

TREATMENT OF PAPER AND PULP MILL EFFLUENT BY COAGULATION

A DISSERTATION

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requirements for the award of the degree
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By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"TREATMENT OF PAPER AND PULP MILL EFFLUENT BY COAGULATION"** 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, Roorkee, is an authentic record of my own work carried out during the period from June 2004 to June 2005 under supervision of Dr. Shri Chand, Professor, Department of Chemical Engineering, Indian Institute of Technology, Roorkee, Roorkee.

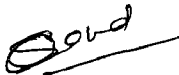
The matter, embodied in this dissertation has not been submitted by me for the award of any other degree.

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ABSTRACT

This dissertation work deals with the removal of chemical oxygen demand (COD) and colour of paper mill effluent due to the chemical precipitation of dissolved solids using different coagulants (such as, aluminium chloride and poly aluminium chloride and copper sulphate). Stephenson et. al. (1994) found that alum based coagulant were effective in treating paper and mill effluent. Ganjidousta et. al. (1997) shown in his paper that polyelectrolyte were also effective. After treating with poly aluminium chloride, results were found as 82.85% COD removal and 91.81% colour removal corresponding to optimum pH of 5 and coagulant dose of 8 g/l. Aluminium chloride was examined for compairing it to PAC. At an optimum pH=4 and dose 7 g/l, it removed 75.5% COD and 83.18% colour. Thus PAC was found more suitable for Colour and COD removal in comparison to aluminium chloride. Garg et. al. (2005) has shown Copper sulfated as new coagulant in his paper. The results found, by using copper sulphate as coagulant, were very impressive. At an optimum pH of 6 and mass loading of 5 g/l, 75% COD reduction and 75.96% colour reduction were obtained.

It is very important in industrial operations to have such coagulated slurries which settle down quickly and the supernatant is therefore separated. So, the settling behavior of effluent treated with above coagulants was also studied. It was found that the aluminium chloride treated effluent settled faster in comparison to other two studied coagulants.

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ABBREVIATIONS

AOX	: Absorbable Organic Halides
BCTMP	: Bleached chemi-thermo-mechanical
BOD	: Biochemical oxygen demand
COD	: Chemical oxygen demand
CPCB	: Central Pollution Control Board
DLVO	: Derjaguin, Landau, Verwery and Overbeek
E (P) Act	: Environmental protection act
EIA	: Environment impact assessment
PAHs	: Polycyclic aromatic hydrocarbons
VOCs	: Volatile organic compounds
MEK	: Methyl ethyl ketone
PASS	: Poly aluminum silicate sulfate
P&P	: Paper and pulp
PAC	: Poly aluminium chloride
ppt	: Precipitation
RBC	: Rotating biological contactor
SCR	: Sludge cake resistance
SVI	: Sludge volume index
TC	: Total carbon
TMP	: Thermo-mechanical pulp
TOC	: Total organic compound
TSS	: Total suspended solid
TDS	: Total dissolved solids
TS	: Total solids

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CHAPTER 1

INTRODUCTION

1.1 General

Rapid industrialization and technological advancement is like boon for world but it may become bane also. Environmental degradation due to rapid industrialization has emerged as a major challenge world over in recent year. Industry produces waste water which contaminated rivers and surface water and drinking water. Many rivers are being fully contaminated. Paper industry that represents an important segment of the world economy has not remained unaffected with this phenomenon and is amongst the highly polluting industries. In addition to global competitiveness, a major issue that the paper industry all over the world is facing is the environmental problem. Environmental issues have become one of the important factors controlling the growth of paper industries during recent years.

1.2 Profile of Pulp and Paper Industry:

Over the centuries, paper has been one of the "unsung" drivers of world development, providing the means for people to record and communicate ideas and news and works of art. Even with the advent of the modern world of plastic bags, electronic communication and paperless offices, paper remains an essential ingredient of homes, factories, offices and schools ^[16]. In principle, the process of making paper is simple. Wood chips are converted to pulp which in turn is processed to create paper, cardboard and a range of other products. In reality, the processes are a complex mix of chemical and physical reactions which take place in both batch and continuous mode. The capital cost of the plant is high, skilled operators are required and the potential for environmental degradation throughout the value chain is huge.

World paper industry assumes nearly 3.5 % of the world industrial production and 2% of world's trade. The paper industry is today a 300 million-ton plus industry

valued at over US\$ one hundred billion per year. The world's major pulp and paper producers are: ^[16]

- North America (USA and Canada)
- South America (Brazil, Chile and Argentina)
- Europe (particularly Scandinavia)
- Asia

The consumption of paper and paper related product is increasing day by day. Industrial grades accounted for 171 million tons, or 58% of the world paper consumption. Corrugating materials were the world's largest paper grade group, accounting for 86 million tons (29%). Consumption of graphical papers, such as newsprint, printing and writing papers, totaled 126 million tons in 1997, with uncoated wood frees, at 44 million tons, the single largest grade group in this area. World demand for paper and paperboard is forecast to grow from the current 300 million tons to over 420 million tons by the year 2010 or an average growth rate of 2.8% per annum. The estimated demand of paper and boards will reach 640 million times in 2020.

For developing countries like India, consumption of paper per unit income has increased over the years. India has over 16% of the world's population but consumes only 1% of the world's paper and paperboard. The pulp and paper industry, now well over 40 years old, (With merely 17 units in 1950 with production of 0.11 million tonnes paper,) has about 400 paper mills with an installed capacity of 4 million tonnes per year. Twenty-eight mills are forest-based, occupying 37% of total production capacity whereas 242 mills, 32%, are based on wastepaper and 130 units, 31%, are based on agro-residues. The future demand of paper is expected to grow from 5.6 MT at present TO 9.5 MT in 2010 and 13 MT in 2015. Demand for cream wove paper is expected to increase by 7-8%. Demand for different kinds of coated paper has increased by 8% in 2002, duplex board has recorded increase by 6.5%, kraft paper has registered a 6% rise in demand and newsprint an impressive 10%. The paper industry in India has a long history with the first mill, being commissioned in 1832.

Major raw material used by paper industry is bamboo, wood, bagasse, waste paper and agricultural residue like wheat straw, rice straw, jute sticks etc. and other unconventional non-woods from farms/ grassland besides waste paper and market pulp. Apart from this, paper industry consumes large amount of chemicals like caustic soda, sodium sulphide, sodium carbonate, chlorine, hypochlorite, mineral acid; coal, talcum powder etc. Process technology used is Kraft pulping, mechanical pulping and semi chemical pulping. Majority of mills use CEH and CEHH bleaching sequences while very few mills use chlorine dioxide bleaching and oxygen delignification.

Table.1.1 Per Capita Consumption^[16]

Country	Production (Million)	Consumption (Million Tons)	Consumption per capita (kg)
Japan	31.825	31.736	250
China	30.900	36.277	28
Korea	9.308	7.385	156
Indonesia	6.935	3.911	19
Taiwan	4.500	5.110	229
India	5.260	5.220	5
Thailand	2.466	2.114	34
Malaysia	1.078	2.251	101
Philippines	0.750	0.828	11
Hong Kong	0.190	1.041	151
Singapore	0.052	0.577	160

1.3 Environmental Challenges and Control Measures in Pulp and Paper Industry:

1.3.1 General:

The waste water generated from integrated pulp and paper mill is highly polluting because it contains high biochemical and chemical oxygen demands (BOD and COD), toxic substances, recalcitrant organics, and intense color. The effluent originating from the chemical pulping stage is called black liquor, and it contains lignin, organic acids, phenolic compounds, sulfur compounds, terpenes, resin etc. Paper industry is one of the major polluting industries and is amongst top twenty-nine industries for which environmental impact assessment (EIA) has been made mandatory. Paper industry consume large amount of water (about 250-300 cu. m. per tonne of paper) and generate an equal amount of wastewater having high BOD, COD, pH, turbidity, high temperature and color. While society needs paper products, it has to be environmentally sustainable. The environmental pollution problems associated with pulp and paper production are four folds:

- Air pollution.
- Water pollution.
- Solid waste pollution.
- Indirect pollution.

1) Air Pollution:

Many problems arise in the conversion of wood to paper pulp. Mills should be monitored for a range of air emissions, such as particulate matter, carbon dioxide, sulphur dioxide, Hydrogen sulphide, volatile organic compounds, chlorine, chloroform, and chlorine dioxide. Air discharges from pulp mills contain hormone disrupting and carcinogenic chemicals, such as chlorinated phenols, polycyclic aromatic hydrocarbons (PAHs), and VOCs. Table.1.2 shows the common air pollutants from paper and pulp industry.

Table.1.2 Common Air Pollutants from Paper and Pulp Industry. ^[15]

Source	Type
Kraft recovery furnace	Fine particulates, nitrogen oxides
Fly ash from hog fuel and coal fired burners	Coarse particulates
Sulfite mill operations	Sulfer oxides, ammonia
Kraft pulping and recovery processes	Reduced sulfer gases
Chip digesters and liquor evaporations	Volatile organic compounds
Pulp drying (non-integrated mills)	Volatile organic compounds
All combustion processes	Nitrogen oxides

2) Water Pollution:

Pulp mills are voracious water users. Their consumption of fresh water can seriously harm habitat near mills, reduce water levels necessary for fish, and alter water temperature, a critical environmental factor for fish. Table.1.3 shows the water pollution from paper and pulp mill.

Table.1.3. Potential water pollutants from paper and pulp processes ^[15]

Source	Effluent characteristics
Water used in wood handling/debarking and chip washing	BOD, Solids, color
Chip digester and liquor evaporator condensate	Concentrated BOD, reduced sulfur compounds
"White waters" from pulp screening, thickening and cleaning	Large volume of water with suspended solids, can have significant BOD
Bleach plant washer filtrates	BOD, color, chlorinated organic compounds
Paper machine water flows	Solids
Fiber and liquor spills	Solids, BOD, color

3) Solid Wastes pollution:

Quantities of generated solid waste vary widely. In the past, up to 250kg of dry material was produced per tonne of pulp, but today some mills generate as little as 10kg/t. Solid wastes are generally benign biomass comprising bark, rejected fiber and bio-solids, combined with small amounts of lime, clay, wood ash, coal ash and wood yard rejects. The principal issue to date has been the increasing costs of disposal to land, compared to the cost of on-site incineration in an acceptable manner. Trends in solid waste management include cleaner incineration, use of sludge as a soil conditioner, and a better process control for minimal waste generation.

4) Indirect Pollution:

The conversion of pulp to paper sheet requires large amounts of energy. The pulp and paper industry is a major energy consumer, using 2,000-6,500 kWh to produce one tone of dried pulp. Whilst chemical pulping actually requires more energy than mechanical (6,350 kWh/tonne Kraft; 5,400 kWh/tonne sulfite) the processes are largely energy self-sufficient through the burning of waste products to generate steam. Mechanical pulping requires imported electrical energy (2000 kWh/tonne). Different bleaching processes require varying amounts of energy, with ECF requiring most at 4.0 kWh/kg and TCF requiring least at 1.0 - 2.0 kWh/kg .

For Energy Conservation Following measures can be taken for conserving energy:

- Insulation of digesters and steam carrying pipes; Prevent leakages of steam.
- Prevent leakage of steam.
- Recycling steam condensate;
- Recovering heat from hot effluent.

1.3.2 Potential Environmental Exposures:

From the pulping process to paper making to delivering to the end consumer the environmental exposures for this industry are numerous. The potential environmental exposures arise from paper and pulp industry is ^[12]:

- Contaminated wastewater - from process equipment, storm water runoff, cooling water
- Improper disposal of solid waste
- Storage tanks: including old storage yards
- Chemical contamination
- Lack of adequate preventative environmental risk management
- Loading/unloading products
- Soil and groundwater contamination

There are upwards of 50 different environmental contaminants associated with the pulp and paper industry: here's an example of some, based on the process.

Pulping: Sodium hydroxide, sodium bisulfate, sodium sulfate, calcium/magnesium/aluminum bisulfites

Bleaching: Chlorines, hydrogen peroxide, acids, ozone, sodium hydroxide/hypochlorite/dithionite

Additives for fillers, adhesives, to improve strength & color : Talc, alum, clay, dyes, pigments, fuel oil, alcohols, wax emulsions, ammonia, starch, silicones, solvents, recycled oils, latex, rosin, acetates, polyesters, etc.

1.3.3 Process inputs and pollutant output ^[15]:

Kraft chemical pulping and chlorine-based (e.g., hypochlorite or chlorine dioxide) bleaching are both commonly used and may generate significant pollutant outputs. Pollutant outputs from mechanical, semi-chemical, and secondary fiber pulping are small when compared to kraft chemical pulping. In the pulp and paper industry, the kraft pulping process is the most significant source of air pollutants. The following table.1.4 illustrate the process inputs and pollutant outputs for a pulp and paper mill using kraft chemical pulping and chlorine-based bleaching.

Table.1.4 various input and various output pollutant [15].

