

**TREATMENT OF TEXTILE MILL WASTE WATER
BY
FENTON PROCESS**

A DISSERTATION

*Submitted in partial fulfillment of the
requirements for the award of the degree*

of

MASTER OF TECHNOLOGY

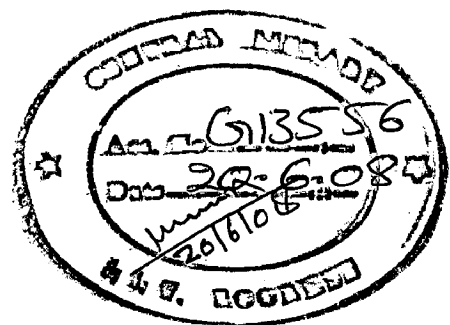
in

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

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JUNE, 2007**

CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled "TREATMENT OF TEXTILE MILL WASTEWATER BY FENTON PROCESS" in the partial fulfillment of the requirements of the award of the degree of Master of Technology in Chemical Engineering with specialization in **Industrial Pollution Abatement**, submitted in the **Department of Chemical Engineering, Indian Institute of Technology Roorkee**, under the kind guidance of **Dr. SHRI CHAND**, Professor and Head, Chemical Engineering Department, Indian Institute of Technology Roorkee, Roorkee.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree of this or any other Institute.


Date: 21 June, 2007.

Place: Roorkee.


(D. KRISHNA SWAMY)

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.


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ACKNOWLEDGEMENT

This is consummated and symbolized not only my efforts but also guidance and vital inputs of different people at crucial junctures in the course of this undertaking to whom I would like to express my gratitude.

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ABSTRACT

Synthetic dyes and pigments released into the environment mainly in the form of wastewater effluents by textile, leather and printing industries cause severe ecological problems. These compounds have a great variety of colors and chemical structures and are recalcitrant to microbial attack.

Biological degradation of different dyestuffs has been extensively studied by both aerobic and anaerobic cultures. However, the degradation of such compounds by either mixed cultures or isolated enzymes is usually very slow. Chemical treatment systems, on the other hand, are generally more effective with respect to biological processes in decolorizing of textile dyestuffs.

Chemical treatment methods adopted in this work are chemical coagulation and Fenton process and both process were compared for COD and color removal efficiencies. Experiments were conducted to investigate the effects of operating variables, including pH, coagulant dose on the color and COD removal efficiency. In first stage of experimental part chemical coagulation has been carried out with coagulants ferrous sulfate, ferric chloride and poly aluminum chloride for removing color and COD from textile mill wastewater. Among the three coagulants, PAC shows highest removal efficiency with a removal of 80.6% and 77.4% for COD and color, respectively. The optimum pH and optimum dose for PAC are 3 and 4g/l, respectively.

In second stage of experimental part Fenton process was carried out to investigate the effects of pH, temperature, H₂O₂ and ferrous sulfate doses on the color and COD removal efficiencies. Maximum removal of COD and color in Fenton process were found to be 84.4% and 93.5%, respectively and the optimum value of H₂O₂/Fe²⁺ ratio was found to be 3.3 for maximum COD and color removal from the textile mill wastewater.

Compared to chemical coagulation Fenton process shows highest removal efficiency for COD and color from textile mill wastewater. Mainly the color removal efficiency is much higher in Fenton process compared to chemical coagulation with PAC.

CONTENTS

	Page No.
CANDIDATE'S DECLARATION	i
ACKNOWLEDGEMENT	ii
ABSTRACT	iii
LIST OF TABLES	vii
LIST OF FIGURES	ix
CHAPTER 1: INTRODUCTION	
1.1 General	1
1.2 Profile of textile industry	2
1.3 Process description of textile industry	3
1.4 Textile mill effluents	6
1.5 Environmental effects of textile mill effluents	8
1.6 Textile mill wastewater discharge standards	10
1.7 Wastewater treatment methods of a textile mill	11
CHAPTER 2: THEORY OF COAGULATION AND FENTON PROCESS	
2.1 Coagulation	13
2.2 Coagulation theory	13
2.3 Fenton process	16
CHAPTER 3: LITERATURE REVIEW	18
Objective of present work	25
CHAPTER 4: EXPERIMENTAL PROGRAMME	
4.1 Effluent characteristics	26
4.2 Chemicals used	26

4.3	Experimental procedure	27
4.3.1	Coagulation	27
4.3.2	Fenton process	28
4.4	Analytical measurements	30
4.4.1	pH measurement	30
4.4.2	Color measurement	30
4.4.3	COD measurement	30
CHAPTER 5: RESULTS AND DISCUSSION		
5.1	General	31
5.2	Coagulation study	31
5.2.1	Effect of pH	31
5.2.2	Effect of coagulant dose	32
5.2.3	Comparison of different coagulants	33
5.3	Fenton process	42
5.3.1	Effect of pH	42
5.3.2	Effect of temperature	42
5.3.3	Effect of H ₂ O ₂ dose	43
5.3.4	Effect of ferrous sulfate dose	43
5.3.5	Comparison of coagulation with Fenton process	44
CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS		
6.1	Conclusions	52
6.2	Recommendations	53
REFERENCES		54
APPENDIX-A		56
APPENDIX-B		60

LIST OF TABLES

Table. No.	Title of Table	Page No:
Table 1.1:	Major Pollutant Types in Textile Wastewaters, Their Origin	7
Table 1.2	Man-made fibre industry: Wastewater discharge standards	10
Table 1.3	Cotton Textile Industry: Wastewater Discharge Standards	10
Table 1.4	Composite Woolen Mill: Wastewater Discharge Standards	10
Table 1.5:	Advantages and disadvantages of methods of COD and color removal from industrial effluents	12
Table A-1	Effect of pH on %COD and %color removal using PAC as coagulant	56
Table A-2	Effect of PAC dose on %COD and % color removal at pH 3	56
Table A-3	Effect of pH on %COD and % color removal using FeCl ₃ as coagulant	56
Table A-4	Effect of FeCl ₃ dose on %COD and % color removal at pH 6	57
Table A-5	Effect of pH on %COD and % color removal using FeSO ₄ as coagulant	57
Table A-6	Effect of FeSO ₄ dose on % COD and % color removal at pH = 8	57
Table A-7	Effect of H ₂ O ₂ dose on %COD and % color removal at pH 3	58

Table A-8	Effect of H_2O_2 dose on %COD and % color removal in Fenton process	58
Table A-9	Effect of $FeSO_4$ dose on %COD and %color removal in Fenton process	58
Table A-10	Effect of pH on % COD and %color removal in Fenton process	59
Table A-11	Effect of temperature on % COD removal in Fenton process	59
Table A-12	Comparison of different coagulants for maximum percentage of COD and color removal	59

LIST OF FIGURES

Fig. No.	Figure title	Page No.
Fig 1	Textile processing flow chart	5
Fig 4.1	Jar test apparatus	29
Fig 4.2	Flow sheet for Fenton process	39
Fig 5.1	Effect of pH on %COD removal using PAC as coagulant	34
Fig 5.2	Effect of pH on %color removal using PAC as coagulant	34
Fig 5.3	Effect of PAC dose on %COD removal at pH 3	35
Fig 5.4	Effect of PAC dose on %color removal at pH 3	36
Fig 5.5	Effect of pH on %COD removal using FeCl ₃ as coagulant	36
Fig 5.6	Effect of pH on %color removal using FeCl ₃ as coagulant	36
Fig 5.7	Effect of FeCl ₃ dose on %COD removal at pH 6	37
Fig 5.8	Effect of FeCl ₃ dose on %color removal at pH 6	37
Fig 5.9	Effect of pH on %COD removal using FeSO ₄ as coagulant	38
Fig 5.10	Effect of pH on %color removal using FeSO ₄ as coagulant	38
Fig 5.11	Effect of FeSO ₄ dose on % COD removal at pH 8	39
Fig 5.12	Effect of FeSO ₄ dose on % color removal at pH 8	39
Fig 5.13	Comparison of different coagulants for maximum COD removal	40
Fig 5.14	Comparison of different coagulants for maximum color removal	41
Fig 5.15	Effect of H ₂ O ₂ dose on %COD removal at pH 3	45
Fig 5.16	Effect of H ₂ O ₂ dose on % color removal at pH 3	45

Fig 5.17	Effect of H ₂ O ₂ dose on %COD removal in Fenton process	46
Fig 5.18	Effect of H ₂ O ₂ dose on %color removal in Fenton process	46
Fig 5.19	Effect of FeSO ₄ dose on %COD removal in Fenton process	47
Fig 5.20	Effect of FeSO ₄ dose on %color removal in Fenton process	47
Fig 5.21	Effect of pH on % COD removal in Fenton process	48
Fig 5.22	Effect of pH on %color removal in Fenton process	48
Fig 5.23	Effect of temperature on % COD removal in Fenton process	49
Fig 5.24:	Comparison of activities different coagulants with Fenton process for maximum COD removal	50
Fig 5.25:	Comparison of activities of different coagulants with Fenton process for maximum Color removal	51
Fig. B-1	Jar test equipment	60
Fig. B-2	Treated and untreated samples	60

CHAPTER - 1

INTRODUCTION

1.1 GENERAL

As a result of rapid industrialization during the last few decades the demand of water from industries has increased tremendously. A large quantity of water used is ultimately discharged into rivers as waste water from the various unit operations of these industrial processes. These waste waters are responsible for the pollution of lakes, rivers, water courses and land on which they are discharged.

The textile processing industry (TPI) is regarded as a water intensive sector as it uses water as the principal medium for applying dyes and finishing agents and removing of impurities. The major pollution load from textile mills can be attributed to the liquid effluents from the various wet processing, operations like scouring, bleaching, mercerizing, dyeing, etc.,. Among the manufacturing operations the textile dyeing and finishing industry are most directly affecting. Wastewaters from fabric and yarn printing and dyeing pose serious environmental problems both because of their color and their high chemical oxygen demand (COD). The color, if not properly dealt with, would have a strongly negative impact on the aquatic environment caused by its turbidity and high polluting strength. The main environmental concern is therefore about the amount of water discharged and the chemical load it carries. To illustrate, for each ton of produced fabric 200–350 m³ of water is consumed.

Color is the most noticeable characteristics of both the raw wastewater and treated effluent from such establishment. Although biological treatment of these waste waters is usually effective in removing a large portion of oxidizable matter, biological treatment is frequently ineffective in removing color. For this reason physico-chemical treatment, primarily aimed at color removal is increasingly appreciable to textile industry.

1.2 PROFILE OF TEXTILE INDUSTRY

The textile industry is one of the most important parts of the Indian economy. The Textile Sector in India ranks next only to Agriculture. Textiles account for 20 % of India's industrial production and around 30 % of its export earnings. It contributes 4% to GDP. From growing its own raw material (cotton, jute, silk and wool) to providing value added products to consumers (fabrics and garments), the textile industry covers a wide range of economic activities, including employment generation in both organized and unorganized sectors. About 16 per cent of the country's work force is employed in this sector.

Manmade fibers account for around 40 % share in a cotton-dominated Indian textile industry. India accounts for 15% of world's total cotton crop production and records second largest producer of silk.

India's position in the world textile economy:

- Third largest producer of raw cotton
- Second largest producer of cellulosic fiber/yarn
- Second largest producer of cotton yarn
- Largest producer of jute
- Second largest producer of silk
- Fifth largest producer of synthetic fibre/yarn

1.3 PROCESS DESCRIPTION OF TEXTILE INDUSTRY

The fibers used in the textile industries may be divided into two types. They are

1. Natural fibers : cotton, wool, jute, silk etc
2. Man- made fibers

Man made fibres are again classified in to two sub categories. They are

- **Natural or regenerated fibres:** cellulosic fibers created by reacting chemicals with wood pulp. Ex: acetate, rayon.
- **Synthetic fibres:** synthesized from organic chemicals. Ex: polyester, polyamide.

In general processing of textile includes four major steps. They are

1. Yarn formation
2. Fabric formation
3. Wet processing
4. Fabrication

YARN FORMATION

Textile fibres are converted into yarn by grouping and twisting operations used to bind them together. Natural fibres need to go through different preparation steps before being spun into yarn. These steps are opening/blending, carding, combing, drawing and drafting. For manmade fibres, just one step of texturizing is needed before spinning.

FABRIC FORMATION

The two major methods used are weaving and knitting. Weaving is the most common process and consists of interlacing yarns. Knitting is also frequently used. The main difference between knitting (dry process) and weaving is the sizing/desizing and mercerizing operations (wet processes). So, no waste water emissions at knitting as in weaving. Tufting is a process used to make most carpets.

WET PROCESSING

Wet processing enhances the appearance, durability and serviceability of fabrics by converting undyed and unfinished goods into finished goods. For simplification, this stage can be divided in three main steps:

- Fabric preparation or pre-treatment (e.g. desizing, scouring, bleaching etc.)
- Dyeing and/or printing
- Functional finishing.

Sizing: The sizing agents serve to smooth and strengthen the fibers, preventing them from being broken and getting tangled during the high-speed weaving process.

Desizing: Removal of sizing material before the cloths can be further processed.

Mercerizing: In this process textiles are treated with concentrated solution of caustic soda in order impart lustre and strength to the fabric or yarn.

Scouring: In order to prepare the fabric for dyeing, it is scoured to remove the excess chemical, processing oils and waxes.

Bleaching: This process is required, if fabric is to be white or dyed a light color.

Dyeing and printing: Textiles are fed continuously into a dye range. Continuous dyeing processes typically consist of dye application, dye fixation with chemicals or heat and washing.

Finishing: To meet requests for special "effects" the bleached and/or dyed textile material (fibre, yarn or fabric) is submitted to one or more functional finishes. These processes may be chemical (e.g. stiffening, softening, water and soil repellent, fire retardant finishing) or mechanical treatment (smoothness, roughness, shining).

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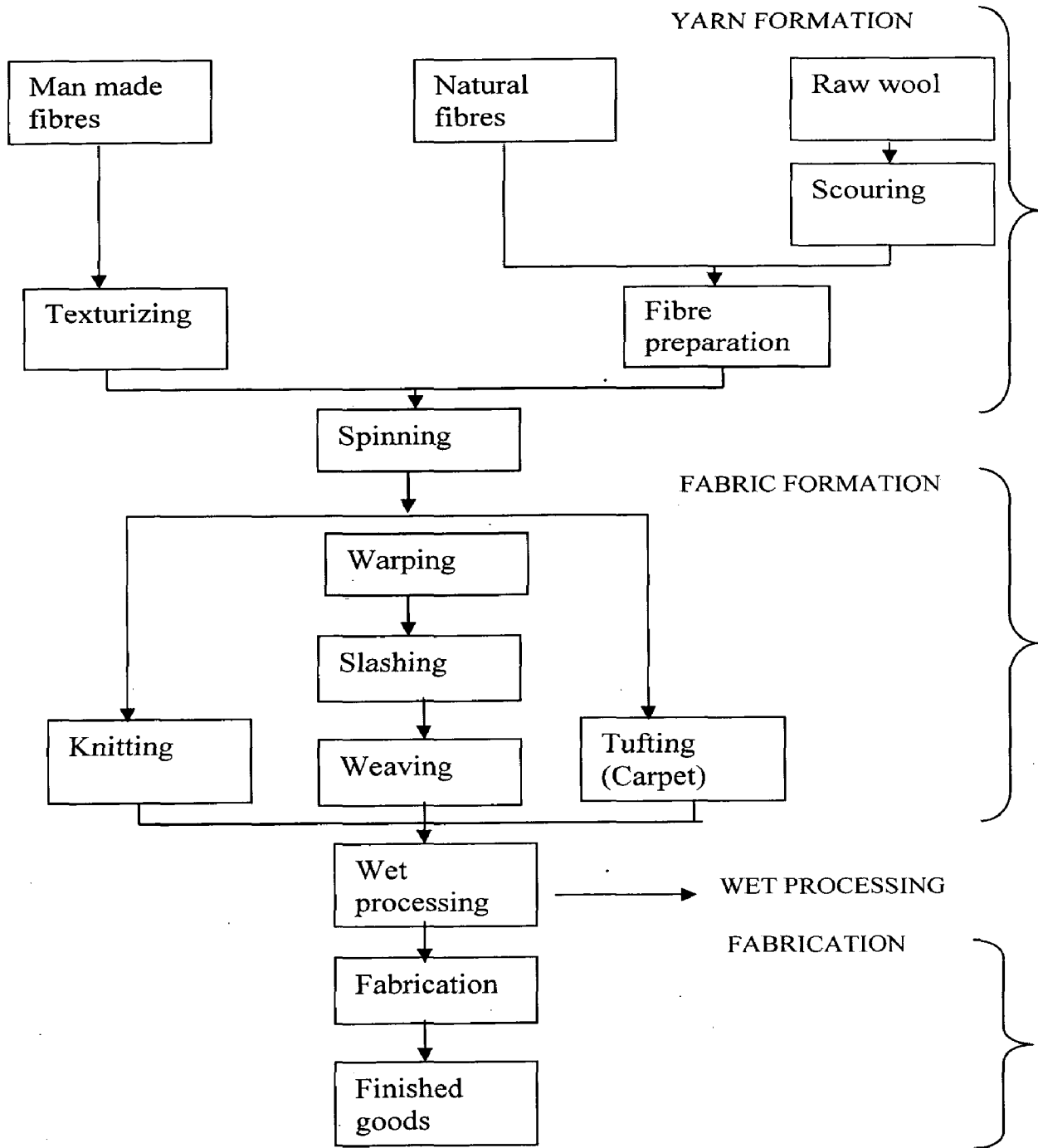


Fig 1: Textile processing flow chart

1.4 TEXTILE MILL EFFLUENTS

Water pollution by the textile mills is mainly attributable to the various waste streams coming out of the wet processing operations. The wet processing stages are slashing or sizing, desizing, scouring, mercerizing, bleaching, carbonizing, dyeing, printing and finishing. The pollutants in the wastewater include the natural impurities in the fibres used, and the processing chemicals.

In sizing or slashing, the yarn is strengthened by loading it with starch or other sizing substances. Waste originates from this section due to spills and the floor washings at the weak end. After slashing, the yarn goes for weaving. The prepared cloth now requires scouring and desizing to remove natural impurities and the slashing compounds. Caustic soda, soda ash, detergents etc. are used in scouring operation. About 50% of the total pollution load of the mill is contributed by the section. Bleaching section contributes about 10% of the total pollution Load. Mercerizing section produce negligible wastes which come out of this section contributes little BOD but high degree of alkalinity.

Wastewater from dyeing section is characterized by high color and COD content. Classes of dyes used include Vat dyes, developing dyes, naphtha dyes, sulfur dyes, basic dyes, direct dyes etc.

