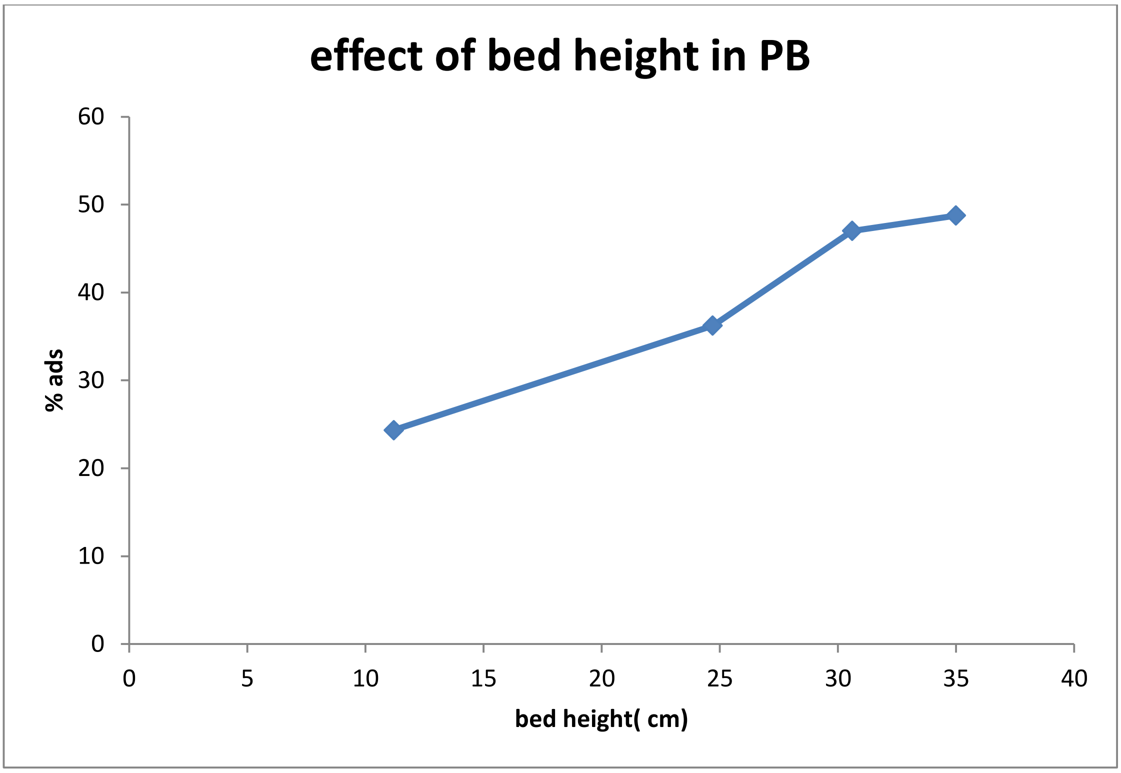


Figure 5.19: Effect of bed height in packed bed

Furthermore the reusability of Fe waste was also tested in batch process so as to estimate the time capacity prior to which a single batch of discarded screws could be used. the results were obtained as shown in fig 5.20.