Process Step	Material Inputs	Process Outputs	Major Pollutant Outputs ^a	Pollutant Media
Fiber Furnish Preparation	Wood logs Chips Sawdust	Furnish chips	dir, grit, fiber, bark	Solid
			BOD	Water
			TSS	
Chemical Pulping Kraft process	Furnish chips	Black liquor (to chemical recovery system), pulp (to bleaching/ processing)	resins, fatty acids	Solid
			color	Water
			BOD	
			COD	
			AOX	
	VOCs [terpenes, alcohols, phenols, methanol, acetone, chloroform, methyl ethyl ketone (MEK)]		Air	
	VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)			
reduced sulfur compounds (TRS)				
Cooking chemicals: sodium sulfide (Na ₂ S), NaOH, white liquor (from chemical recovery)			organo-chlorine compounds (e.g., 3,4,5- trichloroguaiacol)	
Bleaching ^b	Chemical pulp	Bleached pulp	dissolved lignin and carbohydrates	Water
			color	
			COD	
			AOX	
	inorganic chlorine compounds (e.g., chlorate (ClO ₃)) ^c		Air / Water	
	VOCs (acetone, methylene chloride, chloroform, MEK, chloromethane, trichloroethane)			
Hypochlorite (HClO, NaOCl, Ca(OCl) ₂) Chlorine dioxide (ClO ₂)				
Papermaking	Additives, Bleached/ Unbleached pulp	Paper/paperboard product	particulate wastes	Water
			organic compounds	
			inorganic dyes	
			COD	
			acetone	

1.3.4 Paper Mill Effluent Quality and Quantity:

a) Volume of Effluent:

The volume of effluents discharged varies from mill to mill and depends on the production capacity, types of paper manufactured, pulping process, recovery of chemicals and water, economy adopted. It is reported that an integrated pulp and paper mill employing kraft process generates 220 to 320 m³ of effluents per ton of paper manufactured. Mills manufacturing specialty papers generate more volume of effluents as they use more water for washing and bleaching. It is to be mentioned that small mills discharge higher volumes of waste per ton than large mills, as they do not possess recovery units. It is estimated that about 330 m³ of effluent is produced per tonne of paper manufactured in a small mill of capacity 20 ton/day where as 220 m³/ton is generated in a large mill manufacturing 200 tons/day ^[11]. Table 2 shows the volume of effluents discharged by various pulp, paper and board mills.

Since the pulp and paper industry requires large volumes of water, also the bulk of which is released as wastewater. So the most polluting coming from pulp and paper industry is regarding the water pollution.

b) Sources of Waste Water:

All the unit operations, namely, chipping, digestion, pulp washing, bleaching. Papermaking and chemical recovery generate wastewaters. During the manufacture of paper, wastewaters are discharged from: ^[20]

- *Digester house*: leaks and spills of black liquor and gland cooling water.
- *Pulp washing*: the final wash, often referred to as brown stock wash or unbleached Decker wash.
- *Pulp bleaching*: chlorination stage wastewater containing, chloro-lignin etc.

- *Paper machine*: the wastewater contains fibers from felt washing.
- *Chemical recovery*: spills of black liquor and foul condensation.
- *Miscellaneous*: boiler blown down, recausticizer lime mud and lime dredges from lime preparation section.

The figure.1.1 shows Simplified Flow diagram of solid waste and wastewater coming from pulp and paper industry.

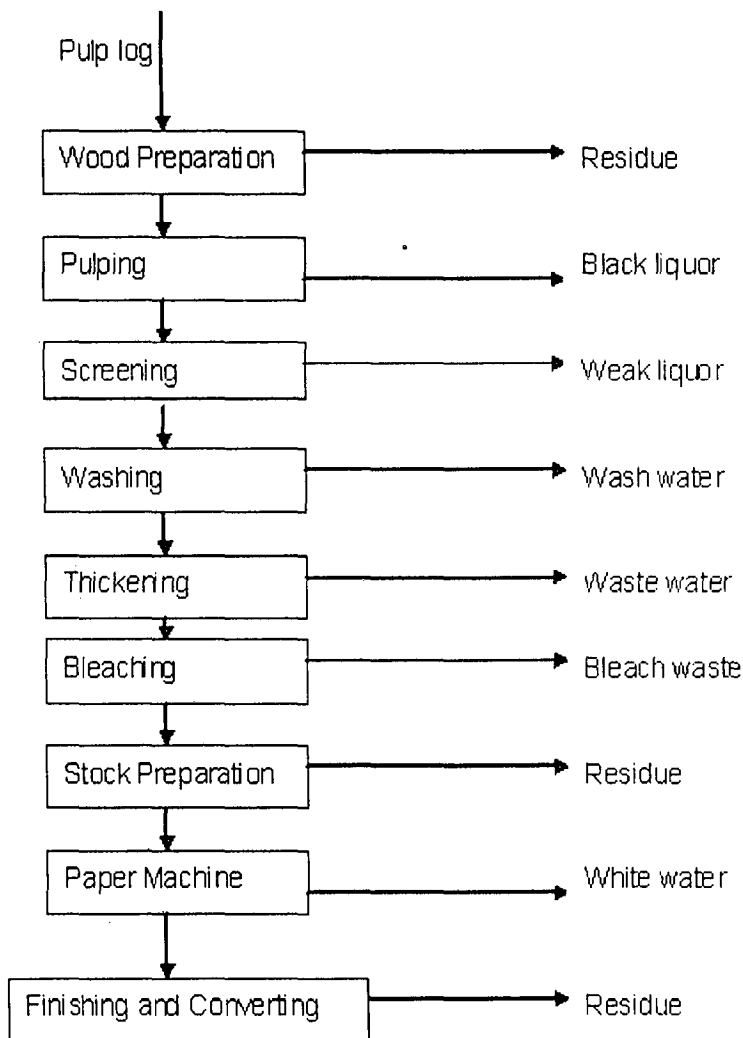


Fig.1.1 Simplified flow diagrams of solid waste and wastewater coming from pulp and paper industry

The major polluting substances present in the effluent are dissolved organics (including coloured and chlorinated substances) and suspended solids. Thus,

pulping and bleaching plants form the major sources of colour in the effluent, washing from the paper machine "white water" dilute these wastes to certain extent. The dissolved compounds, which are partially responsible for the normally high BOD and COD levels in the effluent, originate mainly from the pulping stage where significant losses of wood materials occur. As for paper mills, losses of fibre in repulping of waste paper are generally in the range of 12% to 15%. Loadings of BOD, COD, suspended solids and colour in the P & P mill effluents depend significantly on:

- The nature and cleanliness of the feedstock.
- Whether the P & P mill is equipped with a chemical recovery facility.
- The bleaching techniques employed.
- The efficiency of white water recycle/fiber recovery in the paper line.

Depending on the efficiency of the chemical recovery plant, as much as COD can be removed from the pulp cooking liquor. Modifications in the bleaching sequence can as well reduce the loading of these pollutants. Untreated P & P mill effluents have been shown by many workers as positively toxic to fish and other aquatic organisms. The components of bleached kraft mill effluents, which are most toxic to fish. Using ozone in bleaching instead of chlorine reduces wastewater discharge loadings of Absorbable Organic Halides' AOX', BOD, and Colour from the bleach plant. The major pollutants found in this wastewater are materials that exert oxygen demand and that cause colour in the receiving waters. Oxygen demand results from the biodegradation of carbohydrate components present in the effluent. The colour causing materials are caramelized sugars and lignin degradation products.

1.3.5 Pollution Control in Pulp and Paper Industry:

Treatment that industrial facilities give wastewater before discharging it to the local wastewater treatment facility is referred to as "pretreatment." Methods for

providing pretreatment can be divided into four categories: physical, chemical, biological, and membrane. This briefing addresses the first three categories. A pretreatment system may use one or several pretreatment processes. Following is a brief description of common physical, chemical and biological pre treatment processes: here, brief discussion about different treatment process has been given.

Physical:

- Screening is removal of coarse solids by use of a straining device.
- Sedimentation is gravity settling of pollutants out of the wastewater.
- Flotation is the use of small gas bubbles injected into the wastewater which causes pollutant particles in the wastewater to rise to the surface for subsequent removal.
- Air stripping is removal of volatile and semi volatile organic compounds from wastewater by use of air flow.

Chemical:

- Neutralization is adjustment of alkalinity and acidity to the same concentration (pH 7).
- Precipitation (ppt) is addition of chemicals to wastewater to change the chemical composition of pollutants so that the newly formed compounds settle out during sedimentation.
- Coagulation is use of chemicals to cause pollutants to agglomerate and subsequently settle out during sedimentation.
- Adsorption is use of a chemical which causes certain pollutants to adhere to the surface of that chemical.
- Disinfection is use of a chemical (or other method such as ultraviolet radiation) to selectively destroy disease causing organisms. (Sterilization is the destruction of all organisms.)
- Breakpoint chlorination is the addition of chlorine to the level that chloramines will be oxidized to nitrous oxide and nitrogen, and chlorine will be reduced to chloride ions.

Biological:

- Air activated sludge is an aerobic process in which bacteria consume organic matter, nitrogen and oxygen from the wastewater and grow new bacteria. The bacteria are suspended in the aeration tank by the mixing action of the air blown into the wastewater.
- High purity oxygen activated sludge is an aerobic process very similar to air activated sludge except that pure oxygen rather than air is injected into the wastewater.
- Aerated pond/lagoon is an aerobic process very similar to air activated sludge. Mechanical aerators are generally used to either inject air into the wastewater or to cause violent agitation of the wastewater and air in order to achieve oxygen transfer to the wastewater. As in air activated sludge, the bacteria grow while suspended in the wastewater.
- Trickling filter is a fixed film aerobic process. A tank containing media with a high surface to volume ratio is constructed. Wastewater is discharged at the top of the tank and percolates (trickles) down the media. Bacteria grow on the media utilizing organic matter and nitrogen from the wastewater.
- Rotating biological contactor (RBC) is a fixed film aerobic process similar to the trickling filter process except that the media is supported horizontally across a tank of wastewater. The media upon which the bacteria grow is continuously rotated so that it is alternately in the wastewater and the air.
- Oxidation ditch is an aerobic process similar to the activated sludge process. Physically, however, an oxidation ditch is ring shaped and is equipped with mechanical aeration devices.

1.4 Challenges and Opportunities Faced By Indian Paper Industry ^[8]:

With India's large population, increasing literacy and income the paper industry appears to have a bright future. Presently consumption of about 3 kilograms per annum (which compares to the Asian average of 18 kg and the world average of 45 kg) allows much room for growth.

However, there are many challenges facing the industry. The challenge for the Indian paper industry to meet the ever increasing demand of paper, board and newsprint is getting crippled due to shortage of fibers in the country. And shortage of domestically produced fiber has placed a heavy reliance on foreign sources which leaves it open to price fluctuations and unreliability of supply. Economies of scale make it difficult for the older, smaller, not as technically advanced Indian mills to compete with global operations that have large modern facilities.

The industry is highly fragmented in every sector from production to distribution, and in each area producers, converters and distributors face their own particular problems.

The planned development of the paper industry in India began only in the post-independence period. The growth, however, slowed down in the 1960s owing to the escalation of costs and the scarcity of forest-based raw materials. The stagnation led to frequent shortages of cultural varieties of paper, causing hardships to consumers.

India's newsprint industry is highly capital-intensive and this has restricted the entry of new players and stalled the expansion of existing units. The investment required for setting up a medium-sized plant of 33,000 tons per year is approximately US\$24 million. Modernization and expansion of existing plants is equally expensive. The challenge, which is being faced by Indian paper and pulp mill, is discussed below in different areas.

a) Merchanting Paper:

India has no large retailers of paper, larger stationery stores or nationwide general retail outlets making the merchanting of paper very fragmented. The distributors are medium to small scale and generally restricted to a few grades.

Sources familiar with the industry in India believe that establishing a countrywide paper distribution network in India would be very difficult. The import of fine paper is largely limited to coated and cast coated papers. Publishing grades like LWC and newsprint are the other major imports which are allowed for import by end users only.

b) Fiber:

Sourcing fiber is a serious problem for Indian pulp mills that was compounded when several states banned the felling of trees for the manufacturing of paper. This has forced many producers to shift to alternative raw materials such as recovered paper, and agro-based products. The use of recovered paper has been limited in scale because there is no organized system of collecting wastepaper on a large scale. As most of the existing technology used by larger manufacturers is geared towards the use of wood pulp a shift to agro-based raw materials has been difficult and expensive.

The main alternative raw materials used for manufacturing paper are waste paper and agro-based materials. As the availability of softwood pulp is limited the industry depends on a limited supply of bamboo, which is a poor substitute. Companies are also using tropical hardwood. As of 1999, the furnish used by the industry are approximately 30% hardwood/eucalyptus, 23% bagasse/straw and bamboo/reed; 15% wastepaper; 5% percent of pulp and 4% other materials.

It is estimated that there is 55 million tons of bagasse available, however only 8% is used for paper production. Until recently the high capital cost and non-availability of technology in India has hindered the use of bagasse. Cheap and easy availability of this raw material is forcing many Indian manufacturers to switch to bagasse as an alternative. TNPL was the first commercially successful integrated newsprint manufacturer in the world with bagasse as the primary raw material.

c) Newsprint:

Newsprint manufacturers have been under severe pressure during the past few years due to international newsprint prices being at low levels. Now it would be even more difficult for many of them to sustain business with the import duty on newsprint remaining unchanged at five per cent even though the WTO-bound rate was pegged at 25%. "There are inherent infrastructural inadequacies in upscaling the level of operations, given the problems associated with the availability of appropriate fiber-bearing, high-yielding and quick-yielding pulpwood species.

India has a diverse and growing number of daily newspapers. The print medium is well developed publishing a large number of daily newspapers, including business dailies and a wide selection of weekly, fortnightly and monthly business magazines, news magazines and industry-specific magazines. Circulations are increasing, resulting in an upward trend in newsprint consumption levels.