The finishing section of the mill imparts various finishes to the fabrics. Various types of chemicals are used for various objectives. These include starches, dextrans, natural and synthetic waxes, synthetic resins etc.

Therefore a composite waste from an integrated textile mill may include the following organic and inorganic substances: starch, carboxyl methyl cellulose, sodium hydroxide, detergents, peroxides, hypochlorite, dyes and pigments, sodium gums, dextrans, waxes, sulphides, sulfates soap etc.

Depending upon the process and predominant dye used, the characteristics of mill waste vary widely.

Table 1.1: Major Pollutant Types in Textile Wastewaters, Their Origin

Sl. NO.	Pollutants	Major chemical types	Main Processes of origin
1	Organic load	Starches, enzymes, fats, greases, waxes, surfactants, Acetic acid	Desizing Scouring, Washing Dyeing
2	Color	Dyes, scoured wool impurities	Dyeing, Scouring
3	Nutrients (N,P)	Ammonium salts, urea, phosphate-based buffers and sequestrants	Dyeing
4	pH and salt effects	NaOH, mineral/organic acids, sodium chloride, silicate, sulphate, carbonate	Scouring, Desizing, Bleaching, Mercerising, Dyeing, Neutralisation
5	Sulphur	Sulphate, sulphide and hydrosulphite salts, sulphuric acid	Dyeing
6	Toxicants	Heavy metals, reducing agents (e.g. sulphide), oxidising agents (e.g. chlorite, peroxide, dichromate, persulphate), biocides, quaternary ammonium salts	Desizing, Bleaching, Dyeing, finishing
7	Refractory organics	Surfactants, dyes, resins, synthetic sizes (e.g. PVA), chlorinated organic compounds, carrier organic solvents	Scouring, Desizing, Bleaching, Dyeing, Washing, Finishing

1.5 ENVIRONMENTAL EFFECTS OF TEXTILE MILL EFFLUENTS

The pollutants present in the effluents of the textile mill can be classified into three main groups based on their effects on the receiving bodies.

1. Those which are themselves toxic or harmful; for example free chlorine from bleaching section. These harmful pollutants, if present in appreciable amount, not only will make the receiving water unfit for use; but will also destroy the vegetation and crops where such water is discharged.

2. Those which contribute to the oxygen depletion of the receiving waters. These in turn, can be further sub-classified as follows

a. Chemical reducing agents such as sulpha-dyes and sulphides which will exert immediate oxygen demand because of their reducing characteristic.

b. Biologically liable substances like sizes from grey cloth and other organic solids present in the effluent which will consume dissolved oxygen from water for biochemical stabilization.

c. Surface active agents like greases and detergents which will impede the dissolution of oxygen in the water from the air by forming a preventive barrier.

3. 'Inert' materials in suspension or in dissolved state which are, as such harmless, but can be detrimental in the following ways, if present in high amount.

a. They can blanket the stream bed by way of deposition thereby destroying the plant and invertebrate life.

b. By blanketing the surface of water and thereby preventing oxygen intake which might, in turn, prove harmful for the marine life.

- c. Some of the dyes and coloring impurities present in the water can prevent the penetration of light into the water, because of which the photosynthesis reaction carried out by some micro organisms in the biological treatment of the sewage is hampered.

- d. The dissolved solids of the effluent can clog the porous structure of the soil on which the effluent is discharged. Intake of air from the atmosphere by plants and vegetations on such soil will be hampered, and subsequently their growth also will be retarded

- e. Clogging the pores of the soil by solid content of the effluent can lead to anaerobic fermentation within the soil structure due to inadequate oxygen from intake the atmosphere. Anaerobic fermentation usually produces acid which can have harmful effects on the soil and the plants.

1.6 TEXTILE MILL WASTEWATER DISCHARGE STANDARDS

Table 1.2: MAN-MADE FIBRE INDUSTRY: WASTEWATER DISCHARGE STANDARDS

Process	Parameter	Concentration not to exceed, mg/l (except for pH)
(i) Synthetic	Suspended solids	100
	BOD, 3 days 27°C	30
	pH	5.5 to 9.0
(ii) Semi-synthetic	pH	5.5 to 9.0
	Suspended solids	100
	BOD, 3 days at 27°C	30
	Zinc (as Zn)	5

Table 1.3: Cotton Textile Industry: Wastewater Discharge Standards (Composite & Processing)

Parameter	Concentration not to exceed, mg/l (except for pH & bio-assay)
pH	5.5 to 9.0
Suspended solids	100
BOD, 3 days at 27°C	150
Oil & grease	10
Bio-assay test	90% survival of fish after 96 hrs in 100% effluent

Table 1.4: Composite Woolen Mill: Wastewater Discharge Standards

Parameter	Concentration not to exceed, mg/l (except for pH & bio-assay)
pH	5.5 to 9.0
Suspended solids	100
BOD, 3 days at 27°C	150
Oil & grease	10
Bio-assay test	90% survival of fish after 96 hrs in 100% effluent

1.7 WASTEWATER TREATMENT METHODS OF A TEXTILE MILL

Treatment to be imparted to the effluents of a textile mill is mainly governed by following factors

1. Quantity of effluents to be discharged
2. Different manufacturing processes adopted in the mill
3. Type of receiving bodies e.g., public sewers or river or nallah or irrigation land etc.
4. Legislation imposed by the local municipality.

The treatment of effluents can be generally classified into three main headings.

Physical treatment

This consists of dilution, equalization, separation, filtration, screening, sedimentation etc., and this treatment removes the suspended and precipitated or flocculated solid particles from the effluents.

Chemical treatment

It consists of neutralization of the effluents with acids or alkalies, addition of coagulating agents like alum, ferrous sulphate, ferric sulphate, ferric chloride etc., followed by flocculation and sedimentation. Treatment of the colored effluents with various oxidizing agents like chlorine, ozone, bleaching powder, etc., for removal of various colors present in the effluent as COD is also sometimes carried out. As a result of this treatment, COD of the effluent will come down and its pH might increase in case of treatment with bleaching powder.

Biological treatment

It consists of oxidation by compressed air, trickling filters, activated sludge treatment, lagooning etc. It brings the BOD of the effluent within the stipulated limits.

Table 1.5: Advantages and disadvantages of methods of COD and color removal from industrial effluents

Processes	Advantages	Disadvantages
Photochemical	No sludge production	Formation of by-products
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Adsorption on Activated carbon	Good removal of wide variety of dyes	Very expensive
Membrane filtration	Removes all dye types	Concentrated sludge production
Electro kinetic coagulation	Economically feasible	High sludge production
Ion exchange	Regeneration, no adsorbent loss	Not effective for all dyes
Fenton's reagent	Effective decolorization of both soluble and insoluble dyes	Sludge generation
Biodegradation	Rates of elimination by oxidizable substances about 90%	Low biodegradability of dyes
Coagulation–flocculation	Elimination of insoluble dyes	Production of sludges Costs
Ozone treatment	Good decolorization	No reduction of the COD Additional costs
Reverse osmosis	Separation of organic compounds of low molecular weight and divalent ions from monovalent salts. Treatment of high concentrations	High pressure

CHAPTER - 2

THEORY OF COAGULATION AND FENTON PROCESS

Waste waters from textile dyeing operations are characteristically high in color and organic content. Biological systems are usually installed to stabilize the waste water organics, but additional facilities are typically required to achieve sufficient color removal. The removal of color caused by settleable solids is readily achieved by sedimentation, but color due to colloidal or dissolved substances are more difficult to eliminate. Chemical coagulation or other floc producing processes can be used to remove colloidal materials by adsorption and may even partly remove true dissolved coloring compounds, especially when the color is caused by large organic matter molecules, such as dye stuff. Hence, chemical coagulation is particularly suitable method of color removal from textile waste effluents.

Hence, physico-chemical methods of treatment are supposed to prove better than biological methods, since biological methods of treatment are also not very efficient because of low BOD content of the effluent.

2.1 COAGULATION

Virtually all surface water sources contain perceptible turbidity. Plain sedimentation will not be very efficient for the smaller suspended particles. Under conditions normally encountered in settling basins, efficient removal of particles less than 50 μm in diameter cannot be expected.

Agglomeration of particles into groups, increasing the effective size and therefore the settling velocities, is possible in some instances. Knowledge of the nature of colloidal suspensions is essential to this removal.

2.2 COAGULATION THEORY

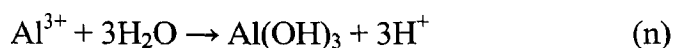
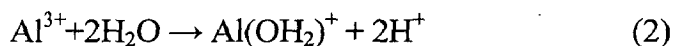
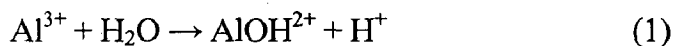
In water-treatment plants, chemical coagulation is usually accomplished by the addition of trivalent metallic salts such as $\text{Al}_2(\text{SO}_4)_3$ (aluminum sulfate) or FeCl_3 (ferric

chloride). Although the exact method by which coagulation is accomplished cannot be determined, four mechanisms are thought to occur. These include ionic layer compression, adsorption and charge neutralization, entrapment in a flocculent mass, and adsorption and inter particle bridging.

Ionic layer compression The quantity of ions in the water surrounding a colloid has an effect on the decay function of the electrostatic potential, high ionic concentration compresses the layers composed predominantly of counter ions toward the surface of the colloid. If this layer is sufficiently compressed, then the van der Waals force will be predominant across the entire area of influence so that the net force will be attractive and no energy barriers will exist. An example of ionic layer compression occurs in nature when a turbid stream flows into the ocean. There the ion content of the water increases drastically and coagulation and settling occur. Eventually, deposits (deltas) are formed from material which was originally so small that it could not have settled without coagulation. Although coagulants such as aluminum and ferric salts used in water treatment ionize, at the concentration commonly used they would not increase the ionic concentration sufficiently to affect ion layer compression.

Adsorption and charge neutralization The nature, rather than the quantity, of the ions is of prime importance in the theory of adsorption and charge neutralization. Although aluminum sulfate (alum) is used, as in the example below, ferric chloride behaves similarly.

The ionization of aluminum sulfate in water produces sulfate anions (SO_4^{2-}) and aluminum cations (Al^{3+}). The sulfate ions may remain in this form or combine with other cations. However, the Al^{3+} cations react immediately with water to form a variety of aquometallic ions and hydrogen.



The aquometallic ions thus formed become part of the ionic cloud surrounding the colloid and, because they have a great affinity for surfaces, are adsorbed onto the surface of the colloid where they neutralize the surface charge. Once the surface charge has been neutralized, the ionic cloud dissipates and the electrostatic potential disappears so that contact occurs freely. Overdosing with coagulants can result in restabilizing the suspension. If enough aquometallic ions are formed and adsorbed, the charges on the particles become reversed and the ionic clouds reform, with negative ions being the counter ions.

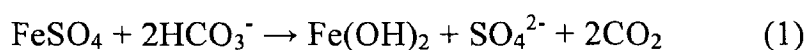
Sweep coagulation According to Eq. (n), the last product formed in the hydrolysis of alum is aluminum hydroxide, $Al(OH)_3$. The $Al(OH)_3$ forms amorphous, gelatinous flocs that are heavier than water and settle by gravity. Colloids may become entrapped in a floe as it is formed, or they may become enmeshed by its "sticky" surface as the flocs settle. The process by which colloids are swept from suspension in this manner is known as sweep coagulation.

Interparticle bridging Large molecules may be formed when aluminum or ferric salts dissociate in water. Synthetic polymers also may be used instead of, or in addition to, metallic salts. These polymers may be linear or branched and are highly surface reactive. Thus, several colloids may become attached to one polymer and several of the polymer-colloid groups may become enmeshed, resulting in a settleable mass.

Coagulation with ferrous sulfate

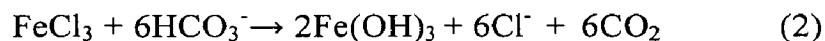
Ferrous sulfate is the least expensive of the iron coagulants and is widely used as a coagulant. Ferrous sulfate does not produce satisfactory flocs until they have been oxidized to the ferric state. The oxidation occurs rapidly in the presence of dissolved oxygen at a $pH > 7$.

Basic equations occurring during the coagulation process for ferrous sulfate salts is given with Eqs. (1) and (2) as follows:



Coagulation with Ferric chloride

Ferric chloride works best at pH below 7. The precipitate formed is ferric hydroxide which has good flocculating and settling characteristics. It is highly hygroscopic in nature.



Coagulation with Poly aluminum chloride

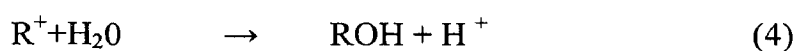
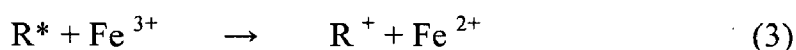
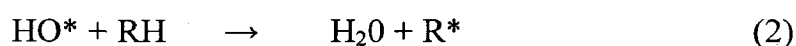
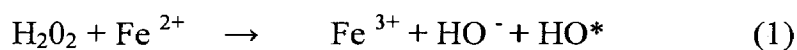
The aluminum derivative is a partially hydrolyzed aluminum chloride solution. Although still not widely used, it has been reported to provide stronger, faster settling flocs than alum in some applications.

Factors affecting the coagulation

1. Type of coagulant
2. Dosage of coagulant
3. Characteristics of waste water such as quantity of suspended matter, temperature and pH of wastewater
4. Time and method of mixing

2.3 FENTON PROCESS

The basic mechanism of the Fenton treatment process consists of chemical oxidation and chemical coagulation of organic compounds. In an acidic environment, the hydrogen peroxide in the presence of excess ferrous ions incurs the following redox reactions:



The hydroxyl radical HO^* attacks the organic compounds RH (the PVA or unsaturated dye molecules) and thus causes chemical decomposition of these compounds. The Fenton process employs ferrous ions and hydrogen peroxide (H_2O_2) under acidic pH conditions.

As shown in reaction (1), strong oxidative hydroxyl radical (HO^*) is produced and the ferrous ions are oxidized to ferric ions. Since both ferrous and ferric ions are coagulants, the Fenton process can therefore have the dual functions of oxidation and coagulation in the treatment process.

CHAPTER-3

LITERATURE REVIEW

This chapter presents a review of the existing literature, to the extent available, on the chemical coagulation and Fenton process. The main emphasis is given to the literature on COD and COLOR removal in textile mill effluent by the chemical coagulation and Fenton process.

Sihorwala and Reddy (1989) conducted jar test for the treatment of cotton textile waste of a textile unit, which discharges its waste through two channels. The treatability of waste by coagulation was studied separately and also by combining both the channel wastes in a ratio of 1:1. The coagulants tested were alum, FeCl_3 and Catfloc – T (liquid cationic poly electrolyte), APH – 35 (liquid anionic polyelectrolyte). Catfloc – T is much effect in a removal of color, COD and TS from cotton textile waste at pH above 10.0. The removal also occurred with anionic polyelectrolyte but to a less extent. Catfloc – T is found to be more economical than alum and FeCl_3 as this did not involve the reduction of pH as required in case of alum and FeCl_3 .

Karthikeyan and Niranjana (1992) conducted coagulation experiments for removal of color from 2 acid dyes (monoazo acid red and anthraquinone acid blue) and 2 direct dyes (disazo direct red and direct blue) with coagulants alum, ferric chloride, lime and ammonium ferrous sulphate and found that monoazo acid red did not respond favorably to chemical coagulation, where as all other dyes exhibited good removal. The optimum dose of coagulant for maximum color removal was less in case of ferric chloride and more for lime. System pH has no influence in affecting color removal but the coagulant dose requirements were less at high system pH values.

Kuo et al. (1992) conducted the experiments with a hydrogen peroxide-ferrous ion system, known as Fenton's reagent for decolorization of five types of simulated dye wastewater, separately prepared with disperse, reactive, direct, acid and basic dyes. The results found are that the best pH value for decolorization is below 3.5, the average percent removal of chemical oxygen demand (COD) is about 90%, the transparency of wastewater is above 25 cm and the average percent decolorization is above 97%. All the results of treating the dye wastewater of actual dyeing and

finishing mills are similar to those in the laboratory. Temperature mainly influences the speed of decolorization, i.e. the lower the temperature, the longer the time for decolorization.

Lin and Lin (1993) conducted ozonation experiments in a multiple reactor system to investigate the efficiency of this process in reducing the color and chemical oxygen demand of the textile waste effluents. They observed that decolorization of those waste effluents can be achieved in less than 10 min in all tested cases. They reported, in conjunction with chemical coagulation, the chemical oxygen demand of those waste effluents can be consistently reduced by up to 70% or more and Ozonation is capable of decomposing the highly structured dye molecules into smaller ones which can be easily biodegraded in an activated sludge process. They investigated that the combination of ozonation, chemical coagulation and the activated sludge processes can provide a very effective means for dealing with this particular type of industrial waste effluent.

Bhole and Pawels (1997) conducted the coagulation experiments for the treatment of textile wastewater. They investigated the use of synthetic polyelectrolyte for treatment of wastewater from textile industries and found that 200 mg/l aluminum chloride with 0.3 mg/l Setlyte N10 produced 97.5 % and 96.4% removal in color and S.S. respectively from textile mill. Dose of 0.3 mg/l EA 1533 with 300 mg/l magnesium chloride gave 93.3 and 94.2% removal in color and S.S. respectively from handloom mill wastewater.

Lin and Lo (1997) investigated the treatment of simulated desizing wastewater by the Fenton process along with chemical coagulation. The simulated wastewater contained less than 0.2% polyvinyl alcohol (PVA) and Blue G (a direct dye) or Black B (a reactive dye). They conducted the experiments to investigate the effects of operating variables, including pH, temperature and the treatment time, on the COD removal efficiency. Optimal operating conditions were experimentally determined. Experimental results show that there exists an optimal pH at 3 and an optimal temperature at 30°C for the Fenton treatment process. When operated at these optimal pH and temperature conditions, the Fenton treatment process is capable of reducing the COD concentration of the wastewater to the discharge standard. The Fenton treatment was found Chemical coagulation using poly aluminum chloride and

polymer was found to complement the Fenton treatment process in reducing the floc settling time, enhancing color removal and reducing Fe ion concentration. A two-step Fenton treatment process intended separately for chemical coagulation and chemical oxidation was observed to be only marginally better than the single-step one.

Lin and Chen (1997) conducted experiments for the treatment of wastewater effluent from the secondary wastewater treatment plant of a dyeing and finishing mill for possible reuse. The treatment system employed consists of the Fenton process, chemical coagulation and ion exchange. The Fenton process and chemical coagulation are intended primarily to remove color, turbidity (NTU) and COD concentration of wastewater effluent while ion exchange is used to further lower the COD and Fe ion concentrations, total hardness, conductivity, alkalinity, SS and TDS of wastewater. Experimental results throughout the study indicated that the combined chemical treatment methods are very effective and are capable of elevating water quality of the treated wastewater effluent to the reuse standard of the textile industry.