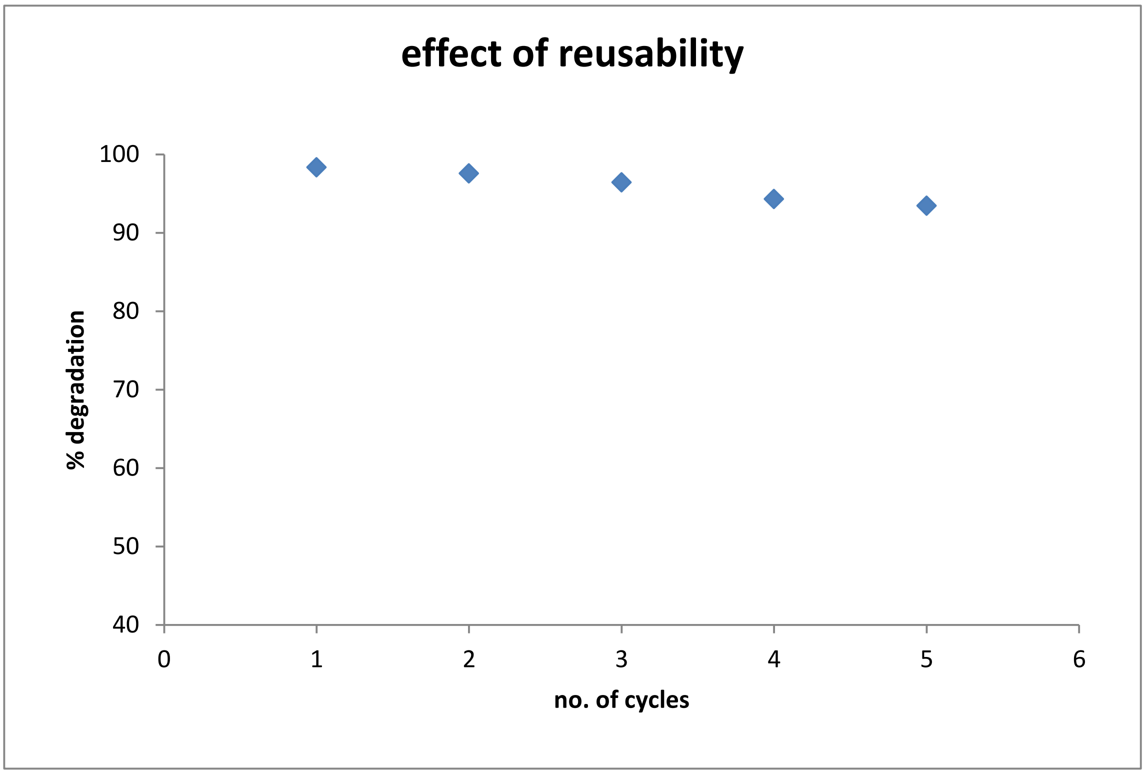


Figure 5.20 : effect on degradation efficiency by reusability of iron waste

Figure 30 clearly stipulates that the iron waste (discarded screws) can be used around 3-4 times [2.9] though the activity decreased gradually during successive runs. However, the removal rate was rather comparable for all the runs at longer reaction times. Around 94 % decolorization of MO was still achieved after catalyst being consecutively used for 5 cycles for 30 minutes.

5.3 **Future scope**

In the present investigation, attempts were made to compare the efficiency of the various processes and select the best one and apply for the removal of methyl orange . much light is thrown on to extend the further research on the following:

i) Another possible development of this work would be to go on exploring the efficiency of different types of fenton processes rather than the classical one like trying electro fenton or photo fenton even photo electro fenton for the removal of methyl orange dye .

ii) By properly combining different possibilities, hybrid techniques can be developed for specific problems. Finally different hybrid techniques can be incooperated to remove not just one but a combination of dyes.

Chapter - 6

Conclusion

Degradation of methyl orange by classical homogenous and heterogenous fenton process was carried out in batch reactor and in continuous packed bed column. In homogenous batch mode, the percentage degradation was commendatory but with recirculation in continuous mode the percentage degradation might improve with the increase of reaction time as waste water treatment of a large volume can be done more efficiently in a continuous process. This appears to be a substantial possibility of saving a large amount of time and energy by abiding to continuous rather than batch process. Pseudo 1st order kinetics is seen to be the best rate equation. In the study Iron containing waste was utilized as heterogenous fenton catalyst. Moreover heterogenous fenton process can be considered better than classical homogenous fenton owing to the fact that no sludge is generated and easy recovery of catalyst from the treated stream. Besides in heterogenous fenton, in addition to the elementary degradation occurrence , adsorption is also involved and can be seen to play an consequential role in dye removal process. The sorption data was fitted into Linear, Langmuir, Freundlich, Temkin isotherms out of which Tempkin Adsorption model was found to have the highest regression value and hence the best fit. It is apparent that the catalyst along with an accurate amount of H_2O_2 in an acidic pH range contributes immensely (around 98%) in the degradation of methyl orange. Furthermore the iron containing solids (discarded screws) used for heterogenous fenton also had a high catalytic activity towards the degradation of methyl orange dye and the catalyst could be consecutively used for about 5 cycles providing almost 94% degradation efficiency within 30 minutes. Hence it appears to be good plausible reason for the use of low cost materials as catalysts in heterogeneous Fenton process for degradation of pollutants.

Chapter - 7

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