The Indian newsprint industry has built up a production capacity of 773,000 t/y, with an investment of more than US\$ 4 billion over the past 40 years. Consumption is about 700,000 tons per year whereas local production is estimated at 400,000 tons. Six mills, with a production capacity of 418,000 tons are in the public sector, and approximately 30 companies, with a capacity of 315,000 tons are in the private sector. Some of these mills have the capability to produce newsprint and cultural varieties of paper on the same machines, using wastepaper as raw material.

1.5 Environmental Standards:

For the preservation of natural resources of earth and protection and improvement of human environments, several acts, rules, regulations and standards have been enforced. Minimal national standards and emission standards for pulp and paper industry are given in Table 1.3.

Table.1.5 Minimum National Standards for wastewater discharge in India [Central Pollution Control Board (CPCB) 2000]

Parameter	Large paper mills	Small paper mills
PH	6.5 to 8.5	5.5 to 9.0
Suspended solids (mg/L)	100	100
BOD at 27°C (mg/L)	30	Inland: 30 Land: 100
COD (mg/L)	350	No limit
Total organic chlorine (TOCL) (Kg/ton paper 1992 onwards)	2.0	No limit

Table.1.6 Environmental standards for pulp & paper mills in India

Table.1.6.1 MINAS for small pulp and paper industry

Parameter	Discharged on to surface water	Disposal on land
pH	5.5 - 9.0	5.5 - 9.0
Suspended solids, mg l ⁻¹	100	100
BOD, mg l ⁻¹	30	100
Sodium absorption ratio	26	26

Table.1.6.2 MINAS for large integrated pulp and paper industry

Parameter	Concentration
pH	7.5 - 8.5
Suspended solids, mg l ⁻¹	50
BOD, mg l ⁻¹	30
COD, mg l ⁻¹	350
Total organic chloride kg per tonne of product	2.0

Table.1.6.3 Effluent discharge standards for pulp and paper mills under E (P) Act. 1986

Category	Standard	Note
Large (writing & printing) pulp and paper mills	200 m ³ /tonne of paper	Standards of discharge for the large pulp & paper mills established from 1992 onward to meet standard of 100 m ³ /tonne of paper
Large (Rayon grade / Newsprint) Pulp and paper mill	150 m ³ /tonne of paper	
Agro-residue based	200 m ³ /tonne of paper	Agro-residue based mills established from January 1992 onward to meet the standards of 150 m ³ /tonne of paper
Wastepaper based mills	75 m ³ /tonne of paper	Wastewater based mills established from January 1992 onward to meet the standards of 50 m ³ /tonne of paper

1.6 Objective:

The aim of this work is to demonstrate the efficacy of chemical coagulation and precipitation for the removal of COD and colour from a pulp and paper mill effluent. In order to meet this goal, four specific objectives were identified:

1. Compare the efficacy of different coagulants (such as PAC, aluminum chloride and copper sulfate) for coagulating and precipitating a paper and pulp mill effluent.
2. Identify the optimum dose of each coagulating agent for maximum COD removal.
3. Locate the optimum pH adjustment.
4. Study the settling characteristics of each coagulant.

CHAPTER 2

FUNDAMENTALS OF COAGULATION

2.1 General

The removal of suspended matter from water is one of the major goals of water treatment. Only disinfection is used more often or considered more important. In fact, effective clarification is really necessary for completely reliable disinfection because microorganisms are shielded by particles in the water.

Clarification usually involves:

- Coagulation
- Flocculation
- Settling
- Filtration

Coagulation and flocculation processes are used to separate the suspended solids portion from the water or waste water. Coagulation includes addition of reagents to a waste for the sole purpose of producing a flocculants precipitate that removes fine suspended matter and colloidal substances by adsorption or mechanical agglomeration. Coagulation and flocculation occur in successive steps intended to overcome the forces stabilizing the suspended particles, allowing particle collision and growth of floc. If step one is incomplete, the following step will be unsuccessful.

2.2 Fundamental of Coagulation

Coagulation has been defined as the addition of a positively charged ion such as Al^{3+} , Fe^{3+} or catalytic polyelectrolyte that results in particle destabilization and charge neutralization. Coagulation involves the formation of complex oxides that form flocculant suspensions, which subsequently are separated from the liquid by sedimentation.

The coagulation target is a colloid particle (See Fig.2.1) of a size 10^{-7} to 10^{-4} cm in diameter. Generally, colloid particles exhibit Brownian movement in the water, their surface is negatively charged so they repel one another, and they form a

stable dispersed suspension. If colloid particles or ions of positive electric charge are added to neutralize the electric charge of coagulation target, physical attractive force (the van der waals force) will exceed the electrical repulsion force, causing the particles to coagulate. The (zeta) potential is used as an index for measuring the magnitude of this repulsive force. This potential is normally form -30 mV to +30 mV, but coagulation starts when it is brought within 10 mV.

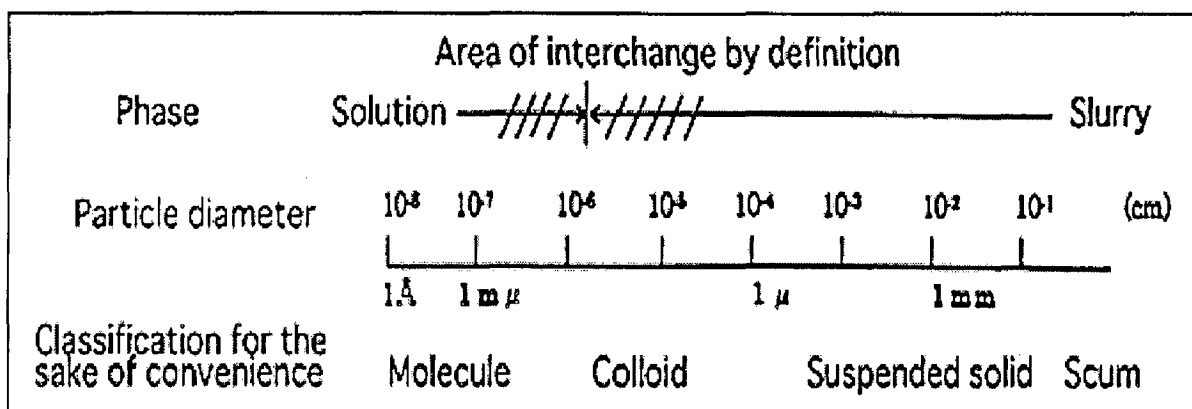


Fig.2.1 Classification of particle by size

Coagulation refers to addition of coagulant which neutralizes charged particle and results in lowering of DLVO energy barrier called destabilization. It is written above that coagulation and flocculation are successive steps.

Flocculation refers to the successful collisions that occur when the destabilized particles are driven toward each other by the hydraulic shear forces in the rapid mix and flocculation basins. Agglomerates of colloids then quickly bridge together to form microflocs which in turn gather into visible floc masses.

The key to effective coagulation and flocculation is an understanding of how individual colloids interact with each other. The behavior of colloids in water is strongly influenced by their electrokinetic charge. Each colloidal particle carries a like charge, which in nature is usually negative. This like charge causes adjacent particles to repel each other and prevents effective agglomeration and flocculation. As a result, charged colloids tend to remain discrete, dispersed, and in suspension (see in fig.2.2).

On the other hand, if the charge is significantly reduced or eliminated, then the colloids will gather together. First forming small groups, then larger aggregates and finally into visible floc particles which settle rapidly and filter easily (see in fig.2.3).

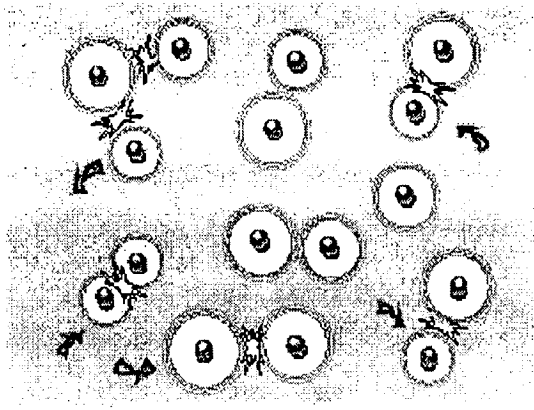


Fig.2.2 Charged particles^[2]

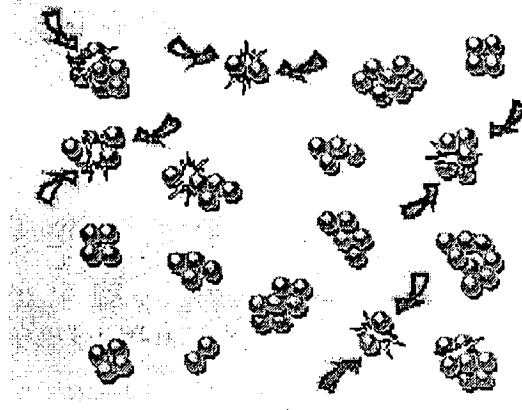


Fig.2.3 Uncharged particles

Double layer

The double layer model is used to visualize the ionic environment in the vicinity of a charged colloid and explains how electrical repulsive forces occur. Initially, attraction from the negative colloid causes some of the positive ions to form a firmly attached layer around the surface of the colloid. This layer of counter-ions is known as the Stern layer. Additional positive ions are still attracted by the negative colloid but now they are repelled by the positive Stern layer as well as by other nearby positive ions that are also trying to approach the colloid. A dynamic equilibrium results & forms a diffuse layer of counter-ions. The diffuse positive ion layer has a high concentration near the colloid which gradually decreases with distance until it reaches equilibrium with the normal counter-ion concentration in solution.

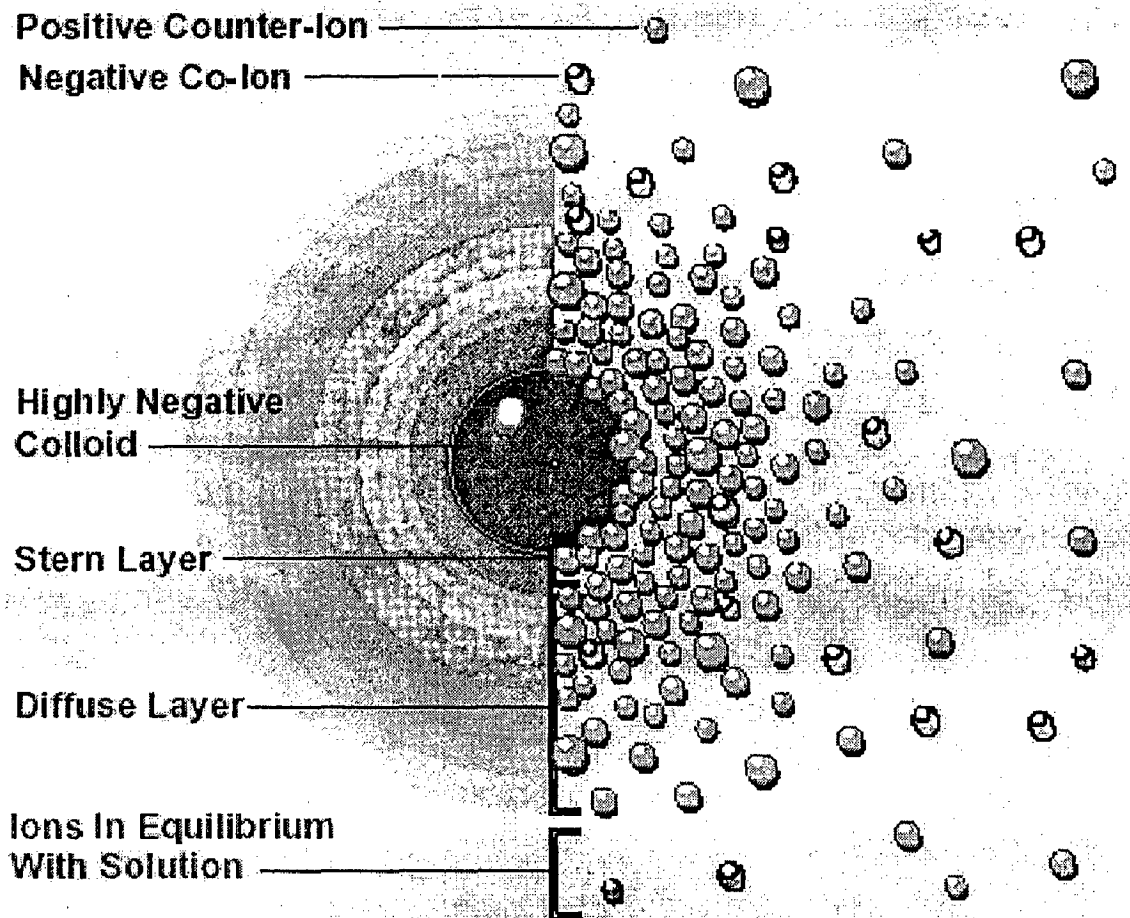


Fig.2.4 Two ways to visualize the double layer: The left view shows the change in charge density around the colloid. The right shows the distribution of positive and negative ions around the charged colloid.^[2]

The attached counter-ion in stern layer and charged atmosphere in diffused layer are referred as double layer.