Shyh et al. (2002) studied the Fenton process, involving oxidation and coagulation, for the removal of color and chemical oxygen demand (COD) from synthetic textile wastewater containing polyvinyl alcohol and a reactive dyestuff, R94H. The experimental variables studied include dosages of iron salts and hydrogen peroxide, oxidation time, mixing speed and organic content. They investigated that color was removed mainly by Fenton oxidation. The color removal reached a maximum of 90% at a reaction time of 5 min under low dosages of H_2O_2 and Fe^{2+} . In contrast, the COD was removed primarily by Fenton coagulation, rather than by Fenton oxidation. The ratio of removal efficiency between Fenton process and ferric coagulation was 5.6 for color removal and 1.2 for COD removal. They investigated that Fenton process for the treatment of textile wastewater favors the removal of color rather than COD.

Tak Hyun et al. (2004) studied the decolorization of some of the most commonly used disperse and reactive dyestuffs by destabilization using ferric chloride as a coagulant. Dye removal, distributions of zeta potential, concentration of suspended solids, changes of the Soluble COD/Total COD ratio and distributions of sludge volume (SV) and SVI (sludge volume index) values were investigated in this work. Compared to reactive dyes, disperse dyes have lower solubility, higher suspended solids concentrations and lower SCOD/TCOD ratios. It was concluded that disperse dye

solutions are more easily decolorized by chemical coagulation than reactive dye solutions. The increasing coagulation efficiencies of the disperse dyes were attributed not only to their low solubility, but also to the final floc formation and their settling quality. The SV and SVI of disperse dyes were lower than those of reactive dyes.

Tak Hyun et al. (2004) studied the decolorization of some of the most commonly used disperse and reactive dyestuffs by combination of chemical coagulation and Fenton oxidation. In addition, performances between Fe^{3+} coagulation and Fenton oxidation of dye solutions were compared by measuring COD and dye removals, distributions of zeta potential, concentration of suspended solid were investigated. They investigated that Fenton oxidation in combination with Fe^{3+} coagulation effectively removes COD and dye. About 90% of COD and 99% of dye removals were obtained at the optimum conditions. Compared to reactive dyes, disperse dyes have lower solubility, higher suspended solids concentrations and lower SCOD/TCOD ratios. The COD and dye removed per unit Fe^{3+} coagulant added for disperse dye solutions were higher than those for reactive dye solutions. Therefore, the disperse dye solutions are more easily decolorized by chemical coagulation than reactive dye solutions. Conversely, reactive dye solutions have higher applicability of Fenton oxidation than disperse dye solutions due to their higher solubility, lower suspended solids concentrations and higher SCOD/TCOD ratios. The COD and dye removed per Fe^{2+} Fenton reagent added for reactive dye solutions are respectively higher than those for disperse dye solutions.

Xiang et al. (2004) investigated the degradation of 20 different dyes in aqueous solutions by the Fenton process. These dyes include 6 types: acidic, reactive, direct, and cationic, disperse and vat dyes. The catalytic activities of four metal ions on the degradation efficiencies of Vat Blue BO, which was chosen as a model dye because of its lowest color and TOC removals, were compared in the dark and under the ultraviolet light irradiation. The catalytic ability of different metals was $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ag}^+$ in the dark, and the same sequence was obtained under irradiation condition with greater degradation efficiency. Furthermore, the efficiencies of three oxidation processes, including $\text{H}_2\text{O}_2/\text{UV}$, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ were compared. The results showed that the oxidation by $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ was the strongest,

and even greater than the arithmetic sum of the other two processes, which suggests the synergistic effect of ultraviolet and ferrous ions on the degradation reaction.

Sureyya et al. (2004) studied the removal of Reactive Black 5 (RB5) from synthetic wastewater using Fenton's oxidation (FO) process. They conducted experiments on the samples containing 100 and 200 mg l⁻¹ of RB5 to remove the dye toxicity and found that Seventy-five milligram per litre of RB5 caused 25% toxicity on 24-h born Daphnis whereas 100 mg l⁻¹ of RB5 displayed 100% toxicity on Daphnia magna. The study was performed in a systematic approach searching optimum values of FeSO₄ and H₂O₂ concentrations, pH and temperature. Optimum pH and temperature for 100 mg l⁻¹ of RB5 observed as 3.0 and 40⁰C, respectively, using 100 mg l⁻¹ of FeSO₄ and 400 mg l⁻¹ of H₂O₂ resulted in 71% chemical oxygen demand (COD) and 99% color removal. For 200 mg l⁻¹ of RB5, 84% COD removal was obtained using 225 mg l⁻¹ of FeSO₄ and 1000 mg l⁻¹ of H₂O₂ yielding 0.05 molar ratio at pH 3.0 and 40⁰C. Color removal was also more than 99%. FeSO₄/H₂O₂ ratios found were not changed for both concentrations. The temperature affected the COD removal significantly at high degrees. Toxicity was completely removed for each concentration of RB5 at optimum removal conditions.

Huseyin Selcuk (2005) evaluated and compared the performance of ferrous and aluminum sulfate coagulations and ozonation treatment techniques. The evaluation of treatment efficiency was made using the parameters of oxygen demand (COD), color absorbance at 436 nm, 525 nm and 620 nm and Daphnia magna toxicity test. Approximately 50-60% color, 60% COD and 70-80% toxicity were removed at 1000 mg/ L and 1500 mg/ L ferrous and aluminum sulfate, respectively. However, these required doses for optimum toxicity reduction are not economical due to the chemical sludge production. Ozonation was relatively effective in reducing color absorbance and toxic effects of textile effluents. Almost complete color absorbance (over 98%) was removed in 20 min ozone contact time, while COD removal (37%) was very low and almost stable in 30 min ozonation period. The toxicity of wastewater reduced after color degradation by 85% at the transferred ozone (TrO₃) concentration of 82.3 mg/ L.

Meric et al. (2005) investigated a systematic approach to optimize pH, temperature and the doses of FeSO_4 and H_2O_2 for Fenton's reagent (FR) to decolorize and detoxify the solutions containing of Remazol Red 120 (RR) dye and its mixture with Remazol Brilliant Blue (RB) and Remazol Yellow 84 (RY) reactive dyes. The acute toxicity of each dye composition was measured using *D. magna*. Optimum pH for RR singly used and for the dye mixture was found 3.5 while optimum temperature was determined 50°C, 40°C and 30°C for 100 mg/l of RR, 200 mg/l of RR and the dye mixture, respectively. More than 98% of color and 92% of COD removal were obtained for the dye solutions. For obtaining high color and COD removal H_2O_2 concentration had to be increased 3 times when RR concentration was doubled whereas FeSO_4 was to be increased 2.5 times for the dye mixture. The results obtained indicate that FR can be assuredly used for complete toxicity removal and obtaining high color and COD efficiency with no toxic effluent on *D. magna* for the dye solutions studied. Acute toxicity test with H_2O_2 was useful to evaluate the complete oxidation resulting in practically no residual H_2O_2 (<3 mg/l) in the solution.

Bali and Karagozoglu (2006) reported the Fenton process (involving oxidation and coagulation), ferric coagulation and H_2O_2 /pyridine/Cu (II) system for the removal of color from a synthetic textile wastewater containing polyvinyl alcohol and a reactive dyestuff, Remazol Turquoise Blue G-133. Experiments were conducted to investigate the effects of operating variables such as pH, coagulant dose, polyelectrolyte type, H_2O_2 and Fe (II) concentrations, optimum pyridine and Cu (II) dosages on decolonization efficiency. Optimal operating conditions were experimentally determined. A decolonization efficiency of 96% was possible to achieve with Fenton's reagent at an optimum [Fe (II)]: [H_2O_2] molar ratio of 1.21:1. However, 27% of initial Fe (II) was still in the effluent which required further treatment. Optimum pH and coagulant dose were found to be 7 and 100-125 mg l^{-1} , respectively, and the corresponding efficiency was approximately 100%. Cationic polyelectrolyte was found to be the most suitable type and 2 mg l^{-1} of it enhanced the decolonization by 10% and 75% for filtered and no filtered samples, respectively. The maximum efficiency achieved by H_2O_2 /pyridine/Cu (II) system was about 92% with a high initial reaction rate different from the H_2O_2 /pyridine system which also led to 92% removal.

Gulkaya et al. (2006) investigated the effectiveness of the Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) in the treatment of carpet dyeing wastewater under different operational conditions, namely, H_2O_2 and FeSO_4 concentrations, initial pH and temperature. Up to 95% COD removal efficiency was attained using 5.5 g/l FeSO_4 and 385 g/l H_2O_2 at a pH of 3, temperature of 50 °C. The $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio (g/g) was found to be between 95 and 290 for maximum COD removal. It was reported that, keeping $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio constant within the range of 95–290, it became possible to decrease FeSO_4 concentration to 1.1 g/l and H_2O_2 concentration to 96.3 g/l, still achieving nearly the same COD removal efficiency. The relative efficiencies of Fenton's oxidation and coagulation stages revealed that Fenton's coagulation removed organic compounds which were not removed by Fenton's oxidation, indicating that the Fenton's coagulation acted as a polishing step.

Salman Ashraf et al. (2006) studied the degradation of Methyl Red, an azo dye, using the ferrous-hydrogen peroxide system. They investigated that oxidation and subsequent degradation of the dye dependent on both the amount of Fe^{2+} ions as well as hydrogen peroxide. In order to study the effect of other salts that are normally present in textile waste streams, a systematic study was carried out using 10 different salt solutions. Some of the ions tested enhanced the rate and extent of degradation of the dye, whereas some had an inhibitory effect. The rates of degradation were found to fit to first-order kinetics.

Baoyou Shi et al.(2007) investigated removal of three direct dyes (Direct Black 19, Direct Red 28, and Direct Blue 86) by coagulation with three different Al based coagulants. The main purpose of this paper is to examine the coagulation features of polymeric aluminum coagulants in treatment of dye-polluted waters and the emphasis was placed on the roles of preformed Al species, particularly Al_{13} . The performance of Al_{13} in coagulation of dyes was observed through jar tests by comparing traditional Al salt, poly aluminum chloride (PACl), and purified Al_{13} . The results showed that under most cases Al_{13} had significantly higher efficiency in removal of direct dyes than traditional Al salt and commercial PACl with the exception of Direct Red 28 removal under high pH range. For traditional Al coagulant, efficient dye removal only occurred in a relatively narrow pH range of near 6.0.

OBJECTIVE OF THE PRESENT WORK

Most of the research has been done in the area of Fenton process using synthetic wastewater. But, limited applications of this method to industrial effluent were reported. So, the main aim of this work was to investigate the efficiency of Fenton process in decreasing COD and color of the industrial effluent and to compare the result with chemical coagulation. In order to achieve this goal, three specific objectives were identified. They were

- a. To determine the effectiveness of chemical coagulation and precipitation for the removal of COD and color from textile mill effluent using different coagulants by conducting Jar test. The coagulants tested were PAC, ferrous sulfate and ferric chloride.
- b. To investigate the effect of operating variables, pH, temperature, H₂O₂ dosage, FeSO₄ dosage on the removal of COD and color from textile mill wastewater by Fenton process.
- c. To compare the COD and color removal efficiencies of chemical coagulation with Fenton process.

CHAPTER-4

EXPERIMENTAL PROGRAMME

Experimental details on coagulation and Fenton process for the removal COD and color from the textile mill wastewater has been presented in this chapter.

4.1 Effluent Characteristics

The textile effluent used in this study was obtained from a nearby by cotton textile mill. The effluent was characterized for the BOD, COD, pH, total suspended solids as per standards methods. The characteristics of the effluent are presented below

Characteristics of the effluent

Chemical oxygen demand	:	2540 mg/l
Biological oxygen demand	:	550 mg/l
pH	:	10.3
Total suspended solids	:	152.1 mg/l
Conductivity	:	32.6 $\mu\text{mhos cm}^{-1}$
Appearance	:	Dark green
Color units	:	3150 Pt-Co units
Zn	:	0.115 mg/l
Cu	:	0.013 mg/l
Chlorides	:	60 mg/l

4.2 CHEMICALS USED

Chemicals used for the experiment were Poly aluminum chloride (PAC), Ferric chloride, Ferrous sulfate, H_2O_2 , Sodium hydroxide, Hydrochloric acid. All chemicals were of AR grade and obtained from S.D. fine chemical ltd. Mumbai.

Among these chemicals PAC, ferric chloride and ferrous sulfate were used as coagulants. H_2O_2 has been used in Fenton process for oxidation process. Sodium hydroxide and hydrochloric acid were used for pH adjustment.

4.3 EXPERIMENTAL PROCEDURE

4.3.1 COAGULATION (JAR TEST)

The experiment consists of three steps

1. Optimizing pH for maximum COD removal
2. To get optimum dose for maximum COD removal

Chemical coagulation and flocculation studies were carried out by laboratory flocculator as shown in the figure. This is called as **JAR TEST**. The procedure is given as follows:

1. Take 200 ml of sample in a glass vessel on a magnetic stirrer. Adjust pH of sample to 6 with 1N H₂SO₄ and 1N NaOH solutions. Add coagulant in small increments. After each addition, provide 10 min rapid mix followed by a 30min slow mix. Continue addition until a visible floc is formed.
2. Using this dose, place 200 ml sample in each of six cylinders of the Jar test apparatus, as shown in figure 4.1
3. Adjust the pH of sample in each cylinder to required value with 1N H₂SO₄ and 1N NaOH solutions
4. Mix each sample rapidly for 10 min, followed by 30 min flocculation at slow speed.
5. Measure the COD and color of the supernatant of each sample.
6. Plot the percentage removal of COD as well as color verses pH and determine the optimum pH.
7. At this pH repeat the steps 2, 4 and 5 varying the coagulant dosage.
8. Plot the % removal v/s the coagulant dosage and determine the optimum dosage.

4.3.2. FENTON PROCESS:

This process involves the oxidation and coagulation for the removal of color and chemical oxygen demand from textile wastewater

Chemicals required in the experiment: Ferrous sulfate, H_2O_2 , Sodium hydroxide, Hydrochloric acid. All chemicals were of AR grade and obtained from S.D. fine chemical ltd. Mumbai.

The Fenton process serves both oxidation and coagulation functions. The Fenton process was carried out by laboratory Jar test and the procedure is given as follows:

- In the oxidation step, 200 ml of wastewater sample was taken in a 500 ml glass cylinder and pH was adjusted to 3 by standard alkali and acid solutions.
- Hydrogen peroxide and ferrous sulfate were added to the wastewater sample, and then the sample was mixed rapidly for 45 min, depending on the designated oxidation time.
- In the coagulation step, the above oxidized sample was mixed slowly and then allowed to stand still for sedimentation to take place.
- After the sedimentation process, the supernatant was separated from sludge and analyzed for COD and color measurements.
- The pH of the sample for both Fenton oxidation and coagulation experiments was controlled at 3.0 with 1 N H_2SO_4 and 1N NaOH.
- The temperature effect experiments were conducted in a 3-necked glass reactor provided with heat and speed controllers.
- The above process was repeated for different pH and doses.

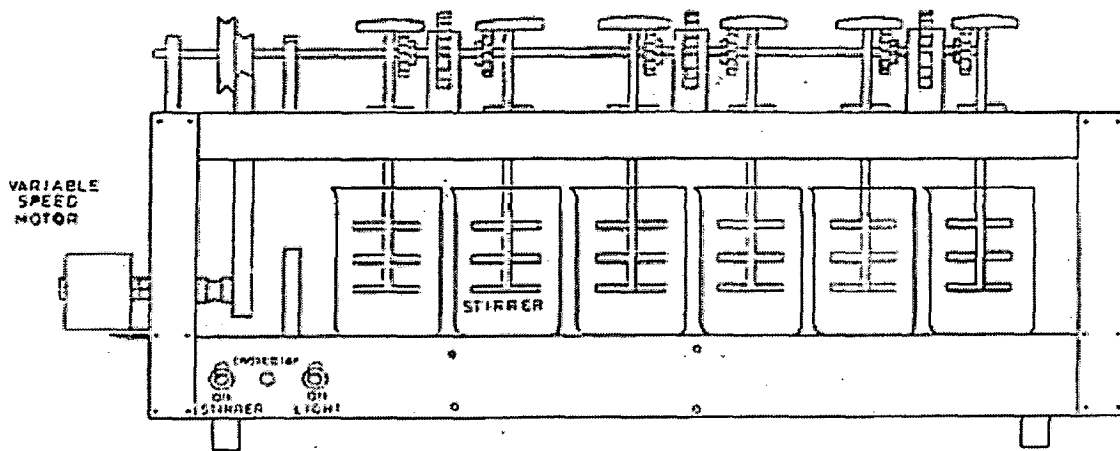


FIG. 3.1 LABORATORY JAR TEST APPARATUS

Fig 4.1: Jar test apparatus

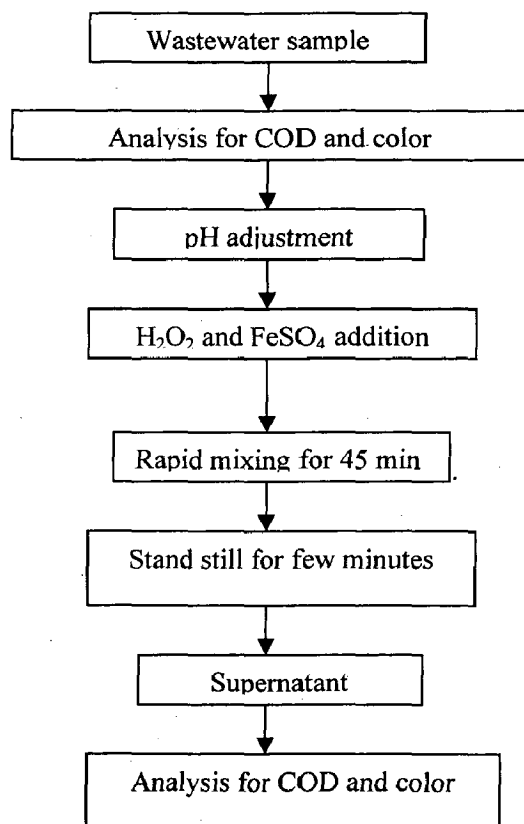


Figure4.2 Flow sheet for Fenton process

4.4 ANALYTICAL MEASUREMENTS

Physical and chemical analysis of the waste water as well as supernatant was made in accordance with the procedures detailed in standard methods (1985) using AR grade reagents.