Double layer thickness

The thickness of the double layer depends upon the concentration of ions in solution. A higher level of ions means more positive ions are available to neutralize the colloid. The result is a thinner double layer. Decreasing the ionic concentration (by dilution, for example) reduces the number of positive ions and a thicker double layer results. The type of counter-ion will also influence Double layer thickness. Type refers to the valence of the positive counter-ion. For Instance, an equal concentration of aluminum (Al^{+3}) ions will be much more

effective than sodium (Na^+) ions in neutralizing the colloidal charge and will result in a thinner double layer.

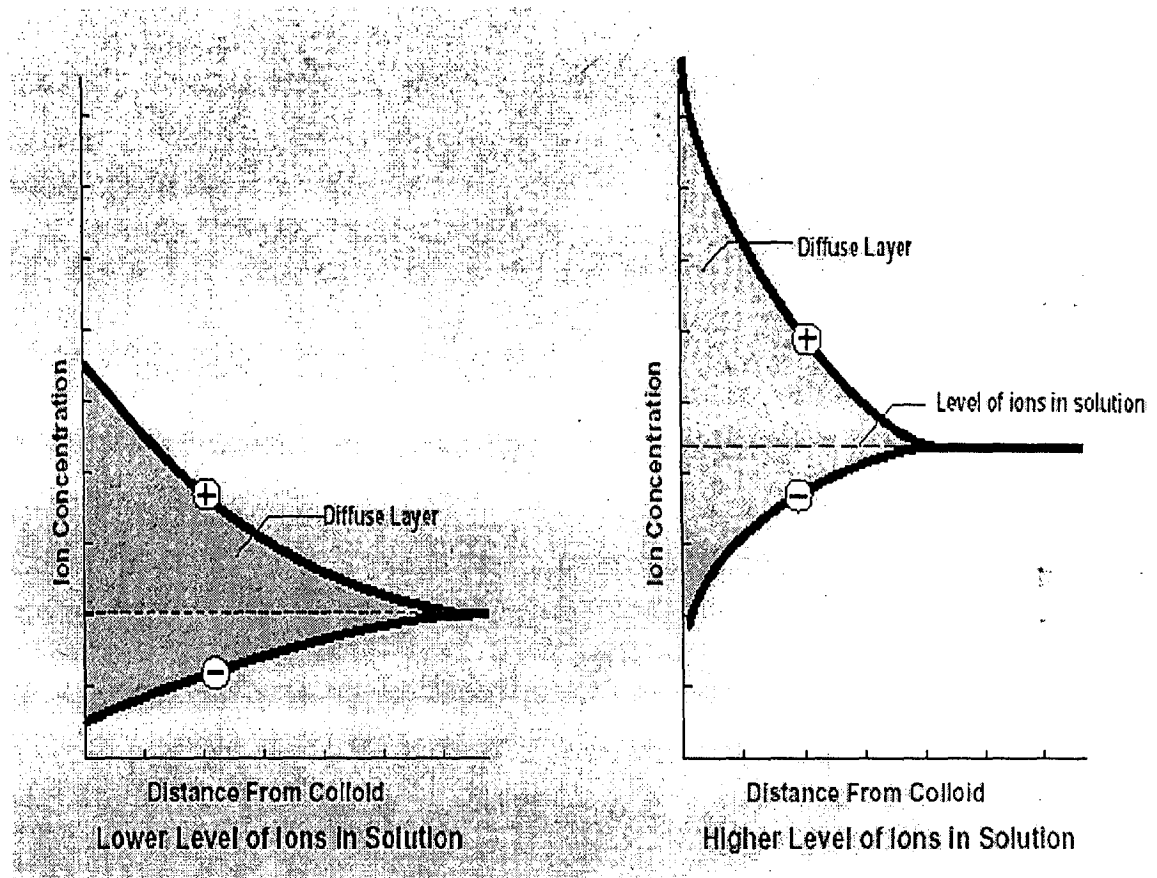


Fig.2.5 Variation of Ion density in the diffuse layer^[2]

Zeta potential:

The negative colloid and its positively charged atmosphere produce an electrical potential across the diffuse layer. This is highest at the surface and drops off progressively with distance, approaching zero at the outside of the diffuse layer. The zeta potential and surface potential are shown in fig.2.6.

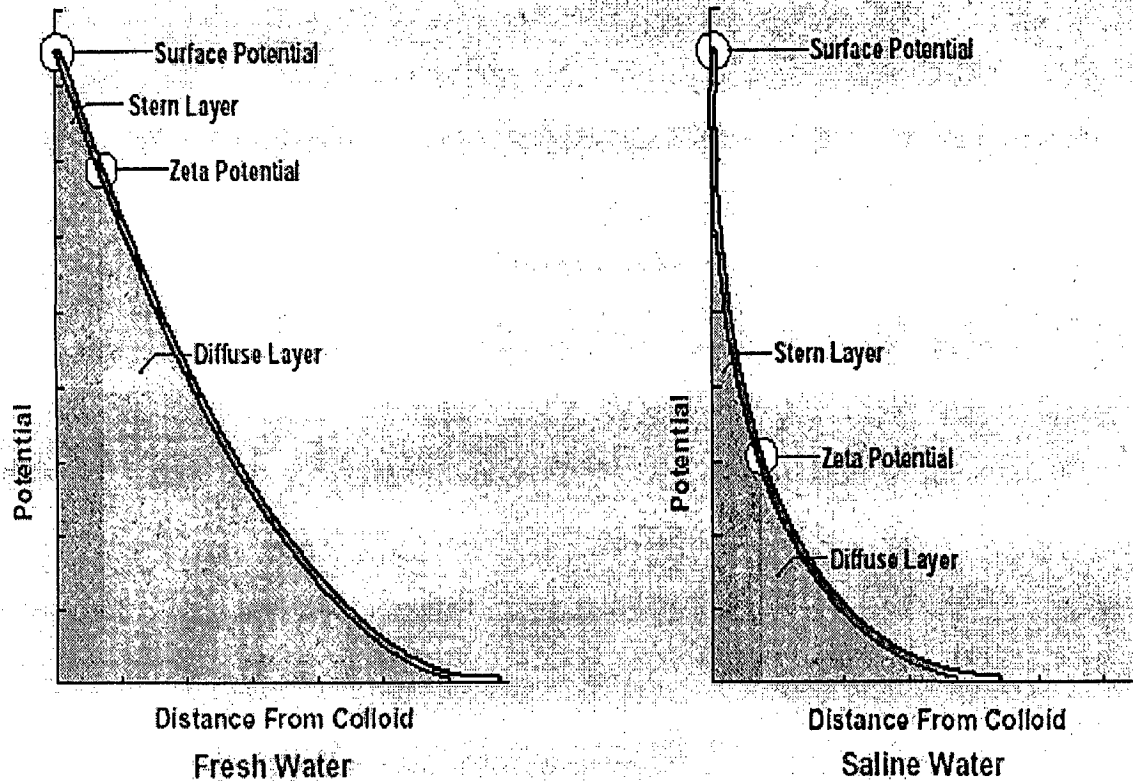


Fig.2.6 Zeta vs. surface potential^[2]

The ratio between zeta potential and surface potential depends on double layer thickness. The low dissolved solids usually found in water treatment results in a relatively large double layer. In this case, zeta potential is a good approximation of surface potential. The situation changes with brackish or saline waters; the high level of ions compresses the double layer and the potential curve. Now the zeta potential is only a fraction of the surface potential.

The energy barrier:

The DLVO theory combines the van der Waals attraction curve and the electrostatic repulsion curve to explain the tendency of colloids to either remain discrete or to flocculate. The combined curve is called the net interaction energy. At each distance, the smaller energy is subtracted from the larger to get the net

interaction energy. The net value is then plotted - above if repulsive, below if attractive – and the curve is formed.

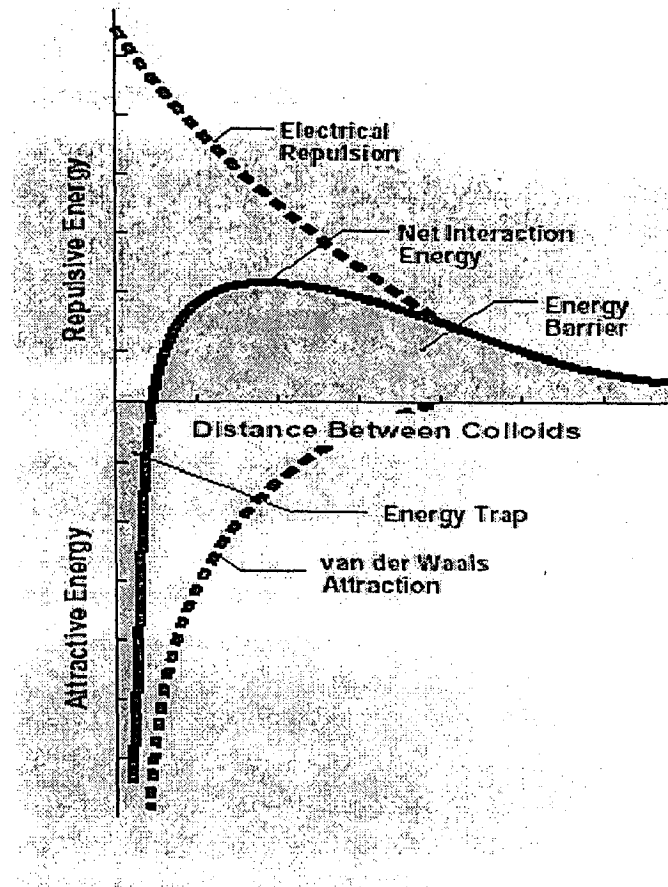


Fig.2.7 Interaction^[2]

The net interaction curve is formed by subtracting the attraction curve from the repulsion curve.

For really effective coagulation, the energy barrier should be lowered or completely removed so that the net interaction is always attractive. This can be accomplished by either compressing the double layer or reducing the surface charge.

Coagulation and flocculation can be caused by any of the following:

- Double layer compression
- Charge neutralization
- Bridging
- Colloid entrapment

2.2.1 Double layer compression:

Double layer compression involves adding salts to the system. As the ionic concentration increases, the double layer and the repulsion energy curves are compressed until there is no longer an energy barrier. Double layer compression involves the addition of large quantities of an indifferent electrolyte (e.g., sodium chloride). The indifference refers to the fact that the ion retains its identity and does not adsorb to the colloid. This change in ionic concentration compresses the double layer around the colloid and is often called salting out. It is important to realize that salting out just compresses the colloid's sphere of influence and does not necessarily reduce its charge. Fig.2.8 shows the double layer compression.

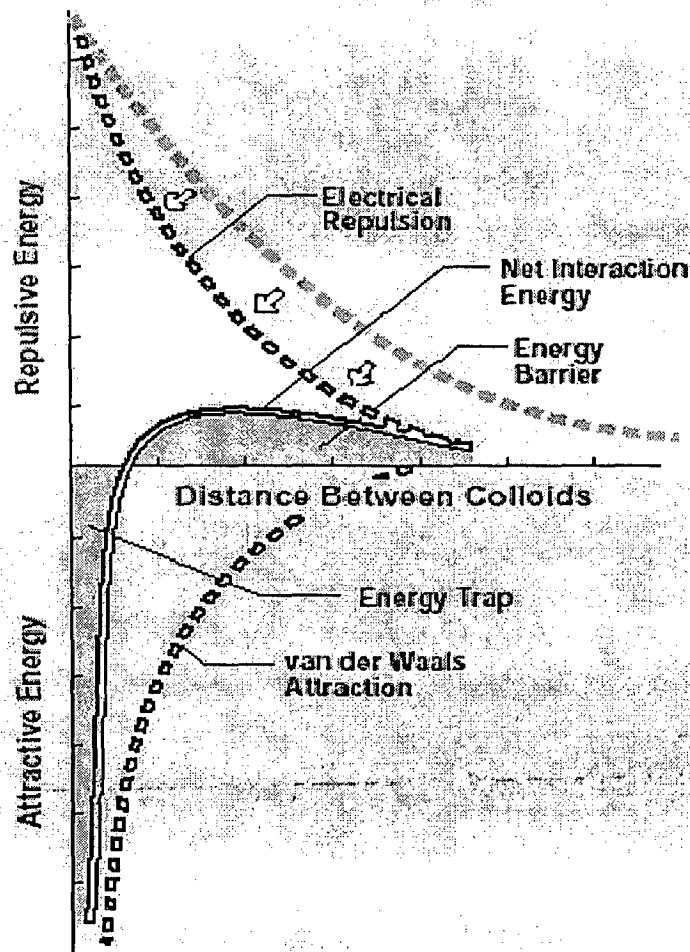


Fig.2.8 Compression^[2]

2.2.2 Charge neutralization

Inorganic coagulants (such as alum) and cationic polymers often work through charge neutralization. It is a practical way to lower the DLVO energy barrier and form stable flocs. Neutralization is the key to optimizing treatment before sedimentation, granular media filtration or air flotation. Charge neutralization alone will not necessarily produce dramatic macroflocs (flocs that can be seen with the naked eye). This is demonstrated by charge neutralizing with cationic polyelectrolytes in the 50,000-200,000 molecular weight range. Charge neutralization involves adsorption of a positively charged coagulant on the surface of the colloid. This charged surface coating neutralizes the negative charge of the colloid, resulting in a near zero net charge. Charge neutralization is easily monitored and controlled using zeta potential. This is important because overdosing can reverse the charge on the colloid, and redispersed it as a positive colloid. The result is a poorly flocculated system. The detrimental effect of overdosing is especially noticeable with very low molecular weight cationic polymers that are ineffective at bridging.

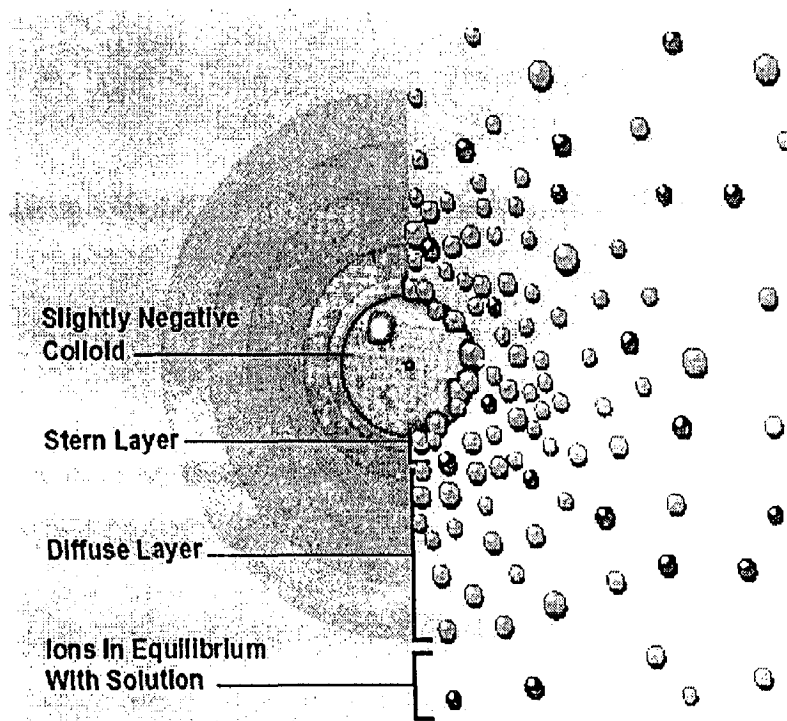
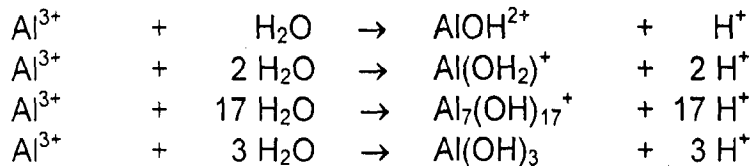


Fig.2.9 Charge reduction^[2]

Lowering the surface charge drops the repulsive energy curve and allows van der Waals forces to reduce the energy barrier.

The ionization of aluminium sulphate in water produces sulphate anions (SO_4^{2-}) and aluminium cations (Al^{3+}). The sulphate 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 the 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 disappears so that contact occurs freely. Overdosing with coagulants can result in restabilizing the suspension. If the 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.

2.2.3 Bridging

Bridging occurs when a coagulant forms threads or fibers which attach to several colloids, capturing and binding them together. Inorganic primary coagulants and organic polyelectrolytes both have the capability of bridging. Higher molecular weights mean longer molecules and more effective bridging. Bridging is often used in conjunction with charge neutralization to grow fast settling and/or shear resistant flocs. For instance, alum or a low molecular weight cationic polymer is first added under rapid mixing conditions to lower the charge and allow microflocs to form. Then a slight amount of high molecular weight polymer, often an anionic, can be added to bridge between the microflocs. The fact that the bridging polymer is negatively charged is not significant because the small colloids have already been captured as microflocs.

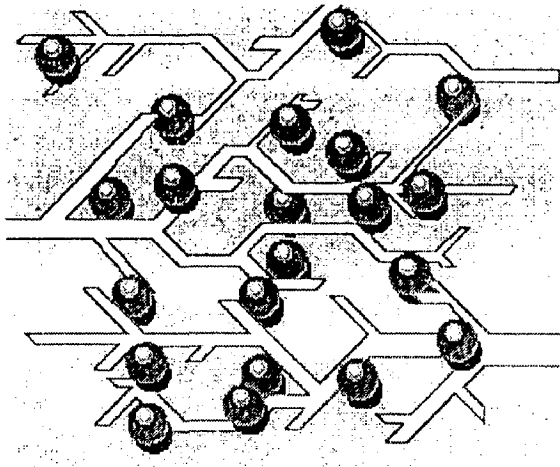


Fig.2.10 Bridging

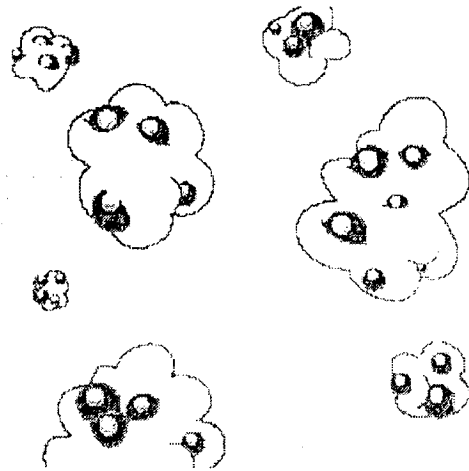


Fig.2.11 Sweep floc

2.2.4 Colloid entrapment:

Colloid entrapment involves adding relatively large doses of coagulants, usually aluminum or iron salts which precipitate as hydrous metal oxides. The amount of coagulant used is far in excess of the amount needed to neutralize the charge on the colloid. Some charge neutralization may occur but most of the colloids are literally swept from the bulk of the water by becoming enmeshed in the settling hydrous oxide floc. This mechanism is often called sweep floc.

2.2.5 Coagulation practice:

With regard to coagulation, surface waters can be grouped into the four general categories described below:

Group 1: High turbidity–low alkalinity. With relatively small dosages of coagulant, water of this type should be easily coagulated by adsorption and charge neutralization. Depression of pH makes this method more effective, since the aquometallic ions are more effective at lower pH values. However, care should be used to prevent excessively low pH.

Group 2: High turbidity-high alkalinity. The pH will be relatively unaffected by coagulant addition. Because of the high alkalinity, adsorption and charge neutralization will be less effective than in waters of low alkalinity. Higher coagulant dosage should be used to ensure sweep coagulation.

Group 3: *Low turbidity-high alkalinity.* The small numbers of colloids make coagulation difficult, even if the particle charge has been neutralized. The principal coagulation mechanism is sweep coagulation with moderate coagulant dosage. Addition of some turbidity may decrease the amount of coagulant needed.

Group 4: *Low turbidity-low alkalinity.* Again, the small number of colloids make coagulation difficult, and low alkalinity prevents effective $\text{Al}(\text{OH})_3$ formation. Additional turbidity can be added to convert this water to that of group 1 or additional alkalinity can be added to convert it to a Group 3 type. It may be advantageous to add both turbidity and alkalinity.

2.3 Coagulant Selection

The choice of coagulant chemical depends upon the nature of the suspended solid to be removed, the raw water conditions, the facility design, and the cost of the amount of chemical necessary to produce the desired result. [Peavy et. al.]

Following factors should be considered in selecting these chemicals:

- Effectiveness.
- Cost.
- Reliability of supply.
- Sludge considerations.
- Compatibility with other treatment processes.
- Environmental effects.
- Labor and equipment requirements for storage, feeding, and handling.

Coagulants generally used are classified as: inorganic and polymers (polyelectrolyte).

2.3.1 Inorganic coagulants

The three main classifications of inorganic coagulants are:

- Aluminum derivatives.
- Iron derivatives.
- Lime.

With exception of sodium aluminates, all common iron and aluminum coagulants are acid salts and, therefore, their addition lowers the pH of the treated water. Depending on the influent's pH and alkalinity (presence of HCO_3^{3-} , CO_3^{2-} , and OH^-), an alkali, such as lime or caustic, may be required to counteract the pH depression of the coagulant. This is important because pH affects both particle surface charge and floc precipitation during coagulation. The optimum pH levels for forming aluminium and iron hydroxide flocs are those that minimize the hydroxide solubility. However, the optimum pH for coagulating suspended solids does not always coincide with the optimum pH for minimum hydroxide floc solubility. Table lists several common inorganic coagulants along with associated advantages and disadvantages.

Aluminium derivatives:

Common aluminium coagulants include aluminium sulphate (alum), sodium aluminate, and polyaluminium chloride.

i. Aluminium sulphate (Alum)

Aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, molecular weight = 666.42) also known as alum, filter alum and alumina sulphate is the most widely used coagulant. It is available in powder or in a lumped form. Alum has no exact formula due to varying water molecules of hydration, which may be attached to aluminium sulphate molecule. When added to the wastewater, several reactions with the naturally present alkalinity and various anionic ligands take place. Dry alum is available in several grades, with a minimum aluminium content (expressed as $\%\text{Al}_2\text{O}_3$) of 17%. Liquid alum is about 49% solution, or approximately 8.3% by weight aluminium as Al_2O_3 .

During coagulation process, it releases hydrogen ions, as well as coagulant species due to series of hydrolytic reactions and forms simple hydroxo complex $Al(OH)^{2+}$. These hydrogen ions neutralize alkalinity. Hydrogen resulting from the addition of 1 mg/l of alum will neutralize 0.5 mg/l of alkalinity, which results in the reduction of pH rapidly. Since optimum pH values must be maintained for best coagulation and since alkalinity must be present for hydroxide floc formation so water is artificially buffered. The aluminium hydroxide floc is less dense than iron floc and therefore requires longer retention times in the sedimentation process. Alum can be effective in the pH range of 5.5-7.8 but seems to work best in most coagulant treatment at 6.8-7.5. Below the pH 5.5, alkalinity in the water is insufficient. The aluminium ions become soluble rather than insoluble and do not participate in hydration to make alum more effective. When the pH level of water is above 7.8 after the addition of alum, the aluminium ions again become soluble and the efficiency of coagulation is decreased.

ii. Sodium aluminate

Sodium aluminate is an alternative to alum and is available in either dry or liquid forms, containing an excess of base. Sodium aluminate provides a strong alkaline source of water-soluble aluminium, which is useful when adding sulphate ions is undesirable. It is sometimes used in conjunction with alum for controlling pH.

iii. Poly aluminium chloride (PAC)

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

Iron derivatives

Iron coagulants include ferric sulphate, ferric chloride, and ferrous sulphate. Compared to aluminium derivatives, iron coagulants can be used successfully over a much broader pH range of 5.0 to 11.0. However, when ferrous

compounds are used, the solution is typically chlorinated before it is sent into the coagulation vessel. As this reaction produces both ferric chloride and ferric sulphate, chlorinated ferrous sulphate has the same field of usefulness as the other iron coagulants. Because ferrous sulphate works better in feeding devices, compared with the ferric coagulants, chlorinated copperas is sometimes preferred. The ferric hydroxide floc is heavier than alum floc and therefore settles more rapidly.

i. Ferrous sulphate

Ferrous sulphate or copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Molecular weight = 278.01), is the least expensive of the iron coagulants and is widely used. Ferrous sulphate 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 $\text{pH} > 7.7$. The optimum pH is greater than 9.

ii. Ferric chloride

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, molecular weight = 270.30) works best at pH below 7, with the optimum at 5.5. The precipitate formed is ferric hydroxide $\text{Fe}(\text{OH})_3$, which has good flocculating and settling characteristics. This chemical can be purchased in anhydrous, lumped solid or solution form; because of its hygroscopic nature and corrosive characteristics, it is fed best as a water solution (27-43% FeCl_3).

Lime

Although lime is primarily used for pH control or chemical precipitation, it is also commonly used as a co-coagulant.

Other coagulating agents

Sulfuric acid is a common reagent for lowering the pH of a waste and occasionally it serves as a coagulant during the process. Its principal action is a coagulating effect on colloidal substances due to decreased pH.

Calcium chloride, CaCl_2 has been used in the treatment of certain industrial wastes, notably those from laundries and textile industries. It makes insoluble calcium flocs having satisfactory flocculating and settling properties.

2.3.2 Polyelectrolytes:

Polyelectrolytes are water-soluble polymers carrying ionic charge along the polymer chain and may be divided into natural and synthetic polyelectrolytes. Important natural polyelectrolytes include polymers of biological origin and those derived from starch products, cellulose derivatives and alginates. Depending on the type of charge, when placed in water, the polyelectrolytes are classified as anionic, cationic or nonionic.

- Anionic—ionize in solution to form negative sites along the polymer molecule.
- Cationic—ionize to form positive sites.
- Non-ionic—very slight ionization.

Molecular weights of polyelectrolytes range from a few hundred thousand to tens of millions. High molecular weight polymers are sheared sensitive that their chains can be broken into smaller fragments by excessive mixing.

(a) Polyelectrolytes function as primary coagulants and also the coagulation aids/flocculents. These are of polyamine type and have high cationic charge density; satisfy the cationic demand of the negatively charged suspended particles and initiate coagulation and formation of flocs. These are low to medium molecular weight polymers, which allow slow building of flocs, and therefore adequately long contact time between the forming floc and the suspended matter is necessary.

The efficiencies of polyelectrolyte primary coagulants depend greatly on the exact nature of the turbidity particles to be coagulated, the amount of turbidity present, and the turbulence (mixing) available during coagulation.

- (b) Coagulation aids / flocculents are low charge density polymers such as polyacrylamide and are used only for building the size of the floc by bridging the primary flocs. They do not satisfy the charge demand. The size of the resulting three-dimensional flocs grows until they can be removed easily by sedimentation.