4.4.1 pH MEASUREMENT

A double electrode digital precise pH meter was used for pH determination. It was standardized by using Analar grade commercial buffer solution prior to recording pH of sample. It is a Cyber scan 510 company model.

4.4.2 COLOR MEASUREMENT

HANNA (Singapore) based instrument was used for measuring color of textile effluent samples. The HANNA instruments measures color of sample at a wavelength of 470 nm. It has 3 vials for measurement. First the distilled water was taken in one vial and it was used to set the initial value to zero. Then filtered wastewater sample was taken in another vial and put into the instrument for color reading. The instrument gives the color reading in Pt-Co units.

4.4.3. COD MEASUREMENT

COD values analyzed with an AQUATIC IC COMPACT COD analyzer. The analytical agent which consists of 0.05 g of HgSO_4 , 3.5 ml 98% H_2SO_4 , 1.5 ml of 1 mol/l $\text{K}_2\text{Cr}_2\text{O}_5$ are mixed with 2.5 ml of wastewater sample and incubated at 150°C for 2 hrs. COD is then analyzed with the COD analyzer.

CHAPTER - 5

RESULTS AND DISCUSSION

5.1 GENERAL

The detailed discussion on the results of the experiments conducted is given in this chapter. These results include

- Coagulation study results
- Fenton process study results

5.2 COAGULATION STUDY

Detailed coagulation studies have been conducted to find the optimum conditions for the maximum removal of COD and Color of the effluent. Effects of various operating parameters like pH and coagulant dose have been studied and are shown in Tables A-1 to A-6 and Figures 5.1 to 5.12.

5.2.1. EFFECT OF pH

The effect of pH on the percentage removal of COD and Color of the effluent at fixed coagulant dose, using different coagulants is shown in Figs. 5.1, 5.2, 5.5, 5.6, 5.9, 5.10 and in Tables A-1,A-3,A-5. The coagulant mass loading for all coagulants kept constant at 3 g/l.

Figs. 5.1 and 5.2 show the effect of pH on %COD and %Color removal using PAC as a coagulant. It is seen from Figs. that, as the pH decreases, the percentage removal of COD and Color increases. But removal percentage does not increase much after the lowering of the pH below 3. The COD reduction found maximum at pH 3. At this optimum pH the COD and Color reduction were 78.7% and 75.6%, respectively. The optimum pH determined on the basis of maximum COD reduction. The maximum color reduction occurred at pH 2.

Figs. 5.5 and 5.6 show the effect of pH on %COD and % Color removal using FeCl_3 as a coagulant. The effluent was examined at different pH conditions i.e., at 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0. The maximum percentage of COD removal was 74.1% at pH 6. The maximum percentage of color removal achieved was 72 % at pH 7. Small changes in the removal efficiencies were observed in the pH range 6-7. As pH increases, percentage removal of COD and Color increases up to a certain limit (up to pH 6), and then removal decreases with increase in pH.

Figs. 5.9 and 5.10 show the effect of pH on %COD and %Color removal using FeSO_4 as a coagulant. It is seen from Figs. that, as the pH increase the percentage removal of COD and Color increases up to pH 8 and small changes in removal efficiencies were observed at pH values above 8. The changes in % COD and %Color reductions were in the range 67.5 % to 68 % and 58.7% to 59.9%, respectively, in the pH range 8 to 10. The %COD and %Color removal at optimum pH 8 were 68% and 59.9% respectively.

5.2.2. EFFECT OF COAGULANT DOSE

The effect of coagulant dose on the percentage removal of COD and Color of the effluent at optimum pH, using different coagulants is shown in Figs. 5.3, 5.4, 5.7, 5.8, 5.11, 5.12 and in Tables A-2, A-4, and A-6.

Figs. 5.3 and 5.4 show the effect of coagulant dose on percentage removal of COD and Color using PAC as a coagulant. The experiments were conducted at optimum pH 3. It is seen from Figs that as coagulant dose increases, the % COD and %Color removal efficiency increases. Maximum percentage of COD and Color removal achieved was 80.6% and 77.8%, at coagulant dose of 4 g/l and 5 g/l respectively. Small changes in percentage removal of COD and Color were observed for coagulant dose range of 4-6 g/l. For optimum PAC dose of 4g/l, 80.6% of COD and 77.4% of Color removal was found.

Figs. 5.7 and 5.8 show the effect of coagulant dose on percentage removal of COD and Color using FeCl_3 as a coagulant. It is seen from the Figs. that as coagulant dose increase the percentage of COD and Color removal increases. The maximum

percentage of COD removal achieved at a coagulant dose of 4 g/l and the maximum percentage of Color removal achieved at a coagulant dose of 3 g/l. 76.2% of COD removal achieved with coagulant dose of 2 g/l. Further increase in coagulant dose (>2g/l) changed the %COD removal efficiency by a small amount. But only 58% Color removal was observed with coagulant dose of 2 g/l. 74.4% of COD and 72.7% of Color removal were found at a dose of 3g/l. The optimum dose of FeCl_3 for maximum COD and color removal was found to be 3 g/l.

Figs 5.11 and 5.12 show the effect of coagulant dose on percentage removal of COD and Color using FeSO_4 as a coagulant. It is seen from the Figs. that as coagulant dose increase the percentage removal of COD and Color increases. The maximum percentage of COD removal i.e., 72.5% achieved at a coagulant dose of 4 g/l and coagulant dose above the 4 g/l, there is no significant change in %COD and %Color removal efficiencies. At 4 g/l of coagulant dose, the %Color removal was 69.8%. Optimum dose for FeSO_4 coagulation for the treatment of textile wastewater was found to be 4 g/l.

5.2.3. COMPARISION OF DIFFERENT COAGULANTS

Table A- 12 and Figs. 5.13 and 5.14 show the comparison of three coagulants i.e., PAC, FeCl_3 and FeSO_4 for the percentage COD and Color removal from the effluent. It is seen from Figs that PAC is more effective in removal of COD and Color from the effluent compared to other two coagulants.

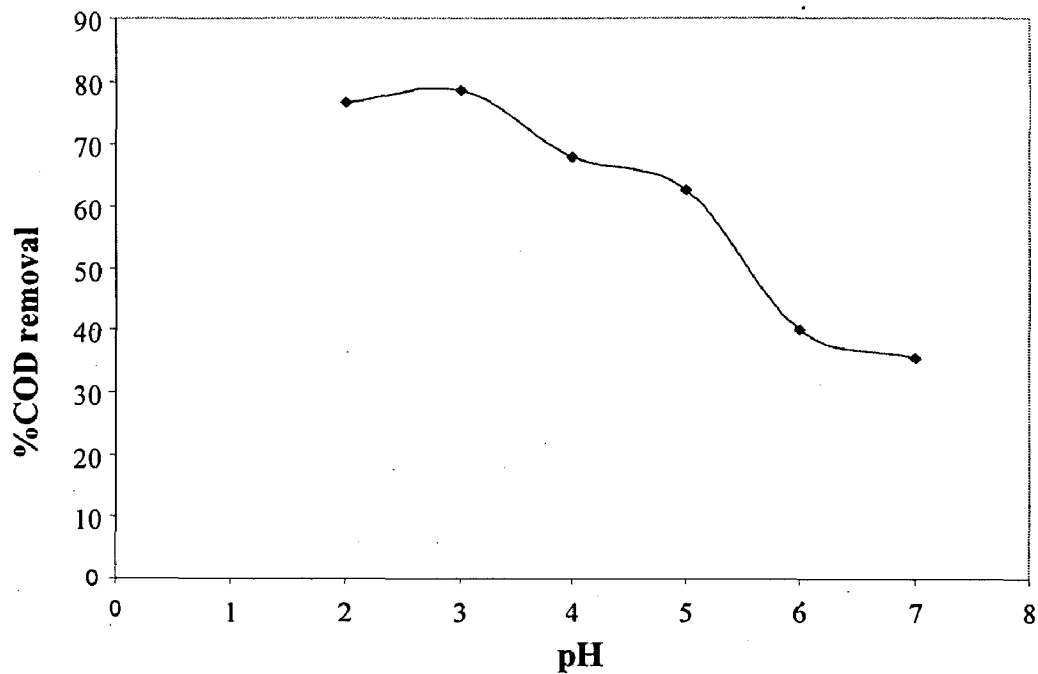


Fig 5.1: Effect of pH on %COD removal using PAC as coagulant (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, PAC dose = 3 g/l)

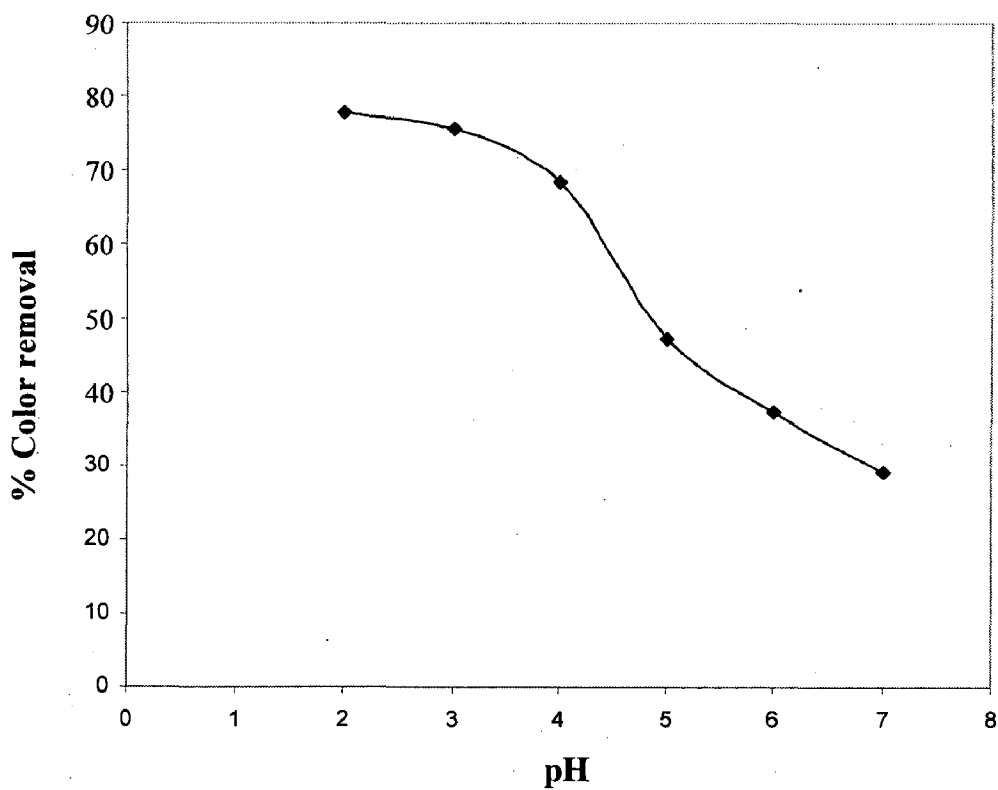


Fig 5.2: Effect of pH on % Color removal using PAC as coagulant (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, PAC dose = 3 g/l)

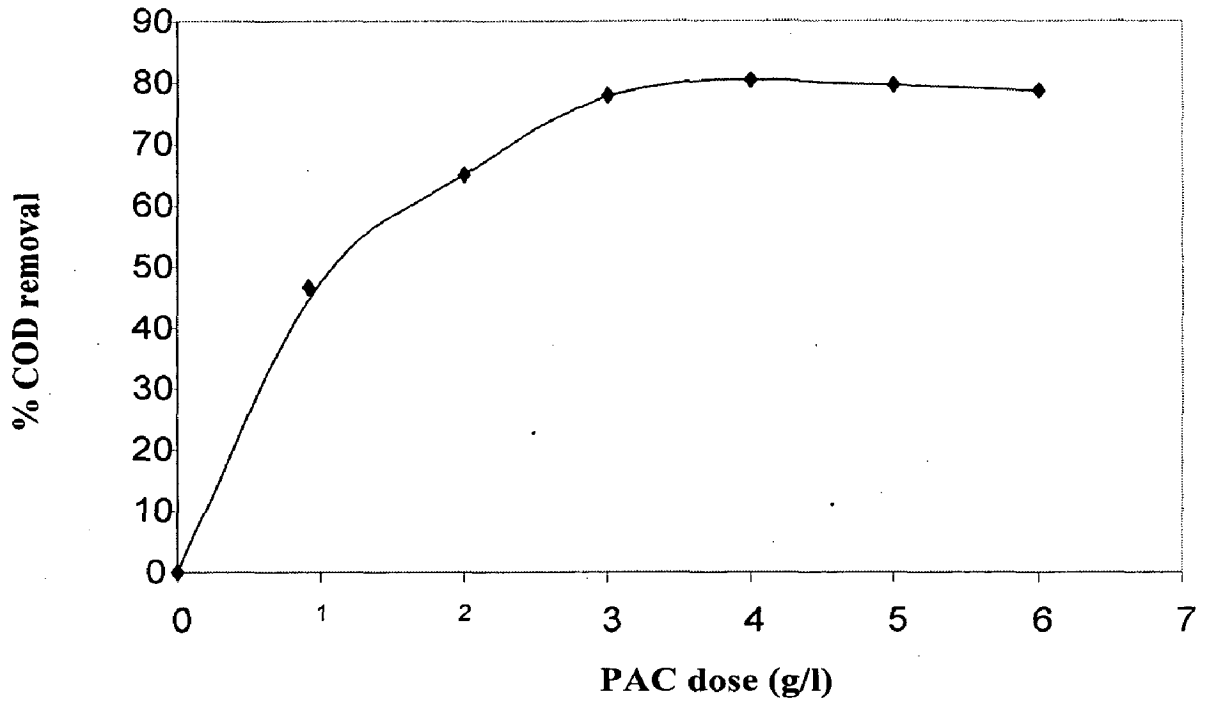


Fig 5.3: Effect of PAC dose on %COD removal at pH 3
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, pH = 3)

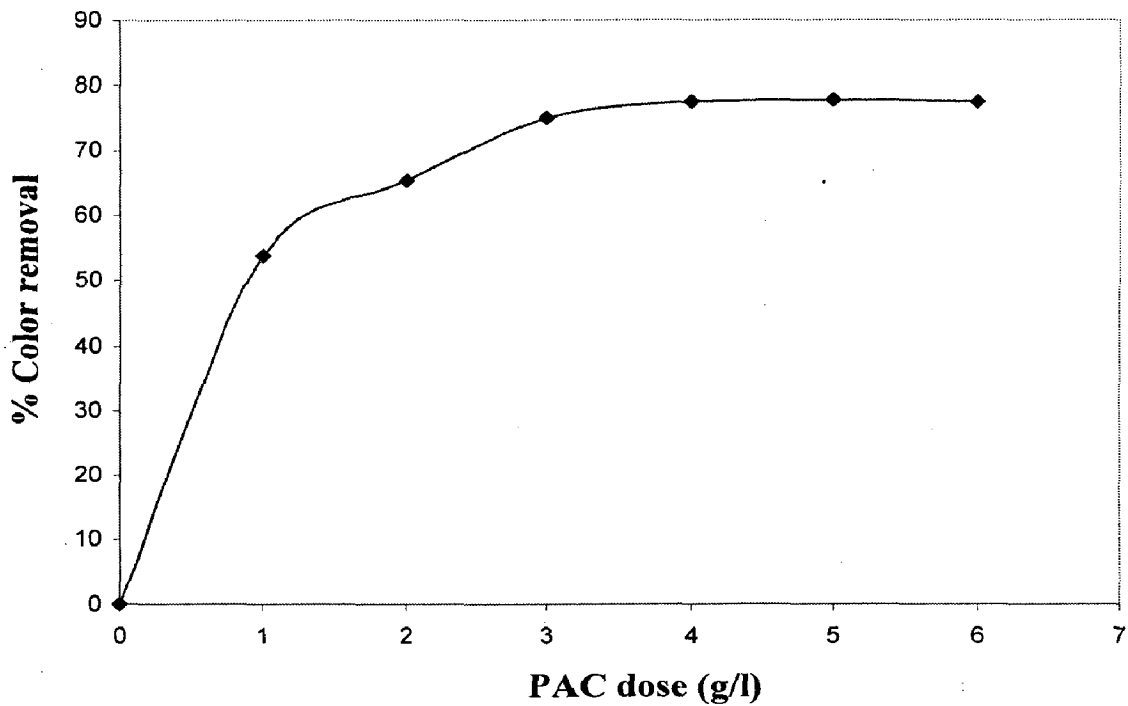


Fig 5.4: Effect of PAC dose on %Color removal at pH 3
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, pH = 3)

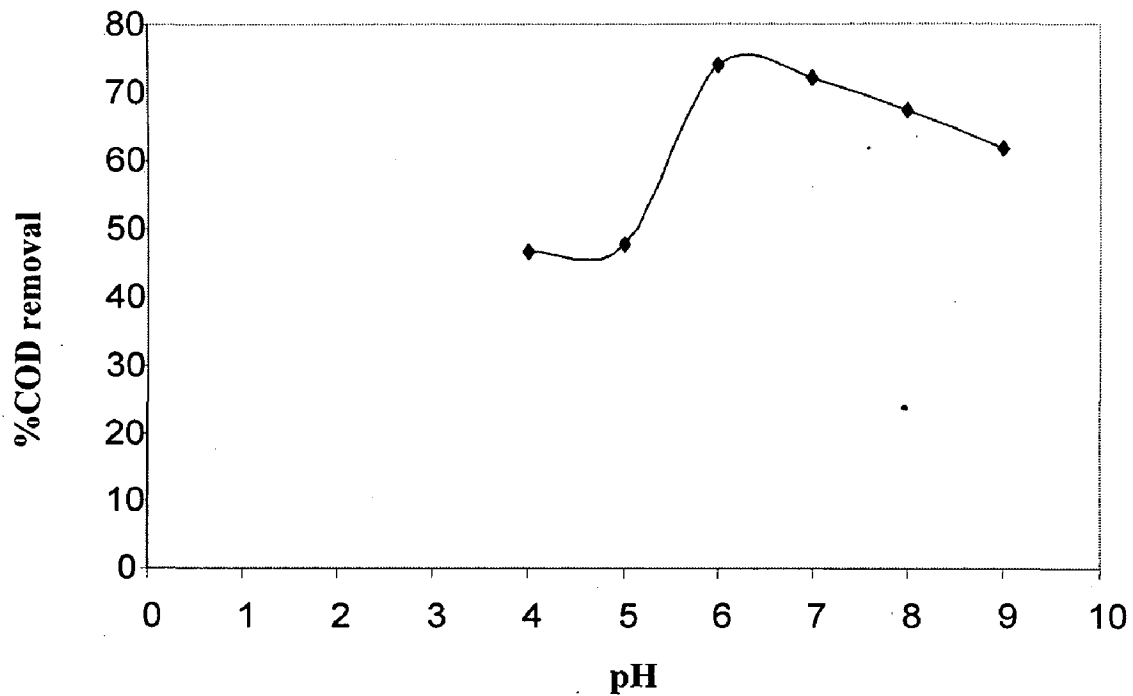


Fig 5.5: Effect of pH on %COD removal using FeCl_3 as coagulant (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, FeCl_3 = 3 g/l)