Anionic polymers

Anionic polymers are usually copolymers, i.e., polymers containing two types of monomer units of acryl amide and acrylic acid. The charge on these polymers is pH sensitive; they function best at a pH above 6. The examples are sodium salt of acrylic acid, known as acrylamide. The acrylic acid unit produces negative charge. The other examples are polystyrene sulfuric acid and 2-acrylamide 2-methylpropane sulfonic acid.

Cationic polymers

Cationic can be copolymers of acryl amide with a cationic monomer, cationically modified acryl amide or a polyamine. The cationic charge in these polymers is derived from nitrogen in the form of secondary, tertiary or quaternary amine group. The charges on these polymers drop off quickly as the pH rises above 6. Poly quaternary amines are pH insensitive and function well over a broad pH range. In these polymers, the charge can be located on a pendant group or may be in the backbone of the polymer chain. Three major cationic monomer, such as Meta acrylamide, propyl trimethyl ammonium chloride, dimethyl diallyl ammonium chloride are stable cationic polyelectrolytes.

High molecular weight polymers have coiled chains. When they are put into solutions, the charged areas on the chain repel each other and force the chain to uncoil. As this occurs, the viscosity of the solution increases. Since charge affects the speed at which the chain uncoils, higher charged polymers will uncoil faster than low charged products. Indeed, nonionic polymers may never fully uncoil since they carry no charge.

Non-ionic polymers

These are large photopolymers of acryl amide with a wide range of molecular weights. Though countless polyelectrolytes are theoretically possible depending upon the charge density and molecular weight, only a few of them have found commercial application.

Common organic polyelectrolytes are shown in Table 2.1 This limits the usage of polyacrylamides of a scientific pattern for a specific application irrespective of the source of supply.

Table 2.1: Advantages and disadvantages of alternative inorganic coagulants

Name	Advantages	Disadvantages
Aluminium Sulphate (Alum) $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	Easy to handle and apply; most commonly used; produces less sludge than lime; most effective between pH 6.5 and 7.5	Adds dissolved solids (salts) to water; effective over a limited pH range.
Sodium Aluminate $\text{Na}_2\text{Al}_2\text{O}_4$	Effective in hard waters; small dosages usually needed	Often used with alum; high cost; ineffective in soft waters
Polyaluminium Chloride (PAC) $\text{Al}_{13}(\text{OH})_{20}(\text{SO}_4)_2 \cdot \text{Cl}_5$	In some applications, floc formed is more dense and faster settling than alum	Not commonly used; little full scale data compared to other aluminium derivatives
Ferric Sulphate $\text{Fe}_2(\text{SO}_4)$	Effective between pH 4–6 and 8.8–9.2	Adds dissolved solids (salts) to water; usually need to add alkalinity
Ferric Chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Effective between pH 4 and 11	Adds dissolved solids (salts) to water; consumes twice as much alkalinity as alum
Ferrous Sulphate (Copperas) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Not as pH sensitive as lime	Adds dissolved solids (salts) to water; usually need to add alkalinity
Lime $\text{Ca}(\text{OH})_2$	Commonly used; very effective; may not add salts to effluent	Very pH dependent; produces large quantities of sludge; overdose can result in poor effluent quality

Table 2.2: Common organic polyelectrolytes

Polymer Type	Name	Mol.wt.	Available form	Typical use
Nonionic	Polyacrylamide	1×10^6 to 2×10^6	Powder, emulsion, solution	As flocculent with inorganic or organic polymers
Anionic	Hydrolyse Polyacrylamide	1×10^6 to 2×10^7	Powder, emulsion, solution	As flocculent with inorganic or organic polymers
Cationic	Poly(DADMAC) Or Poly(DADMAC) polymers	200 to 500×10^3	Solution	Primary coagulant alone or in combination with inorganics.
Cationic	Quaternized Polyamines	10 to 500×10^4	Solution	Primary coagulant alone or in combination with inorganics.
Cationic	Polyamines	10^4 to 10^6	Solution	Primary coagulant alone or in combination with inorganics.

CHAPTER 3

LITERATURE REVIEW

In this section, a detailed report on the study of literature related to the treatment of pulp and paper mill effluent, coagulation and related to different type of coagulants have been given.

Dilek and Gökçay [1994] studied the waste characterization and physico – chemical treatability of effluents from a pulp and paper mill effluent using alum ($\text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$) as a coagulant. They reported COD removals of 96 %, 50 % and 20 % for the paper machine, alkali extraction and bleaching effluents, respectively and 80% colour was removed from the alkali extraction effluent at a coagulant (alum) concentration of 100 mg l^{-1} and at a pH value of 7.0.

Dilek and S Bese [2000] had investigated the effect of clay addition during alum coagulation, on the removal of color from pulp-and-paper industry wastewaters. Four types of clay, namely beige-and brown-sepiolites, calcium- and sodium-bentonites of different mesh sizes were used. Different quantities of alum and clay were applied, either singly or in combination, to the effluents of the wood-based pulpand-paper mill. Colour of the treated wastewater, the sludge volume index (SVI) and sludge cake resistance (SCR) of the sludge produced was monitored. It was observed that the clays tested were not efficient in colour removal when they were applied on their own. When clay was added along with alum, a certain increase in colour removal efficiency was obtained as compared to alum alone. When alum was used in conjunction with clay, settling characteristics of the sludge produced improved substantially, in terms of both SVI and SCR. Acid activation of the clays did not improve the colour removal efficiency further. However, acid activation of sodium bentonite caused the SVI and SCR values to improve considerably compared to virgin sodium bentonite. Use of different mesh sizes of clays did not exert any significant effect on the colour removal. However, it did exert significant effects on SVI and SCR values

as such that the increase in mesh size caused the SVI values to decrease and the SCR values to increase.

Francis et al. [1997] carried out chemical pretreatment of effluent with green liquor followed by air activated sludge biological treatment. The chemical pretreatment reduced the absorbable organic halogen (AOX) in the acid effluents by 50%, thus, reducing the AOX in the influent to the biological treatment plant by 59%. Thus, the chemical pretreatment significantly enhanced the overall treatment versus biological treatment alone.

Garg et al. [2005] reported the efficacy of copper sulfate as a coagulant for the precipitation/ coagulation of kraft pulp and paper mill black liquor having a COD of 7000 mg l⁻¹. 61.4 % COD removal was obtained at a copper sulfate concentration of 5 g l⁻¹. The coagulated sludge was found to have a heating value comparable to that of coal.

Ganjidousta et al. [1997] studied Removal of lignin (black liquor color, and TOC) from pulp and paper industrial wastewater, and used Synthetic polymer (HE, PEI, and PAM), natural polymer (chitosan) and chemical (alum) as coagulant.

J. Oral et al. [2004] described an efficient way of processing sludge including waste-to-energy aspects.

Lee et al. [1989] studied the secondary treatment of pulp and paper mill wastewater for BOD removal by anaerobic treatment processes, including aerated stabilization basins and activated sludge has been accepted worldwide.

M.I. Aguilar et al. [2004] done physicochemical treatment (coagulation flocculation) of slaughterhouse wastewater, using anionic polyacrylamide as

coagulant aid to improve the settling velocity of the flocs formed with the coagulants used: ferric sulphate, aluminum sulphate and polyaluminium chloride.

Pattabhi et al. [2000] studied Coagulation separation of solids from sewage water as well as wastewater from small-scale industries such as milk processing, dyeing and electroplating industries. The chemical treatment involves alum, ferric chloride, mixed sulfate and polyaluminum chloride.

Peter Holt et al. [1999] studied electrocoagulation for treatment of polluted water. This has the major advantage of providing active cations required for coagulation, without increasing the salinity of the water.

Robert J. Stephenson and Sheldon J. B. Duff [1995] have studied coagulation and precipitation of a mechanical pulping effluent- I, for removal of color, carbon and turbidity. They examined the effects of metal coagulant concentration, effluent dilution and pH on the removal of total carbon, colour and turbidity from a combined bleached chemithermomechanical /thermo mechanical (BCTMP/TMP) effluent. Both chloride and sulphate salts of iron and aluminum were effective in treating the mechanical pulping effluent in batch jar screening tests; pH had a pronounced affect on precipitation. In terms of minimizing the total carbon (TC), colour and turbidity levels, the optimum adjusted pH ranges were: 4.0-6.5 for ferric chloride, above 7.4 for ferrous sulphate, 5.0-6.0 for aluminum chloride and 5.8 to 6.8 for aluminum sulphate.

Robert J. Stephenson and Sheldon J. B. Duff [1994] have studied coagulation and precipitation of a mechanical pulping effluent- II. And observed Iron and aluminum coagulating agents were effective in treating a CTMP/BCTMP pulping effluent in batch jar screening tests. Pulp and paper effluents contain a number of compounds which are harmful to receiving waters and which are inhibitory or recalcitrant to biological treatment. For full strength effluent, toxicity was markedly reduced by precipitation, with optimal Microtox EC50 values of approx.

20% being recorded. Dilution of the effluent followed by precipitation further improved toxicity removal, and complete detoxification of ¼ strength effluent was observed using ferric chloride as the precipitant. At higher than optimal levels of addition, iron and aluminum salts contributed to toxicity. The possibility of salt recovery was demonstrated through a fixed solids balance. Ferric chloride appeared to be the most promising candidate for recovery, with less than 20% of the fixed solids lost to the supernatant.

Selvapathy et al. [1994] used Poly aluminum silicate sulfate (PASS) as a coagulant aid with alum and treated Turbidity, residual aluminum of stock turbidity suspension, and found the residual Aluminum in the treated water was found to be fewer when PASS was used as coagulant.

Srivastava et al. [2005] have used PAC as a coagulant and bagasse fly ash as an adsorbent in a two stage chemical coagulation (precipitation) – adsorption method for the removal of COD and colour from the alkaline black liquor and acid waste waters from different sections of the small agri – based pulp and paper mills which do not have chemical recovery units. They reported that the coagulation – flocculation is best at a pH \approx 3 at a PAC dosage of 3 kg m⁻³ with about 80 % and 90 % removals of COD and colour, respectively.

Tarlan et al. [2001] studied the ability of algae to treat a wood-based pulp and paper industry wastewater. Tests were performed in batch reactors seeded with a mixed culture of algae. Under different lighting and initial wastewater strength conditions, changes in COD, AOX and color contents of reactors were followed with time. Algae were found to remove up to 58% of COD, 84% of color and 80% of AOX from pulp and paper industry wastewaters. The study also showed that algae grew mixotrophically, while the main mechanism of color and organics removal from pulping effluents was partly metabolism and partly metabolic conversion of colored and chlorinated molecules to non-colored

and non-chlorinated molecules. Adsorption onto algal biomass was not so effective.

Vinod K. Sharma et al. [1997] investigated the economic, social and environmental impact of international trade of waste paper for recycling purposes between industrialized and developing countries.

CHAPTER 4

EXPERIMENTAL PROCEDURE

Experimental details on coagulation studies for the removal of colour and COD from pulp and paper mill effluent using different coagulants have been presented in this chapter. The characteristics of effluent being examined have also been presented.

4.1. Effluent

Black liquor was obtained from a local integrated kraft pulp and paper mill. This liquor was having a COD of about 7×10^5 mg l⁻¹. Synthetic wastewater was prepared by diluting this black liquor with distilled water to have a COD value of about 7000 mg l⁻¹. The average characteristics of the synthetic wastewater are presented in Table.4.1.

Table.4.1: Characteristics of diluted black liquor

Chemical oxygen demand (COD)	:	7000 mg l ⁻¹
Biochemical oxygen demand (BOD)	:	1400 mg l ⁻¹
pH	:	10.45
Total solids (TS)	:	7 240 mg l ⁻¹
Total dissolved solids (TDS)	:	6 680 mg m ⁻¹
Total suspended solids (TSS)	:	560 mg l ⁻¹
Conductivity	:	51 760 μmhos cm ⁻¹
Color	:	Dark brown
Color unit	:	5095.76

4.2 Coagulants:

Coagulants studied are:

- Aluminium chloride
- Copper sulphate
- Poly aluminium chloride

All the coagulants excepting aluminium chloride (which was LR grade) were of analytical reagent (AR) grade. Aluminum chloride and copper sulphate were purchased from s.d.fine Chemicals Ltd. Mumbai-400025. Poly aluminium chloride (PAC) was obtained from Jubilant Organosys, Gajraula, India.

4.3 Experimental Procedure:

An experimental detail of the coagulation study is given below. Fig.4.1 shows the flow chart of the experimental method.

The initial COD, color and pH of the sample were measured using the methods described later in this chapter. The experiment is carried out in three steps:

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

1. Optimization of pH:

- i. 200 ml of effluent samples were taken in 5 or 6 beakers.
- ii. A constant dose of 5 g/l of coagulant was added in each beaker.
- iii. Different pH were maintained in all the beakers with the help of NaOH/H₂SO₄. The pH range was varied between 2 to 10.
- iv. The contents of beakers were agitated rapidly for 10 minute and gently for 5 minute. Then it was left for 2 hours.
- v. Supernatant was separated and centrifuged.
- vi. COD and Colour of supernatant of each beaker were measured as per the method described later.

- vii. The results thus give % COD/Colour removal as function of initial pH of the effluent.

2. Optimization of coagulant's dose:

- i. The experimental procedure was same as described above except the amount of coagulant dose was varied and pH in all the beakers was maintained constant at their optimum pH value.