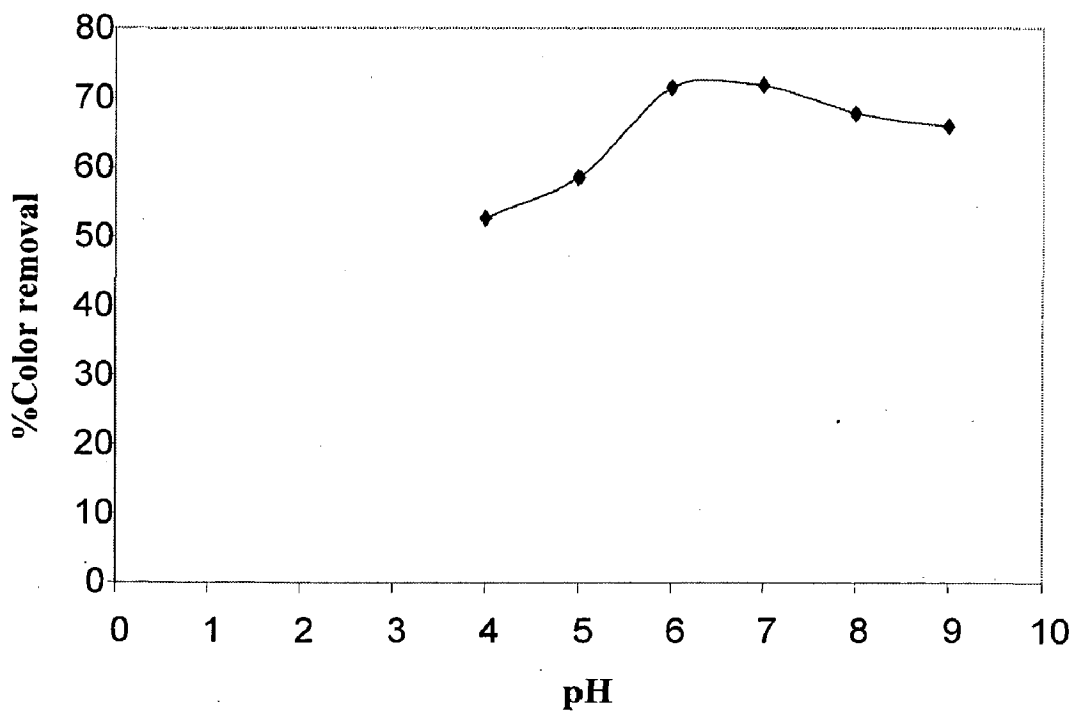
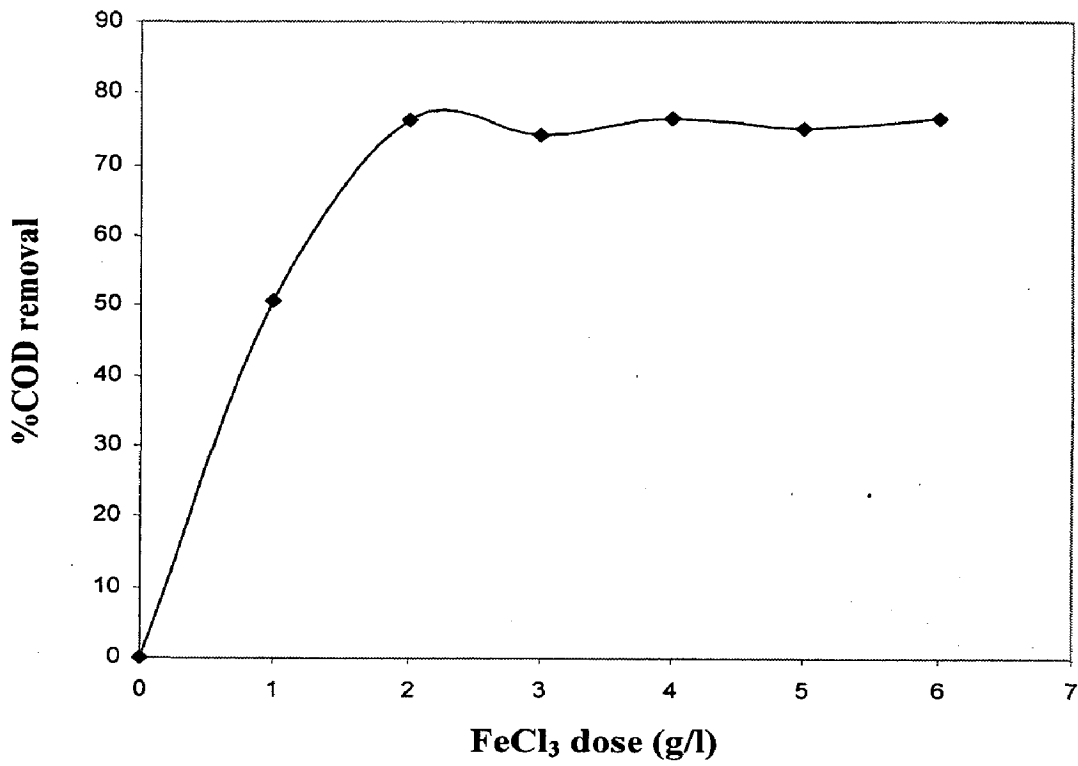
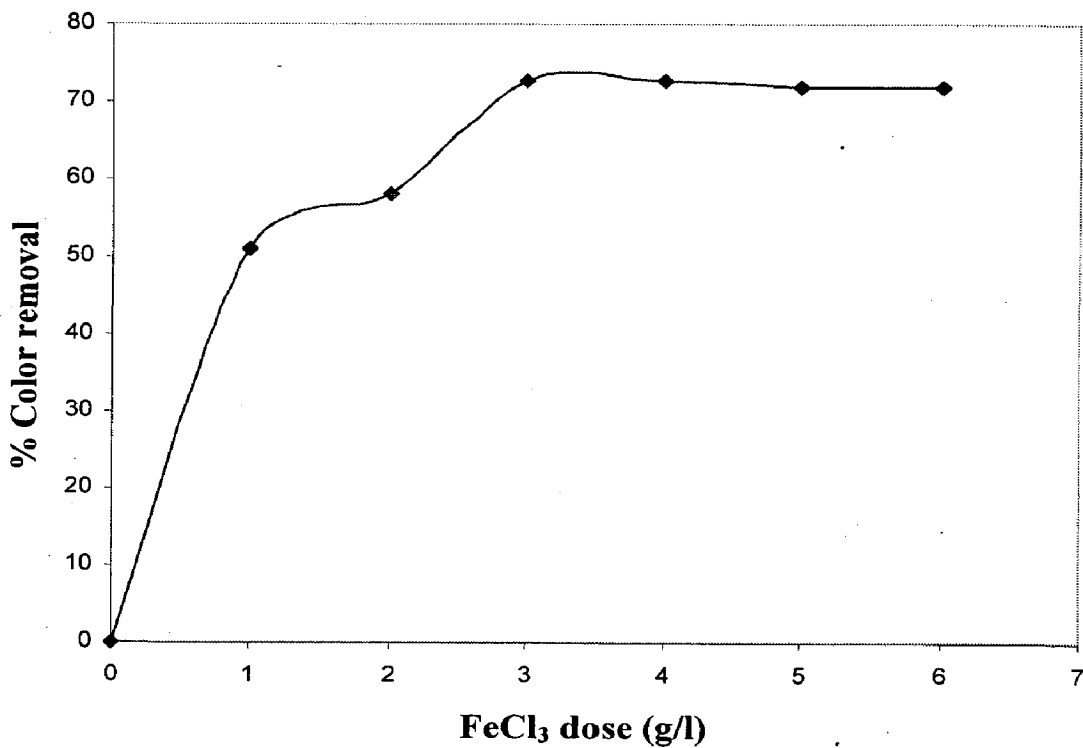


Fig 5.6: Effect of pH on %Color removal using FeCl_3 as coagulant (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, FeCl_3 = 3 g/l)



**Fig 5.7: Effect of FeCl₃ dose on %COD removal at pH=6
(Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, pH = 6)**



**Fig 5.8: Effect of FeCl₃ dose on %Color removal at pH=6
(Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, pH = 6)**

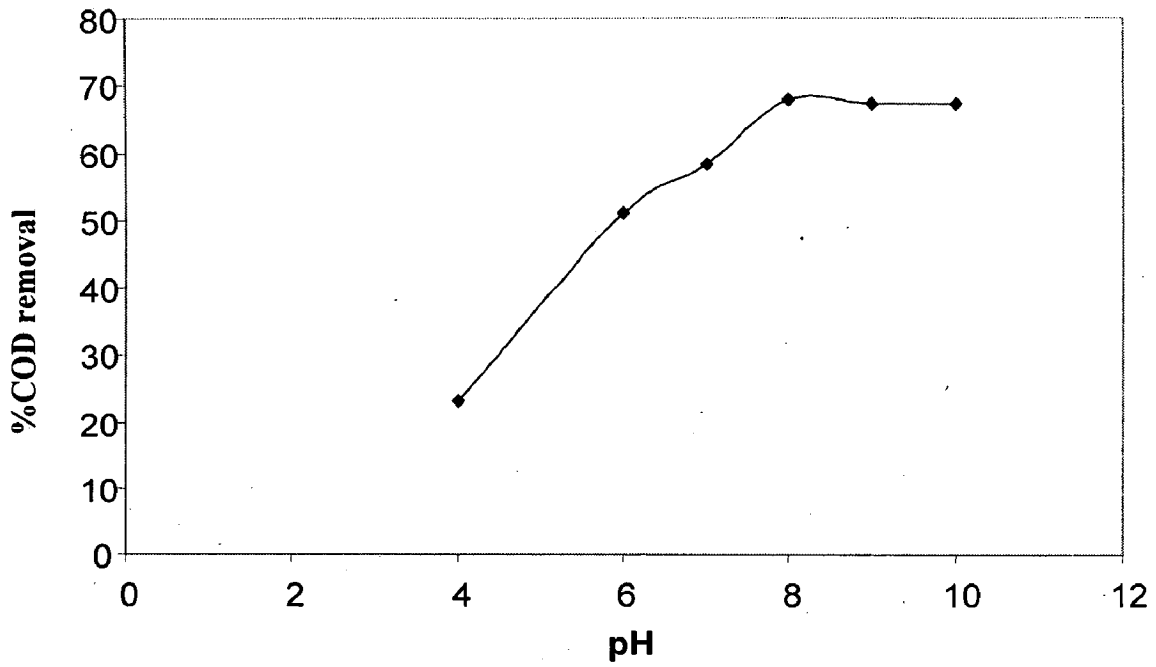


Fig 5.9: Effect of pH on %COD removal using FeSO_4 as coagulant
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, FeSO_4 dose = 3 g/l)

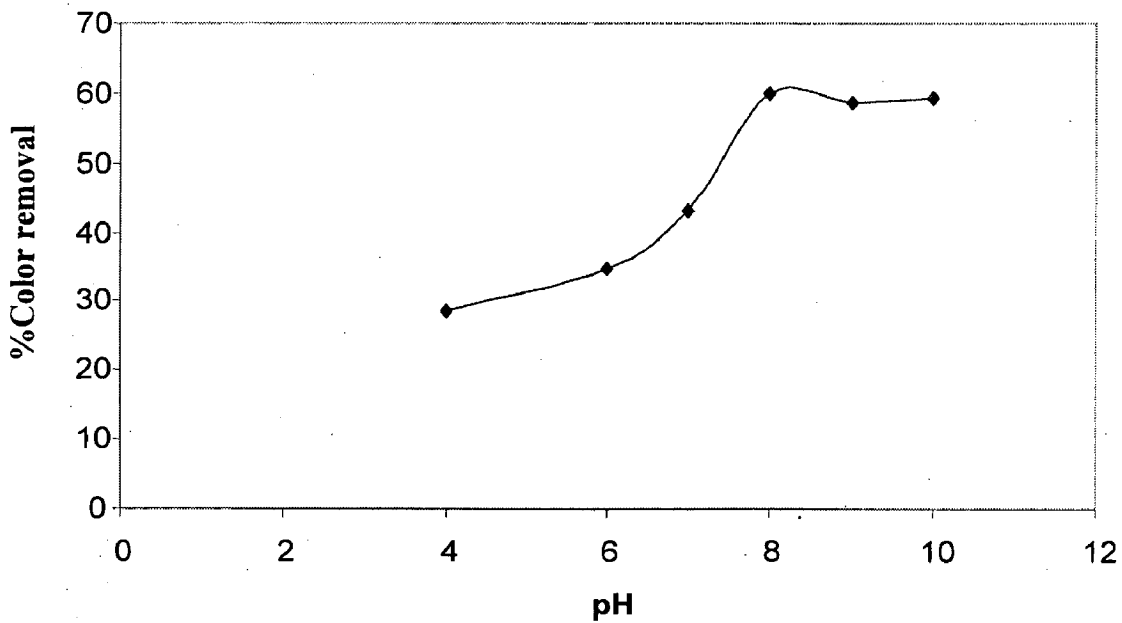


Fig 5.10: Effect of pH on %Color removal using FeSO_4 as coagulant
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, FeSO_4 dose = 3 g/l)

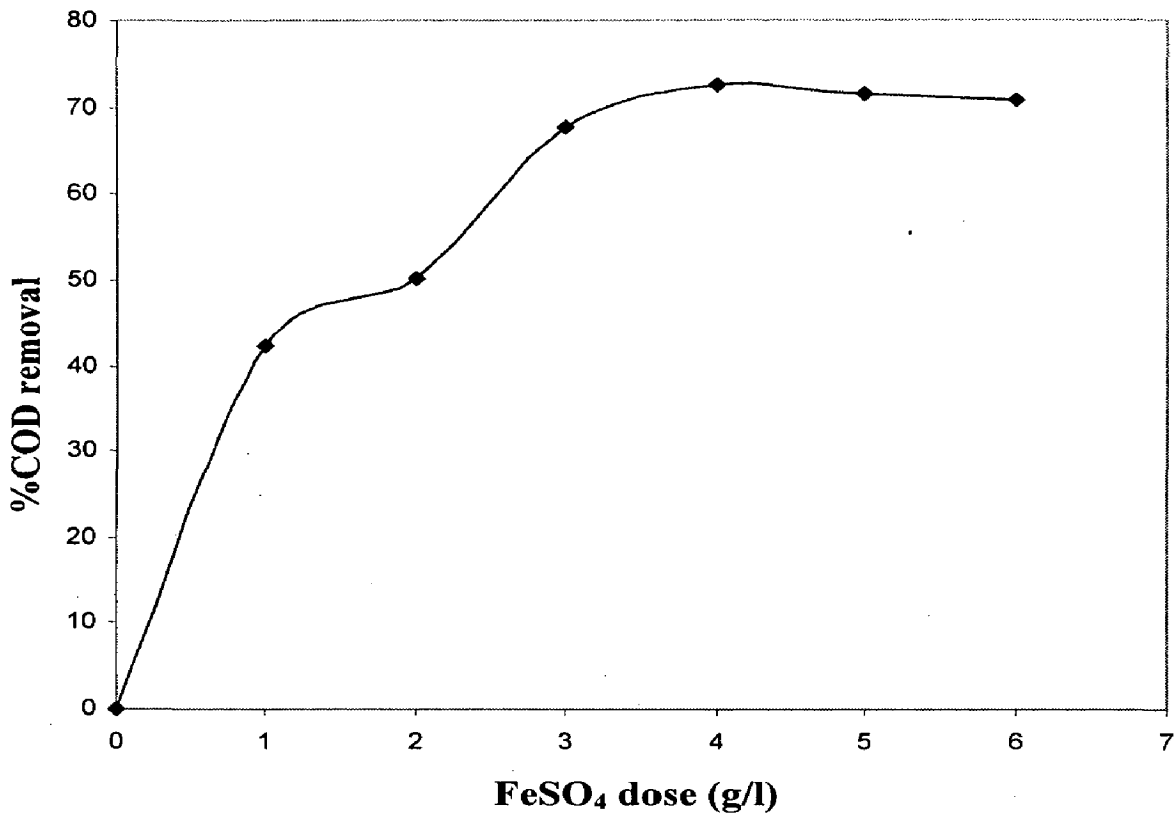


Fig 5.11: Effect of FeSO₄ dose on % COD removal at pH = 8
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, pH = 8)

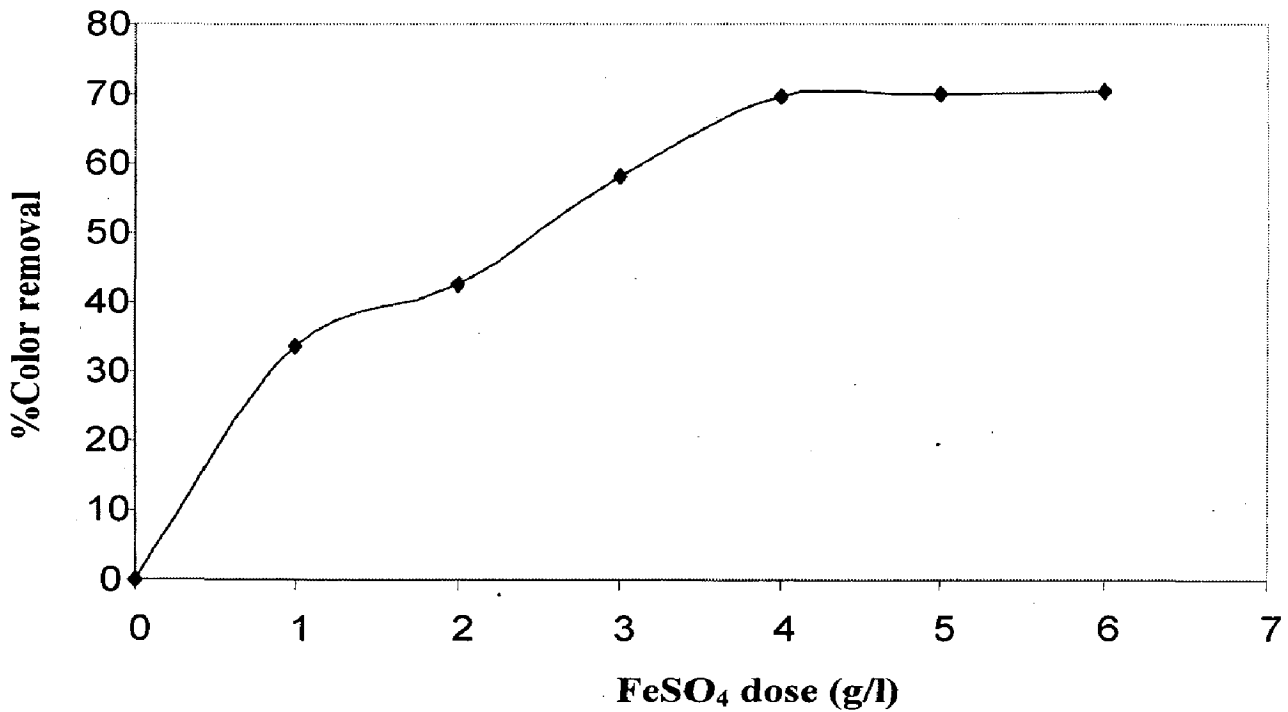


Fig 5.12: Effect of FeSO₄ dose on % Color removal at pH = 8
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, pH = 8)