3. Settling characteristics:

- i. Some of the runs (which gave maximum COD removal) were used to find out settling characteristics. Different types of coagulants produce different type of sludge. It is very important in industrial operations to have such coagulated slurries which settle down quickly and the supernatant is therefore separated. The settling experimentation was carried out in 100 ml measuring cylinder and the data for settling of the suspended matter layer with time was noted.

Settling of the effluent residue after treatment with different coagulants was observed in a 100 ml measuring cylinder. The Kynch theory was used to analyse the settling process ^[20]. Some assumptions were made to use this theory:

- a) The wall effect was not taken in consideration.
- b) Particle concentration was assumed uniform.
- c) No differential settling of particles as a result of differences in shape, size or composition was considered.
- d) The initial concentration was taken either as uniform or it increases towards the bottom.
- e) The velocity of fall of sediments depends on the local concentration of particles, and
- f) The sedimentation velocity tends to zero as the concentration approaches a limiting value.

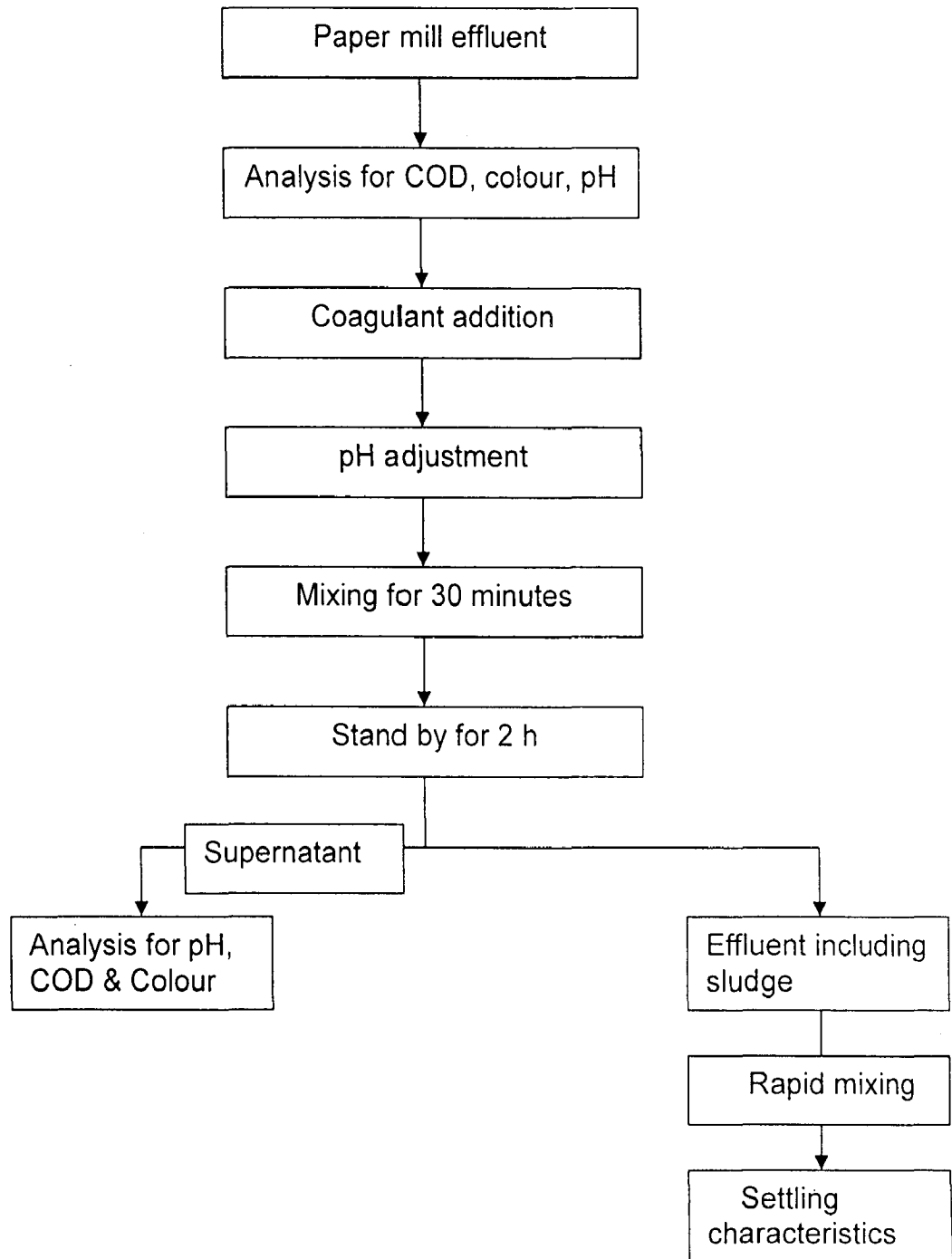


Fig.4.1. Flow chart showing the steps for coagulation studies

4.4 Analytical Methods:

The treated samples were centrifuged in a Remi Centrifuge (Model R 24, Remi Instruments, Bombay, India). The COD of the effluent was determined by dichromate open reflux method as per standard method . The colour of the initial and final effluent after the treatment was measured at a wavelength of 263 nm using UV/VIS spectrophotometer (Model Lambda 35 Perkin Elmer, Switzerland). Conductivity was measured using Conductivity Bridge (Philips PR 9500, India).

4.4.1 COD estimation:

The COD of the samples were determined as per ISI (IS: 3025). Reagents and procedure were described below.

Reagents:

- i. Standard potassium dichromate 0.25 N
- ii. Sulphuric acid (with 1gm of silver sulphate in every 75 ml. acid)
- iii. Ferroin indicator solution
- iv. Standard ferrous ammonium sulphate.

Procedure:

As stated earlier in this chapter, The COD of the effluent was determined by dichromate open reflux method as per standard method. It is described below.

- i. A small amount of sample was diluted to 30.0 ml in reflux flask.
- ii. Glass beads and small amount of HgSO_4 were added.
- iii. 5.00 ml of H_2SO_4 was added slowly to dissolve HgSO_4 .
- iv. 10.00 ml of 0.25 N potassium dichromate was added and solution was mixed.
- v. Remaining acid reagent (25.00 ml) was added and mixture was mixed.
- vi. A mixture was heated and refluxes for 2 hour and then cooled.
- vii. Mixture was diluted to 250 ml and titrated with standard ferrous ammonium sulphate using ferroin indicator.
- viii. Reading of titrant (ml) used were taken carefully.

A blank consisting of distilled water, equal to the volume of sample and reagents, was refluxed. And then, titrated and readings were taken.

The COD of the sample was calculated by the formula.

$$\text{COD (mg/l)} = [(A-B) \cdot C \cdot 8000] / \text{ml of sample}$$

Where,

A= Volume (ml) of Ferrous Ammonium Sulphate for the blank solution.

B= Volume (ml) of Ferrous Ammonium Sulphate for the solution.

C= Normality of the Ferrous Ammonium Sulphate solution.

CHAPTER 5 RESULTS AND DISCUSSION

The detailed discussion on the results of the experiments conducted is given in this chapter. Detailed coagulation studies have been conducted for the removal of COD and colour of the effluent. Effect of various operating parameters, like pH and initial concentration, have been studied and are shown in Tables A-1 to A-6 and Figs. 5.1 to 5.17.

5.1 Effect of pH (on COD and color removal):

Figs. 5.1 through 5.6 shows the effect of pH on the COD reduction as well as colour removal of the waste water having an initial COD value of 7000 mg l^{-1} at ambient temperature (25°C) using different coagulants. The coagulant mass loading was kept constant. The runs were taken at different pH values, i.e., at 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10. A part of the treated waste water was taken out and centrifuged for 10 min at a speed of 10,000 rpm. Then, the supernatant was decanted off and its COD was measured. For aluminium chloride, the COD reduction was found maximum at the pH of 4.0 and the treatment effected a COD reduction of 73.75 % and 86.15% colour reduction. For the coagulants, copper sulphate and PAC, the optimum pH was found to be 6.00, 5.00 respectively and 75%, 69.41% COD removal as well as 77.78%, 81.89% colour reduction respectively. The optimum pH was determined on the basis of maximum COD reduction. The maximum colour reduction may occur at other pH value.

5.2 Effect of Mass loading (on COD and Colour removal):

For different coagulants, the effect of mass loading on the COD reduction of the synthetic waste water ($\text{COD}_0 = 7000 \text{ mg l}^{-1}$) was studied at ambient temperature of 25°C . The coagulant mass loading was varied from 1 to 8 g l^{-1} . Fig. 5.4 shows the effect of aluminium chloride mass loading at constant $\text{pH}=4.00$. Maximum COD removal of 75.5% and color removal of 86.30% was found at mass loading of 7 g/l, 5 g/l respectively. For copper sulphate and PAC, their mass loadings

were varied at their respective optimum pH (6.00 for copper sulphate and 5.00 for PAC). Maximum COD reductions were obtained at coagulant dose of 5 g/l (75% removal) of copper sulphate and 8 g/l (82.85% removal) of PAC. These are shown in Fig.5.5 and 5.6. The corresponding colour removals are shown in Fig.5.10 to 5.12. The maximum colour removal (79.64%) was found at 6 g/l dose of copper sulphate and 8 g/l of PAC dose (91.81%).

5.3 Effect on pH:

Fig.5.13 through 5.15 shows the variation of pH after addition of different dose of coagulants. The decrease in pH after the addition of coagulant may be due to the several hydrolytic reactions, which are taking place during coagulation, forming multivalent charged hydrous oxide species and generating H_3O^+ ion during each step, thus reducing the pH value ^[1]. Stephenson and Duff ^[18] have also reported that the coagulant addition depresses pH to highly acidic levels, as the coagulant dose is highly correlated with pH. Higher doses of coagulants without the need of optimization are reported due to two reasons: one for the increment in the aggregate rate and the other by enmeshing particulates into large aggregates.

5.4 Comparison of Different Coagulant for COD Removal:

Fig.5.16 shows the effect of different coagulants, such as, PAC, aluminium chloride, copper sulfate, on the COD reduction of the waste water at room temperature. PAC was found more effective for COD removal.

5.5 Comparison of different coagulant for colour removal:

Fig.5.17 shows the effect of different coagulants, such as, PAC, aluminium chloride, copper sulfate, on the colour reduction of the waste water at room temperature. The colour compounds present in the paper mill effluent are negatively charged, which get neutralized from the positively charged coagulant and remove the colour of the waste water. The colour reduction increases up to a breakpoint, after which it starts decreasing due to increase in the coagulant concentration.

5.8 Settling characteristics:

Fig.5.18 through 5.20 shows the time Vs height graph of settling sludge of different coagulants. It is seen that the settling of the solids is faster initially and after some time, the rate of settling decreases. The portion, in which settling is faster is known as zone- settling region and the zone, where a compressed layer begins to form at the bottom of the cylinder, is called compression settling region.

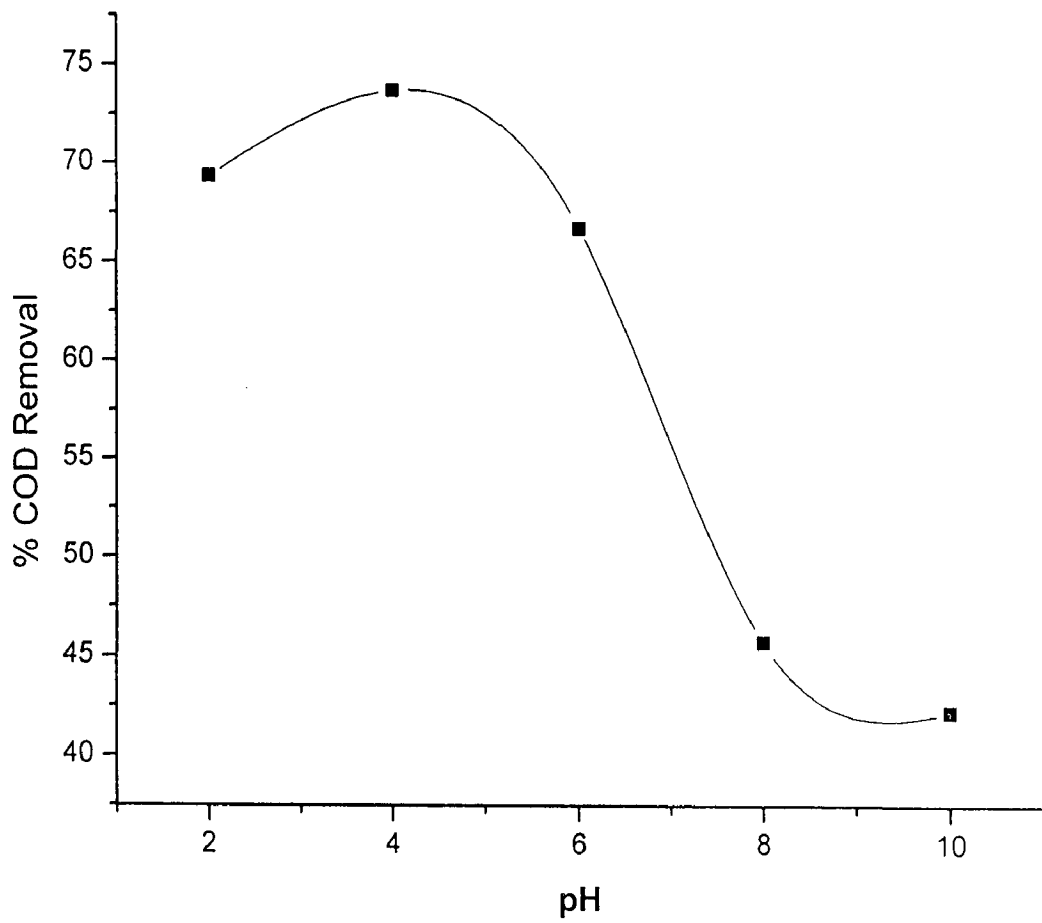


Fig.5.1. Effect of pH on %COD removal with $AlCl_3$ as coagulant.