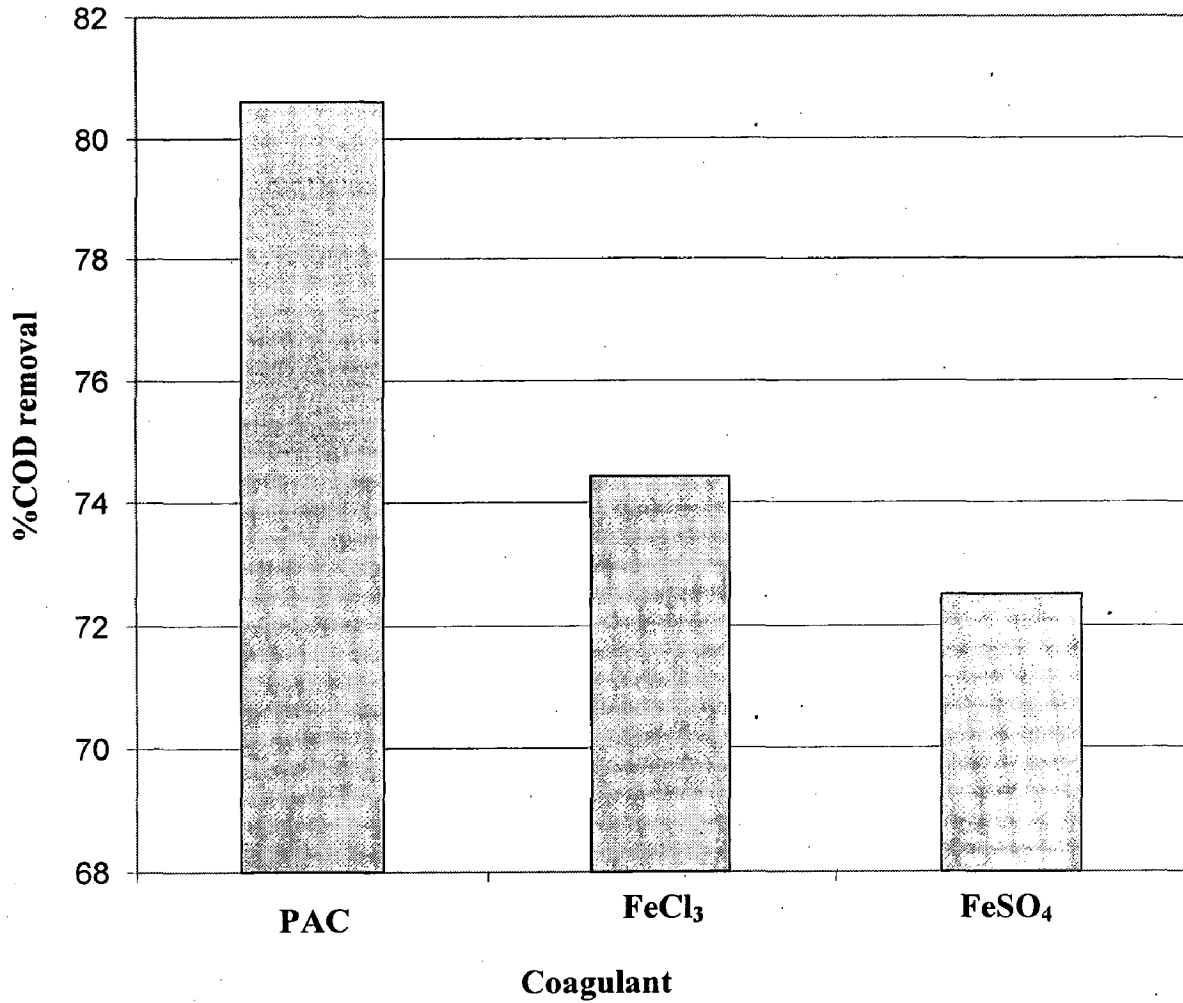


Fig 5.13: Comparison of different coagulants for maximum COD removal (Corresponding to optimum pH and dose)

PAC (pH 3, dose = 4 g/l), FeCl₃ (pH 6, dose = 3 g/l), FeSO₄ (pH 8, dose = 4 g/l)

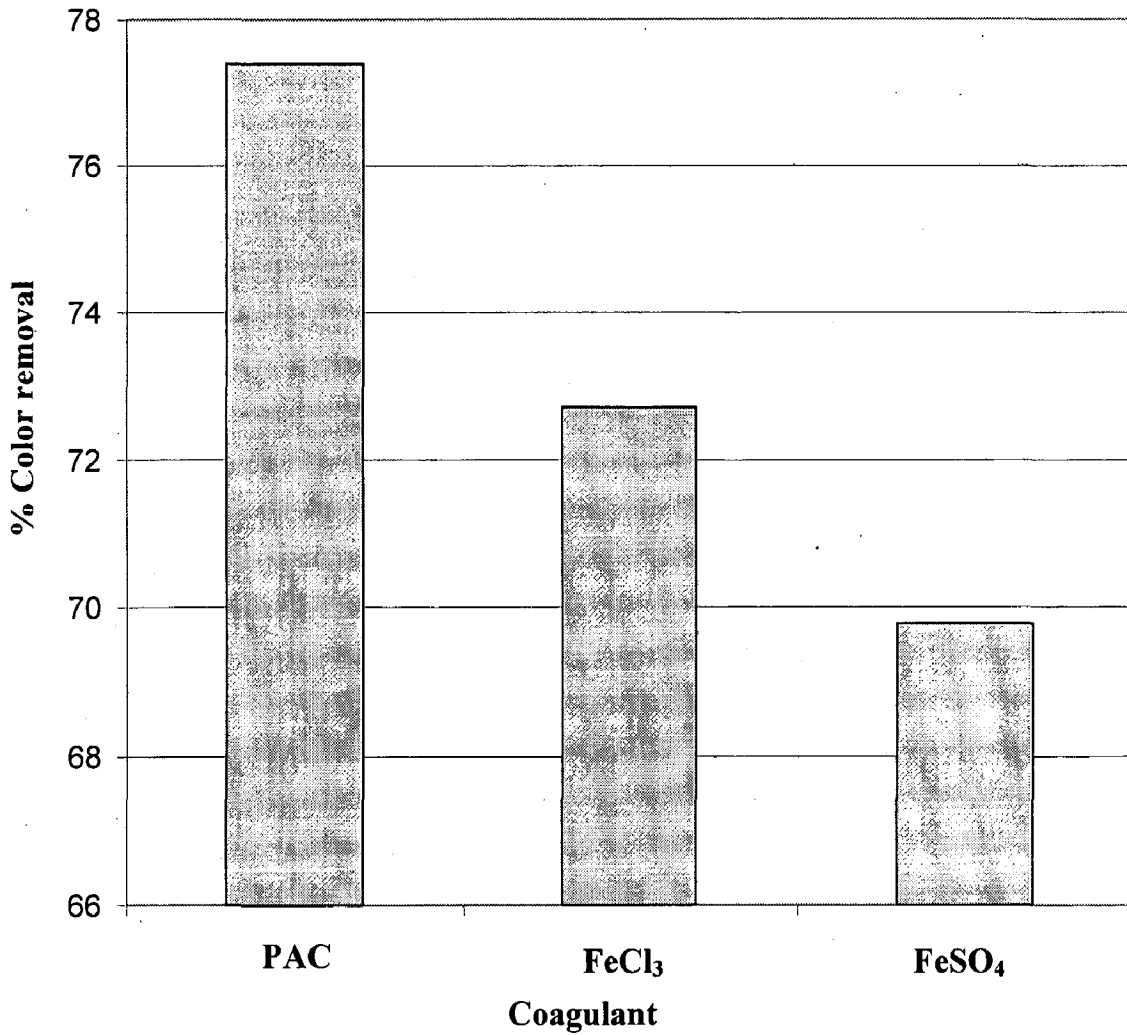


Fig 5.14: Comparison of different coagulants for maximum Color removal (Corresponding to optimum pH and dose)

PAC (pH 3, dose = 4 g/l), FeCl₃ (pH 6, dose = 3 g/l), FeSO₄ (pH 8, dose = 4 g/l)

5.3 FENTON PROCESS

Fenton process has been conducted to find the optimum conditions for the maximum removal of COD and Color of the effluent. The Fenton process serves both oxidation and coagulation functions. In the oxidation step, hydrogen peroxide was added to the effluent sample, the sample was mixed rapidly for 45 min, depending on the designated oxidation time. In the coagulation step, the above oxidized sample was mixed slowly and then allowed to stand still for sedimentation to take place. Jar tests were conducted to find the effects of various operating parameters like pH, temperature, FeSO₄ and H₂O₂ doses on the removal of COD and Color and results are presented here.

5.3.1. EFFECT OF pH

The experimental runs were conducted at ambient temperature at different pH values (2, 3, 4, 5, 6 and 7) with H₂O₂ dose = 10 g/l and FeSO₄ dose = 3 g/l. Fenton oxidation is known as a highly pH dependent process since pH plays an important role in the mechanism of OH^{*} production in Fenton reaction. Fig. 5.21 and 5.22 show the effect of pH on the % COD and %Color removal efficiencies. Both figures show that, as the pH increases above 3, there is a decrease in % COD and %Color removal, indicating an optimal pH 3 for the Fenton process. The decrease was due to the less OH^{*} production at higher pH values. At pH 3 the %COD and % Color removal was 84.2% and 93.9 %, respectively.

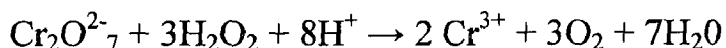
5.3.2. EFFECT OF TEMPERATURE

The experimental runs were conducted at pH 3 for different temperatures i.e., at 25, 30, 40, 50, 60 and at H₂O₂ dose = 10 g/l and FeSO₄ dose = 3 g/l. Fig. 5.23 shows the effect of temperature on the percentage removal COD. The obtained % COD removals after Fenton process were 82.9, 86.9, 82.3, 78.5, and 76.3 at 25, 30, 40, 50, and 60, respectively. It is seen from this values that an optimum temperature for maximum COD removal is 30⁰C and %COD removal is 86.9. Below the optimum temperature, there is a small change in %COD removal, but above that temperature

there is a significant decrease in %COD removal because of rapid H₂O₂ decomposition at higher temperature which is not conducive to COD removal

5.3.4. EFFECT OF H₂O₂ DOSE

Experimental runs were conducted at pH 3 for different H₂O₂ dosage, keeping the ferrous sulfate dose constant at 3 g/l, to study the effect of H₂O₂ dose on %COD and % Color removal efficiency. Results were shown in Table A-8 and in Fig. 5.17 and 5.18. It was seen from the figures that, as the H₂O₂ dosage increases, the %COD and %Color removal increases, because the concentration of HO* is expected to increase with increasing H₂O₂ dosage, leading to increased oxidation rates of color and other organic compounds. The maximum % COD removal was observed at H₂O₂ dosage of 10 g/l with removal percentages were 85.6% and 93.1% for COD and Color respectively. Small changes of removal were observed at dosage above 10 g/l. For higher doses above the optimum value, increases the value of COD in the treated effluent because excess H₂O₂ in the Fenton process can consume K₂Cr₂O₇ according to reaction given below, and leading to the increase of inorganic COD.



The maximum %Color removal was 94.5%, observed at a dose of 12g/l. The optimum dose of H₂O₂ found was 10g/l.

The experiment runs were also conducted at pH 3 to see the effect of only H₂O₂ dose (with out adding ferrous sulfate) on %COD and %Color removal. The results were presented in the Table A-7 and in Figs. 5.15 and 5.16. In the presence of H₂O₂ only, the color removal increased from 23.3% to 51.4% and COD removal decreased from -3.4 to -19.2 as the H₂O₂ dose increased from 2 to 12g/l, respectively. The negative COD removal is due to residual H₂O₂, which consumes K₂Cr₂O₇, according to the reaction given above.

5.3.5. EFFECT OF FeSO₄ DOSE

Experimental runs were conducted at pH 3 for different FeSO₄ dosage, keeping the H₂O₂ dose constant at 10 g/l, to study the effect of FeSO₄ dose on

%COD and %Color removal efficiency. Results are presented in Table A-9 and in Fig. 5.19 and 5.20. It was seen from the figures that, as the FeSO_4 dosage increases, the %COD and %Color removal increases. The maximum percentage of COD and Color removed was 85.1% and 93.5% and at ferrous dose of 6 g/l and 5 g/l, respectively. At doses above 3 g/l, there was a slightly change in %COD removal i.e., 83.3 % to 85.1%. So optimum ferrous dose can be taken as 3 g/l. At this optimum dose the %COD and % Color removal was 84.4% and 93.5% respectively. The $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ for maximum COD and Color removal was found to be 3.3(g/g).

5.3.6. COMPARISION OF COAGULATION WITH FENTON PROCESS

Figs. 5.24 and 5.25 show the comparison of three coagulants i.e., PAC, FeCl_3 and FeSO_4 with Fenton process for the percentage COD and Color removal from the effluent. It is seen from Figs that Fenton process is more effective in removal of COD and color from the effluent compared to chemical coagulation

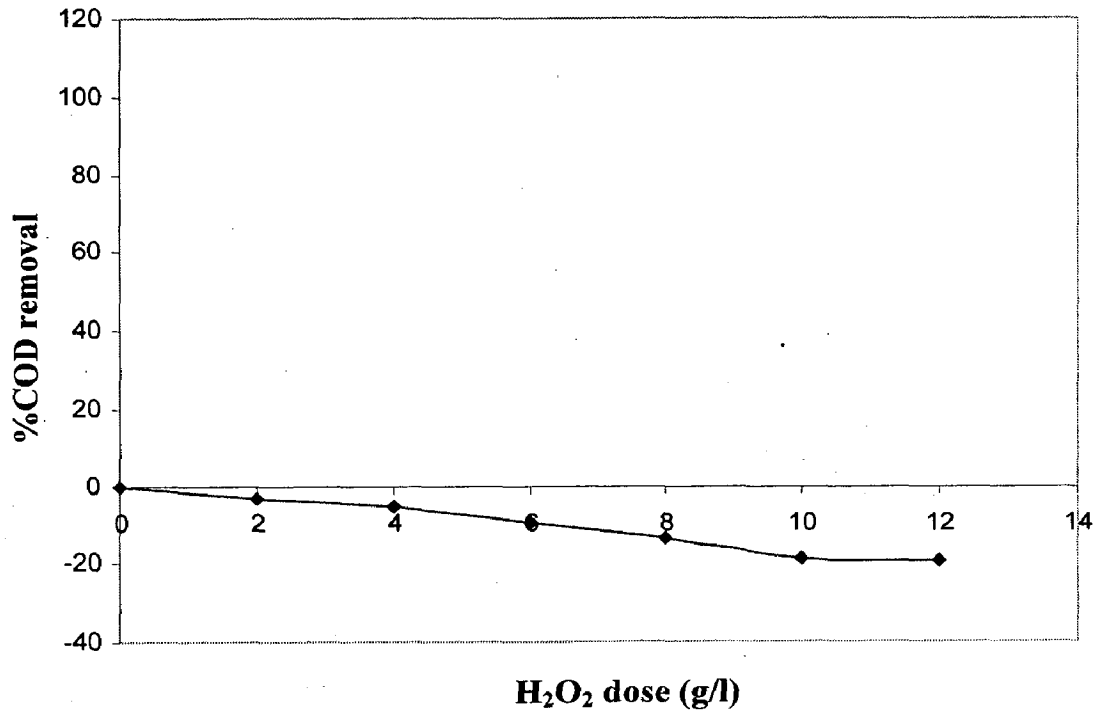


Fig 5.15: Effect of H₂O₂ dose on %COD removal at pH = 3 in Fenton process (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, pH = 3)

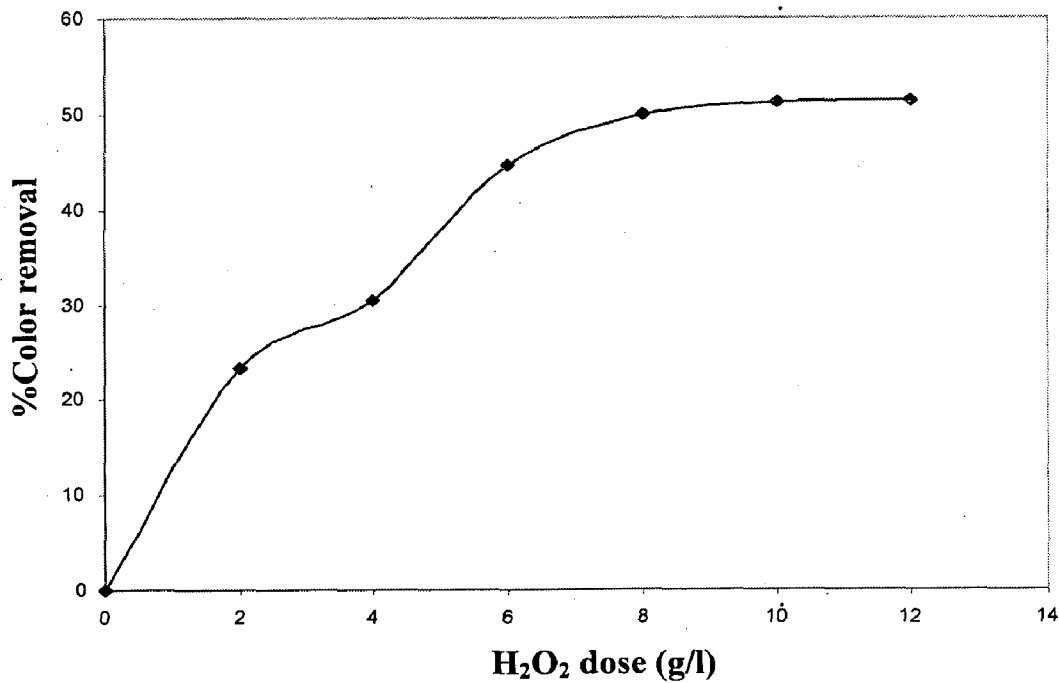


Fig 5.16: Effect of H₂O₂ dose on % Color removal at pH = 3 in Fenton process (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, pH = 3)

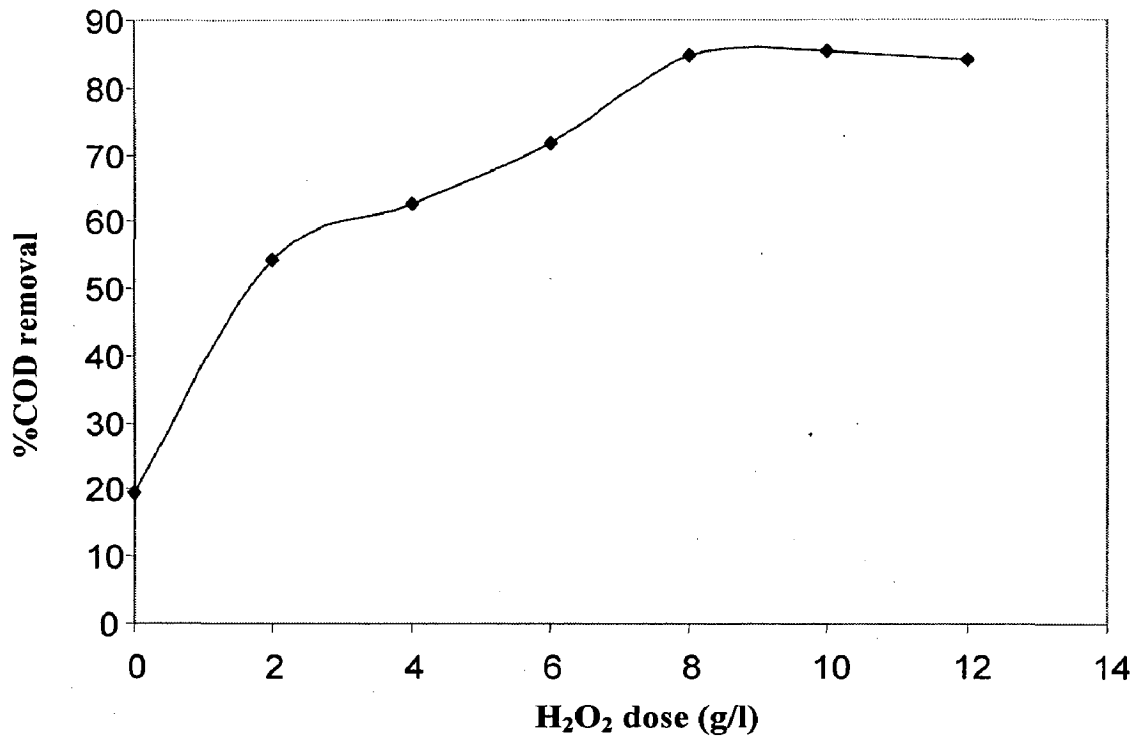


Fig 5.17: Effect of H₂O₂ dose on %COD removal in Fenton process
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, FeSO₄ dose= 3 g/l, pH =3)

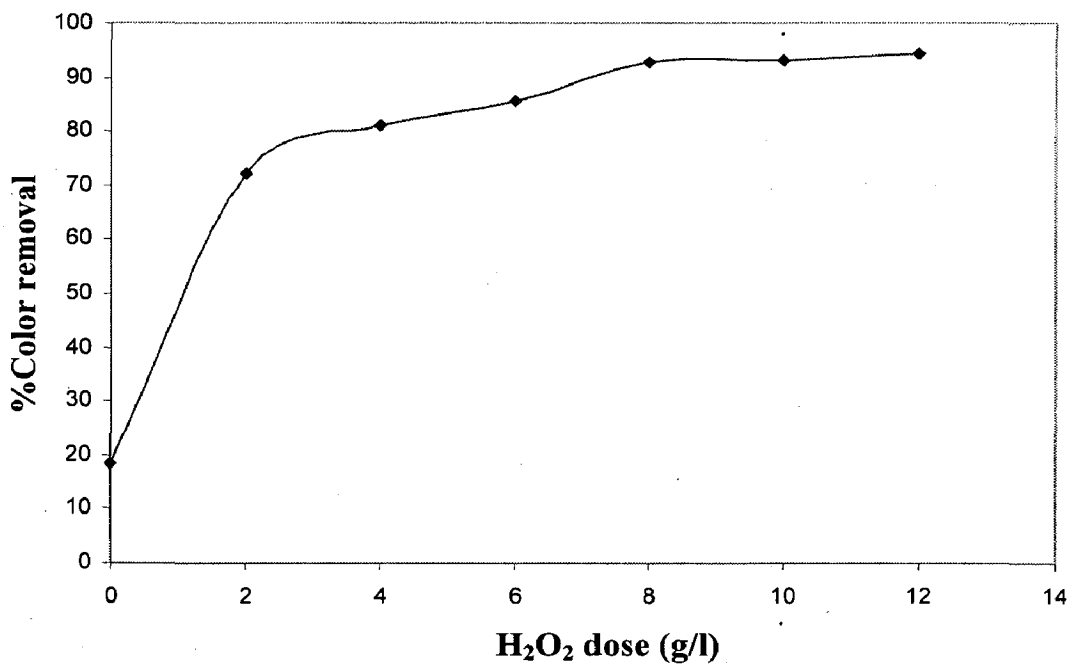


Fig 5.18: Effect of H₂O₂ dose on %Color removal in Fenton process
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, FeSO₄ dose= 3 g/l, pH =3)

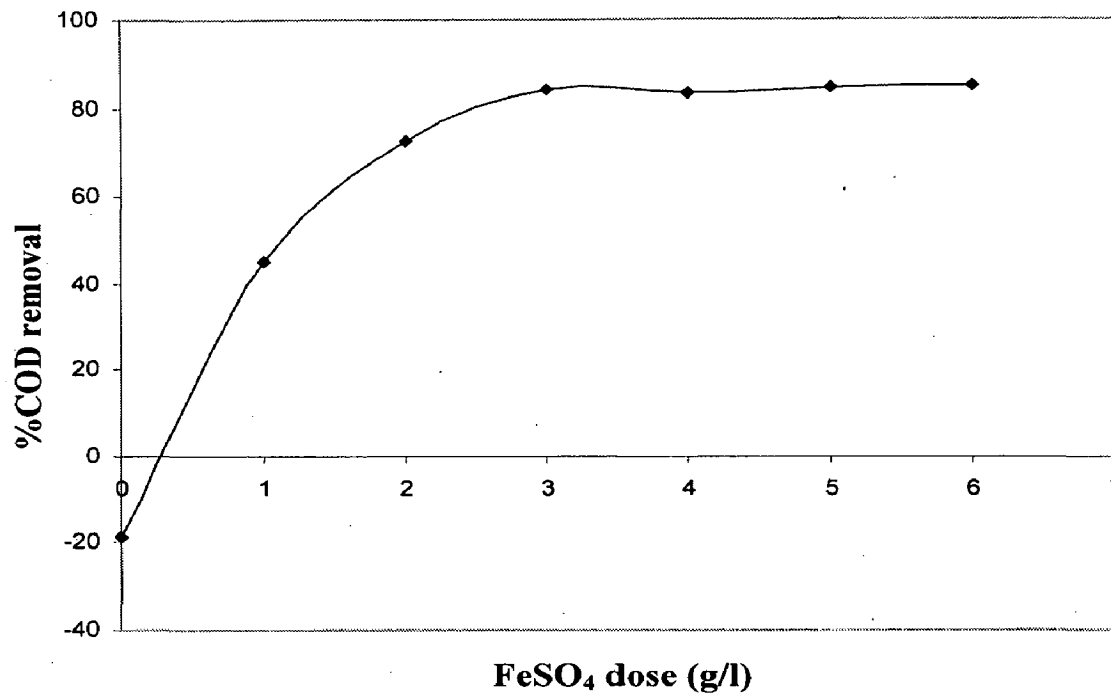


Fig 5.19: Effect of FeSO₄ dose on %COD removal in Fenton process (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, H₂O₂ dose = 10 g/l, pH =3)

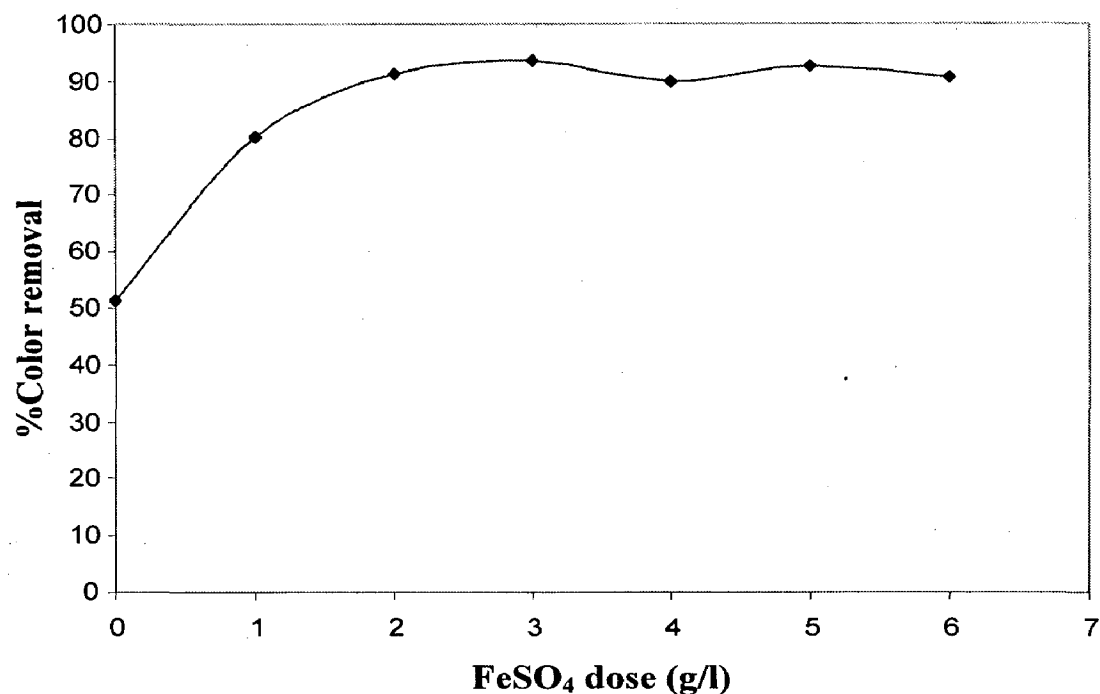


Fig 5.20: Effect of FeSO₄ dose on %Color removal in Fenton process (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, H₂O₂ dose = 10 g/l, pH =3)

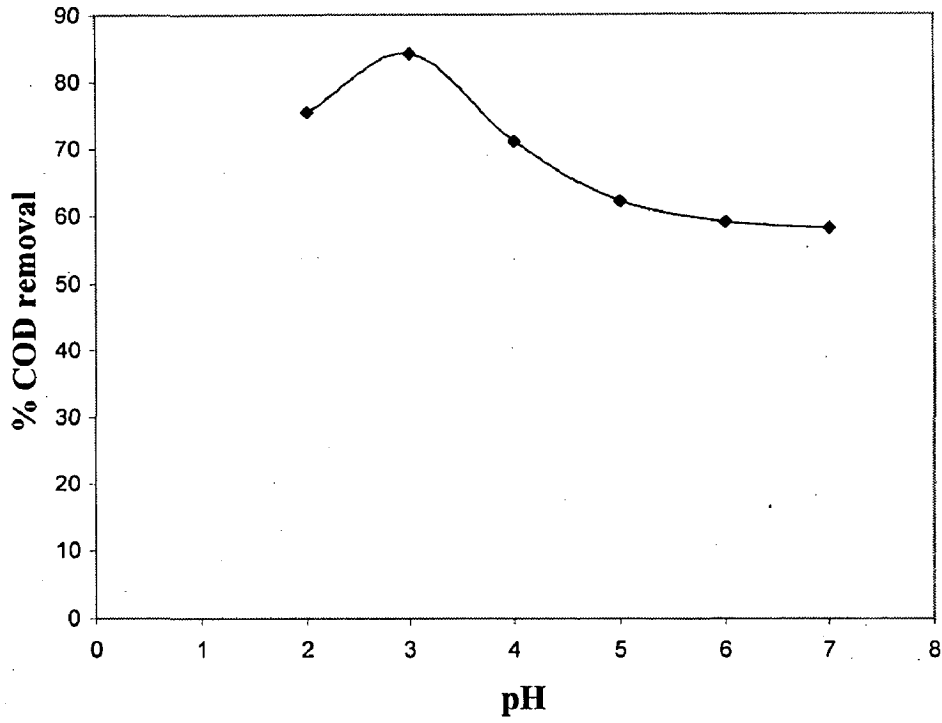


Fig 5.21: Effect of pH on % COD removal in Fenton process.
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, H₂O₂ dose = 10 g/l, FeSO₄ dose= 3 g/l pH =3)

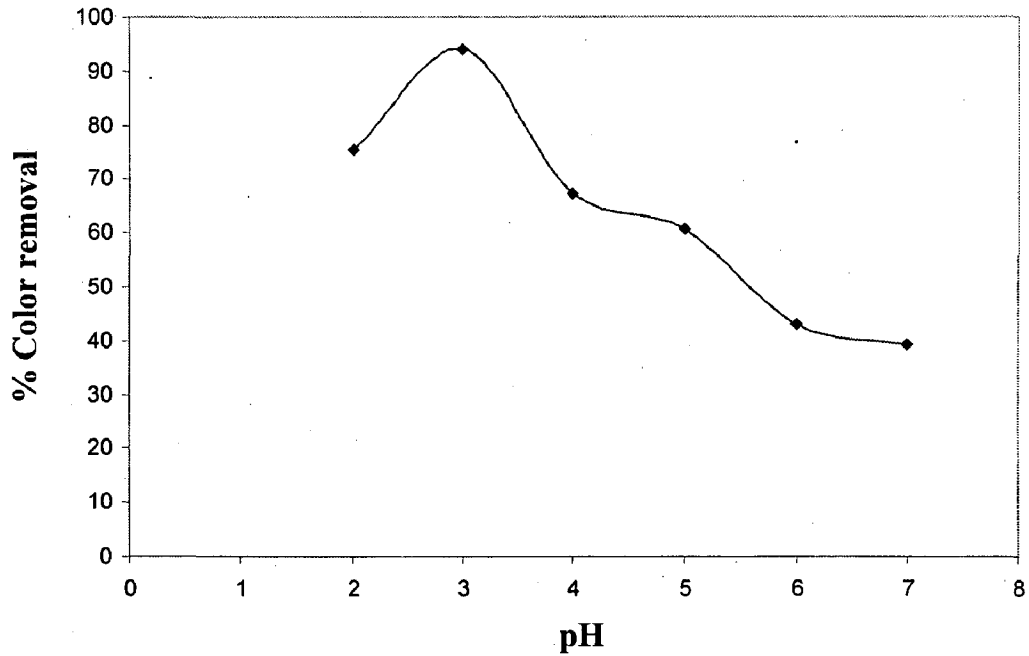


Fig 5.22: Effect of pH on %Color removal in Fenton process.
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit, H₂O₂ dose = 10 g/l, FeSO₄ dose= 3 g/l pH =3)

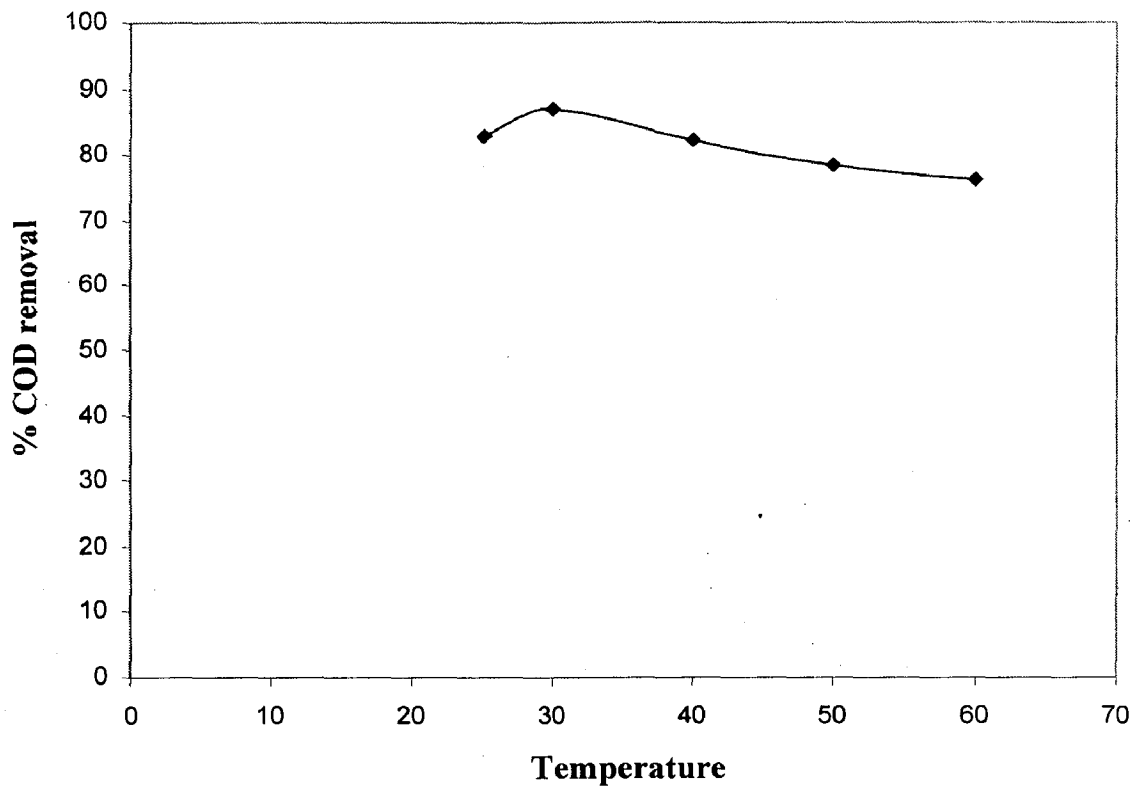


Fig 5.23: Effect of temperature on % COD removal in Fenton process.
(Initial COD = 2540 mg/l, Color = 3150 Pt-Co unit,
H₂O₂ dose = 10 g/l, FeSO₄ dose= 3 g/l pH =3)

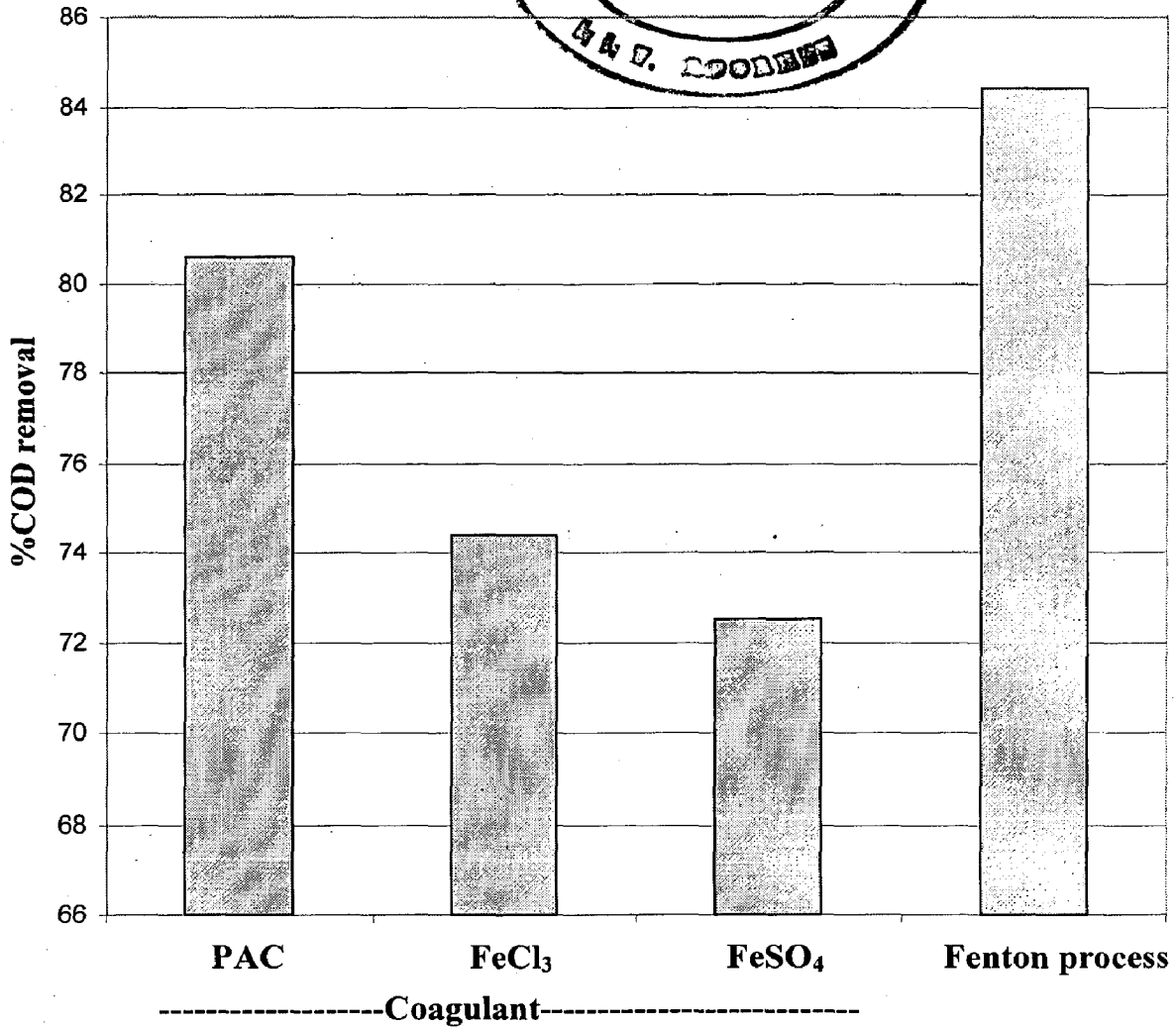
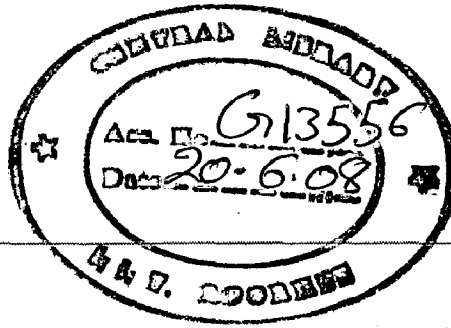


Fig 5.24: Comparison of different coagulants with Fenton process for maximum COD removal (Corresponding to optimum pH and optimum dose)

PAC (pH 3, dose = 4 g/l), FeCl₃ (pH 6, dose = 3 g/l), FeSO₄ (pH 8, dose = 4 g/l), Fenton process (pH 3, H₂O₂ dose = 10 g/l, FeSO₄ dose = 3g/l)

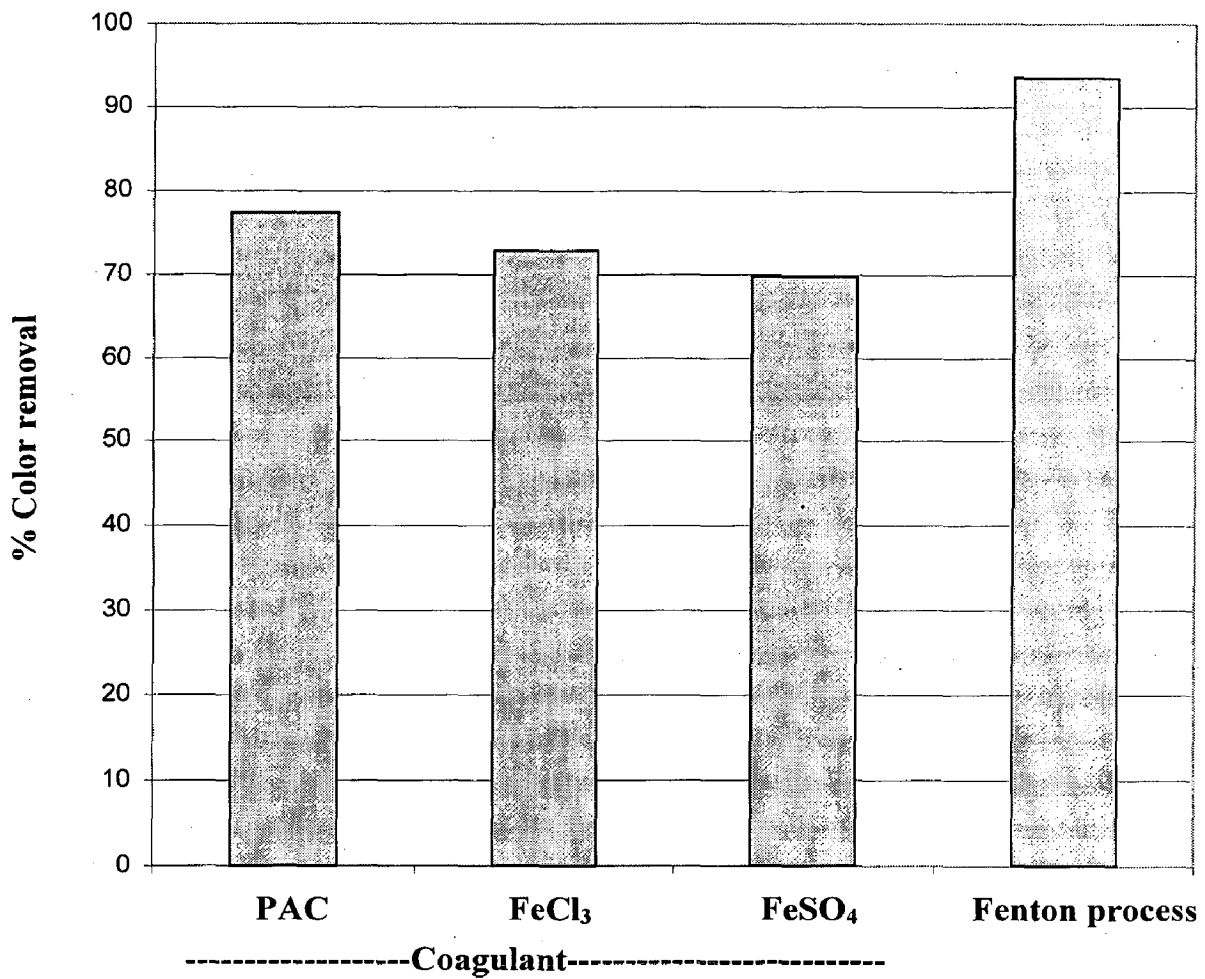


Fig 5.25: Comparison of activities of different coagulants with Fenton process for maximum Color removal

(Corresponding to optimum pH and optimum dose)

PAC (pH 3, dose = 4 g/l), FeCl₃ (pH 6, dose = 3 g/l), FeSO₄ (pH 8, dose = 4 g/l),

Fenton process (pH 3, H₂O₂ dose = 10 g/l, FeSO₄ dose = 3g/l)

CHAPTER-6

CONCLUSION AND RECOMMENDATIONS

6.1 CONCLUSIONS:

The following major conclusions can be drawn from the present work.

1. A comparison of different coagulants at their respective optimum pH shows poly aluminum chloride (PAC) has a greater COD and Color removal efficiency.
2. Removal of COD and Color for PAC treatment increases as the pH of the effluent decreases. The optimum pH for maximum COD and Color removal was found to be 3.
3. Percentage removal of COD and color increases with coagulant dose up to the optimum value, after that no significant change is observed. The optimum dose for PAC was found to be 4 g/l.
4. The optimum pH and optimum dose for maximum COD and color removal for coagulation with FeCl_3 were found to be 6 and 3 g/l, respectively. The optimum pH and optimum dose for maximum COD and color removal for FeSO_4 were found to be 8 and 4 g/l, respectively.
5. The maximum percentage of COD removal achieved, after treatment with PAC, FeCl_3 and FeSO_4 at the optimum conditions were 80.6%, 74.4%, 72.5%, respectively and the maximum percentage of color removal achieved were 77.4%, 72.7%, and 69.8%, respectively.
6. The optimum pH for maximum COD and color removal in Fenton process was found to be 3. At higher pH the COD and color removal were very less due to the less OH^* production at higher pH values. The maximum percentage of COD and color removal, at optimum conditions were 84.4% and 93.5% respectively.
7. The optimum doses of FeSO_4 and H_2O_2 were found to be 3g/l and 10 g/l respectively during Fenton process and the optimum value of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio for maximum COD and color removal was found to be 3.3.

6.2 RECOMMENDATIONS

1. It was observed by this work that poly-coagulants (PAC) have potential for better removal of COD and color. Hence, other polyelectrolyte i.e., poly ion sulfate, poly alumino-iron chloride etc. can be tried for better removal.
2. The combination of H_2O_2 with other coagulants i.e., $FeCl_3$, copper sulfate etc. for the treatment of effluent can be tried to get better removal efficiencies.
3. It is required to find the reaction kinetics for the Fenton process.
4. Further pilot scale studies are required to evaluate the suitability of Fenton process for the treatment of textile mill wastewater on plant scale

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Table A-1: Effect of pH on %COD and %Color removal using PAC
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co units, PAC dose = 3 g/l)

SLNO.	pH	PAC dose(g/l)	COD (mg/l)	Color (Pt-Co units)	%COD removal	% Color removal
1	2	3	594	699	76.7	77.8
2	3	3	541	769	78.7	75.6
3	4	3	777	995	68	68.4
4	5	3	947	1660	62.7	47.3
5	6	3	1524	1975	40	37.3
6	7	3	1638	2227	35.5	29.3

Table A-2: Effect of PAC dose on %COD and %Color removal at pH 3
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co units, pH = 3)

SLNO.	pH	PAC dose(g/l)	COD (mg/l)	Color (Pt-Co units)	%COD removal	% Color removal
1	3	1	1338	1449	47.3	54
2	3	2	884	1093	65.2	65.3
3	3	3	564	784	77.8	75.1
4	3	4	493	712	80.6	77.4
5	3	5	521	699	79.5	77.8
6	3	6	536	709	78.9	77.5

Table A-3: Effect of pH on %COD and %Color removal using FeCl₃
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co units, FeCl₃ dose = 3 g/l)

SLNO.	pH	FeCl ₃ dose(g/l)	COD (mg/l)	Color (Pt-Co units)	%COD removal	% Color removal
1	4	3	1351	1497	46.8	52.5
2	5	3	1323	1301	47.9	58.7
3	6	3	658	904	74.1	71.3
4	7	3	706	882	72.2	72
5	8	3	828	1014	67.4	67.8
6	9	3	968	1077	61.9	65.8

**Table A-4: Effect of FeCl₃ dose on %COD and %Color removal at pH=6
(Initial COD = 2540 mg/l, Color = 3150 Pt-Co units, pH = 6)**

SI.NO.	pH	FeCl ₃ dose(g/l)	COD (mg/l)	COLOR (Pt-Co units)	%COD removal	% Color removal
1	6	1	1252	1537	50.7	51.2
2	6	2	604	1323	76.2	58
3	6	3	650	860	74.4	72.7
4	6	4	597	863	76.6	72.6
5	6	5	632	888	75.1	71.8
6	6	6	597	885	76.5	71.9

**Table A-5: Effect of pH on %COD and %Color removal using FeSO₄
(Initial COD = 2540 mg/l, Color = 3150 Pt-Co units, FeSO₄ dose = 3 g/l)**

SI.NO.	pH	FeSO ₄ dose (g/l)	COD (mg/l)	Color (Pt-Co units)	%COD removal	% Color removal
1	4	3	1951	2255	23.2	28.4
2	6	3	1238	2060	51.2	34.6
3	7	3	1062	1789	58.2	43.2
4	8	3	812	1264	68	59.9
5	9	3	828	1301	67.4	58.7
6	10	3	825	1282	67.5	59.3

**Table A-6: Effect of FeSO₄ dose on % COD and % Color removal at pH = 8
(Initial COD = 2540 mg/l, Color = 3150 Pt-Co units, pH = 8)**

SI.NO.	pH	FeSO ₄ dose (g/l)	COD (mg/l)	Color (Pt-Co units)	%COD removal	% Color removal
1	8	1	1463	2092	42.4	33.6
2	8	2	1262	1805	50.3	42.7
3	8	3	818	1314	67.8	58.3
4	8	4	699	951	72.5	69.8
5	8	5	724	945	71.5	70
6	8	6	739	936	70.9	70.3

**Table A-7: Effect of H₂O₂ dose on %COD and % Color removal at pH = 3
(Initial COD = 2540 mg/l, Color = 3150 Pt-Co units, pH = 3)**

SI.NO.	pH	H ₂ O ₂ dose (g/l)	COD (mg/l)	Color (Pt-Co units)	%COD removal	% Color removal
1	3	2	2626	2416	-3.4	23.3
2	3	4	2672	2189	-5.2	30.5
3	3	6	2776	1745	-9.3	44.6
4	3	8	2893	1575	-13.9	50
5	3	10	3015	1537	-18.7	51.2
6	3	12	3028	1531	-19.2	51.4

Table A-8: Effect of H₂O₂ dose on %COD and %Color removal in Fenton process (Initial COD = 2540 mg/l, Color = 3150 Pt-Co units, FeSO₄ dose= 3 g/l, pH =3)

SI. NO.	pH	FeSO ₄ dose (g/l)	H ₂ O ₂ dose (g/l)	COD (mg/l)	Color (Pt-Co units)	%COD removal	% Color removal
1	3	3	0	2533	2073	19.6	18.4
2	3	3	2	1161	879	54.3	72.1
3	3	3	4	947	598	62.7	81
4	3	3	6	714	454	71.9	85.6
5	3	3	8	386	227	84.8	92.8
6	3	3	10	366	217	85.6	93.1
7	3	3	12	549	173	78.4	94.5

**Table A-9: Effect of FeSO₄ dose on %COD and %Color removal in Fenton process
(Initial COD = 2540 mg/l, Color = 3150, H₂O₂ dose = 10 g/l, pH =3)**

SI. NO.	pH	FeSO ₄ dose (g/l)	H ₂ O ₂ dose (g/l)	COD (mg/l)	Color (Pt-Co units)	%COD removal	% Color removal
1	3	0	10	2893	1537	-18.7	51.2
2	3	1	10	1394	623	45.1	80.2
3	3	2	10	701	271	72.4	91.4
4	3	3	10	396	205	84.4	93.5
5	3	4	10	424	315	83.3	90.0
6	3	5	10	389	236	84.7	92.5
7	3	6	10	378	296	85.1	90.6

Table A-10: Effect of pH on % COD and %Color removal in Fenton process.
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co units, H₂O₂ dose = 10 g/l, FeSO₄ dose= 3 g/l pH =3)

Sl. NO	pH	FeSO ₄ dose (g/l)	H ₂ O ₂ dose (g/l)	COD (mg/l)	Color (Pt-Co units)	%COD removal	% Color removal
1	2	3	10	625	775	75.4	75.4
2	3	3	10	401	192	84.2	93.9
3	4	3	10	734	1027	71.1	67.4
4	5	3	10	958	1241	62.3	60.6
5	6	3	10	1039	1796	59.1	43
6	7	3	10	1059	1909	58.3	39.4

Table A-11: Effect of temperature on % COD removal in Fenton process.
 (Initial COD = 2540 mg/l, Color = 3150 Pt-Co units, H₂O₂ dose = 10 g/l, FeSO₄ dose= 3 g/l pH =3)

Sl.NO.	pH	Temperature	FeSO ₄ dose (g/l)	H ₂ O ₂ dose (g/l)	COD (mg/l)	%COD removal
1	3	25	3	10	434	82.9
2	3	30	3	10	333	86.9
3	3	40	3	10	450	82.3
4	3	50	3	10	546	78.5
5	3	60	3	10	602	76.3

Table A-12: Comparison of different coagulants for maximum percentage of COD and Color removal (Corresponding to optimum pH and optimum dose)

Sl.NO	Type of coagulant	Optimum pH	Optimum dose(g/l)	% COD removal	% Color removal
1	PAC	3	4	80.6	77.4
2	FeCl ₃	6	3	74.4	72.7
3	FeSO ₄	8	4	72.5	69.8
4	Fenton process	3	H ₂ O ₂ = 10 FeSO ₄ =3	84.4	93.5