Dose of $AlCl_3$ = 5 g/l

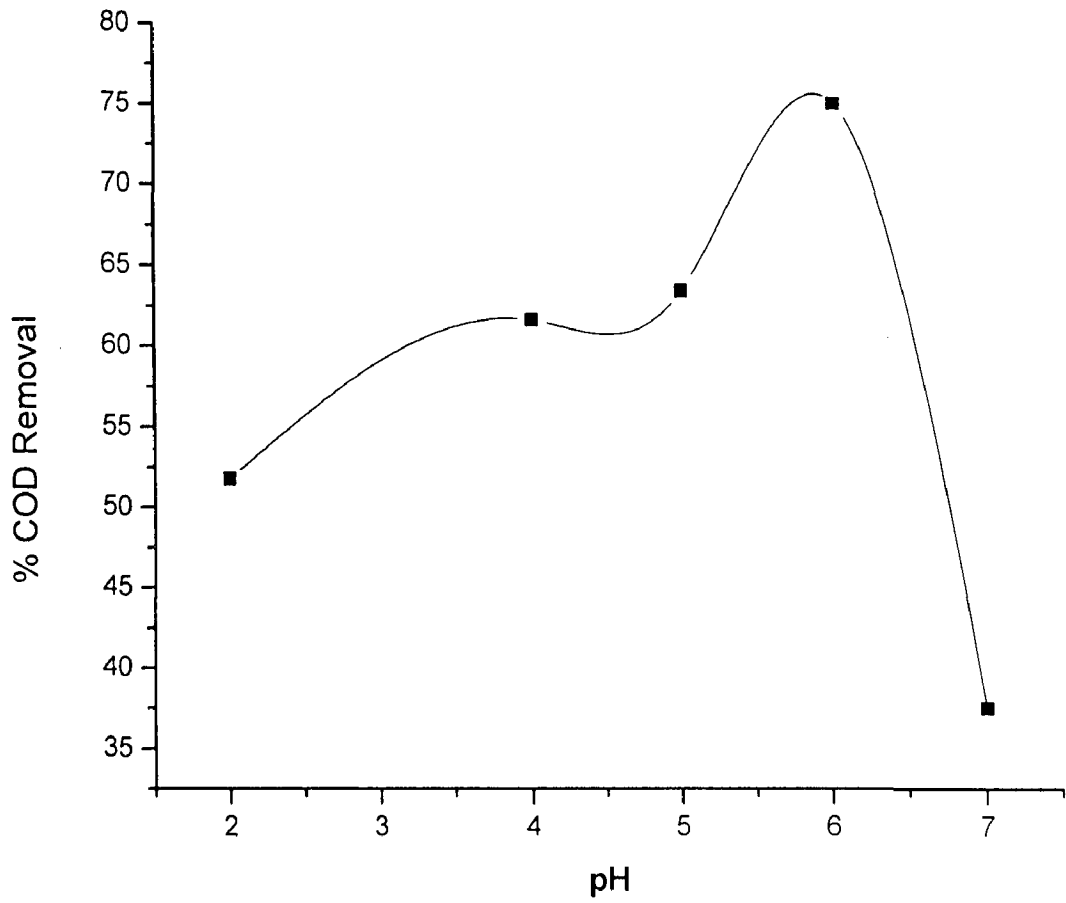


Fig.5.2 Effect of pH on %COD removal with Copper sulphate as coagulant.
Dose of copper sulphate= 5 g/l

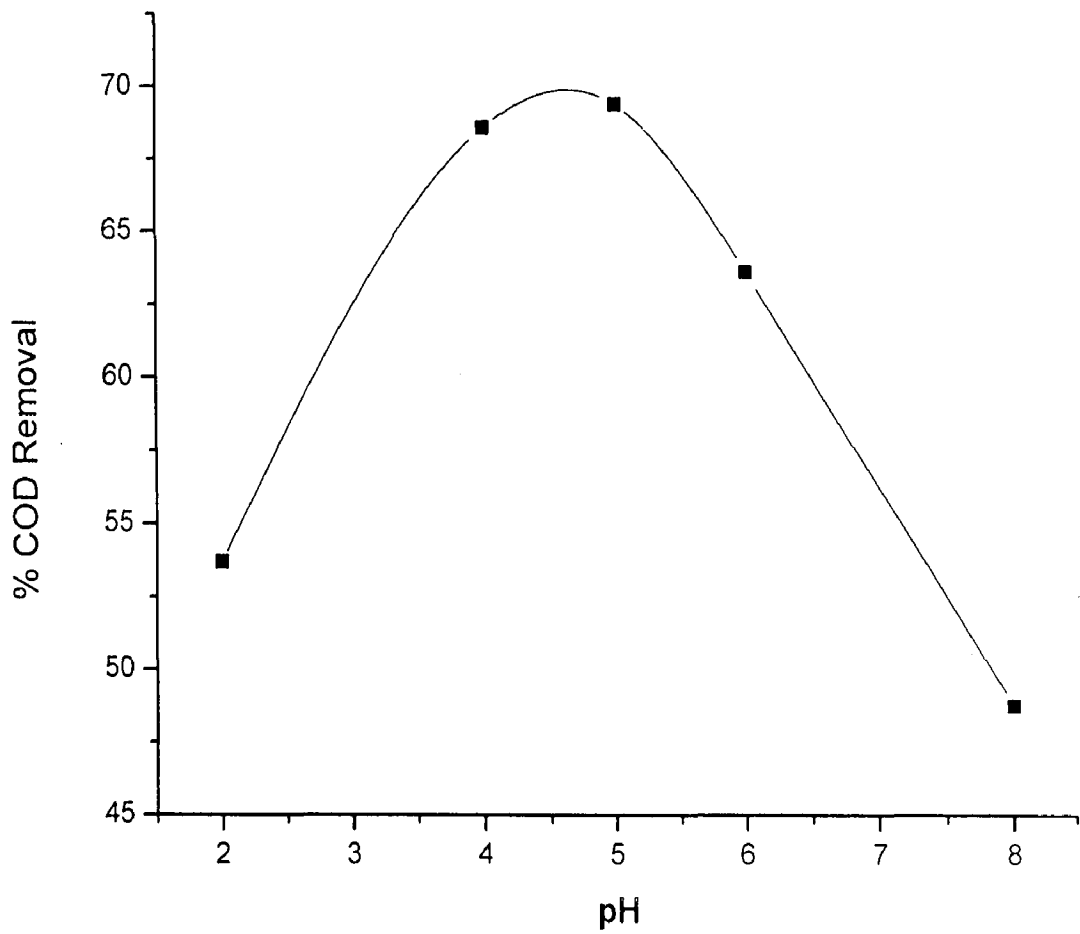


Fig.5.3 Effect of pH on %COD removal with PAC as coagulant
Dose of PAC= 5 g/l

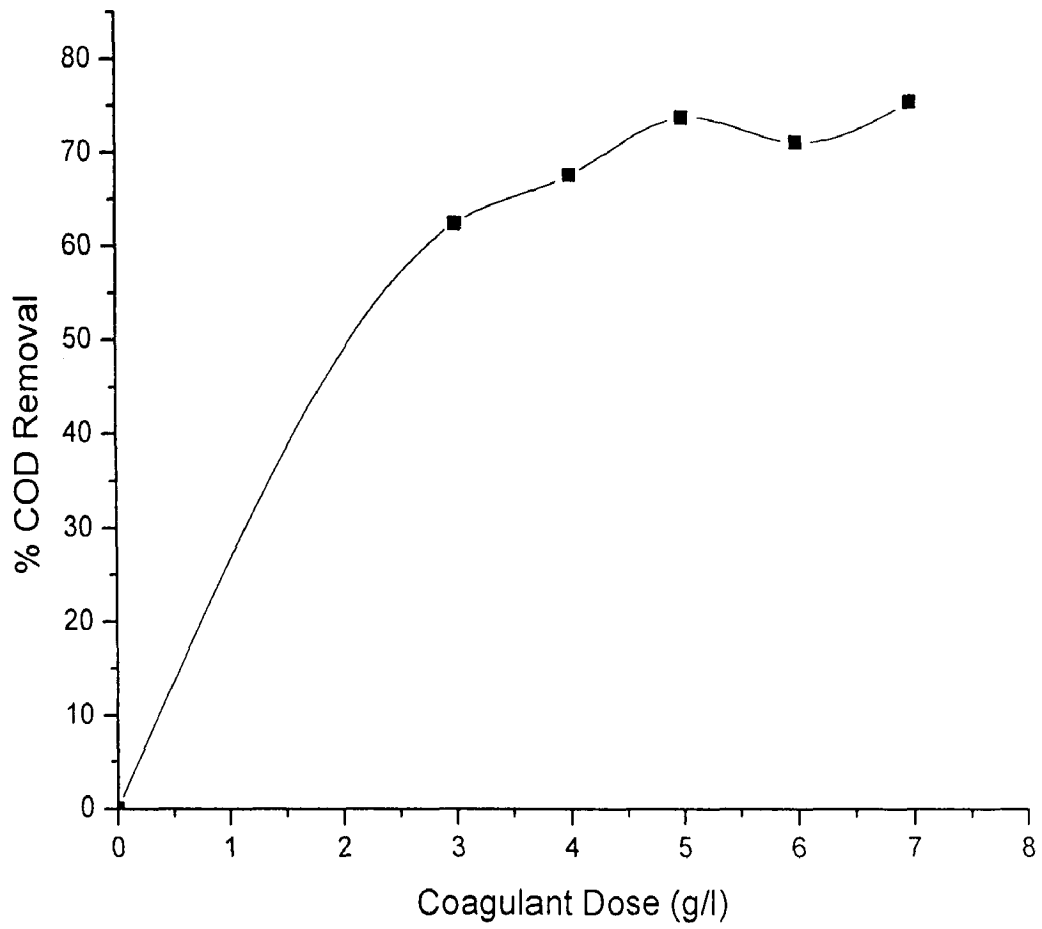


Fig.5.4 Effect of coagulant dosing on %COD removal with $AlCl_3$ as coagulant at pH=4

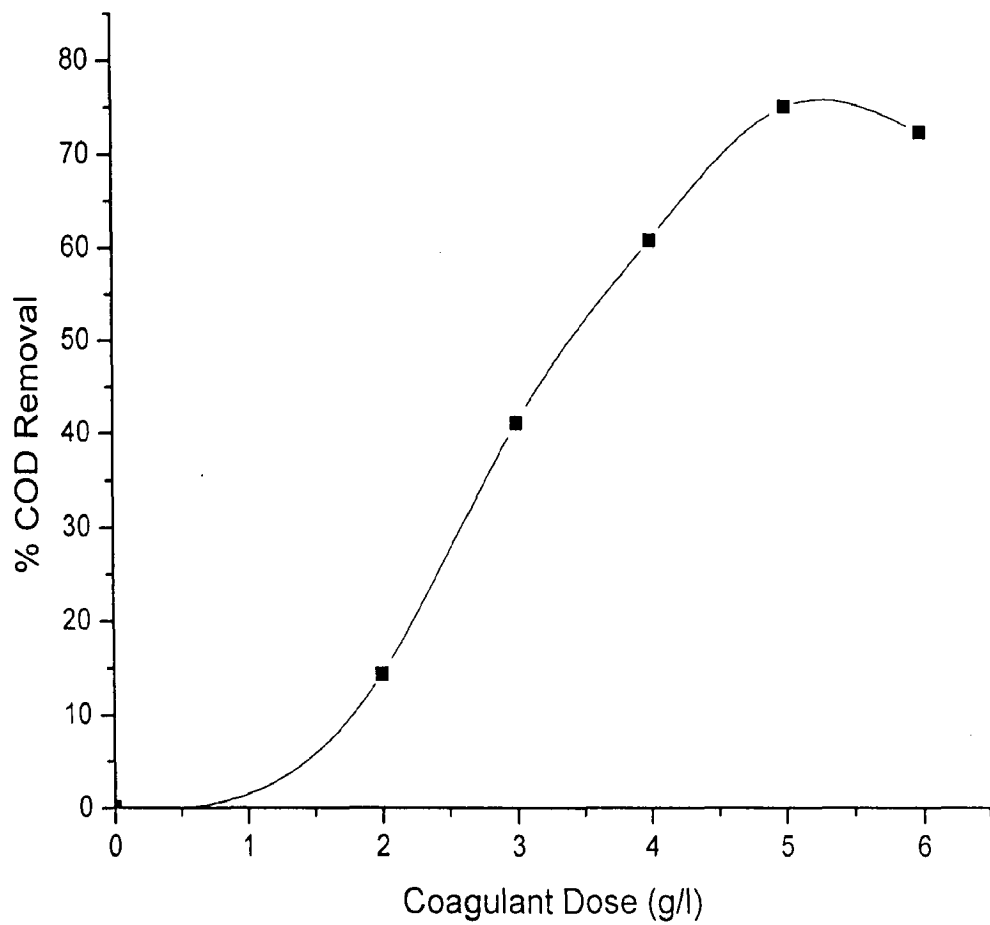


Fig.5.5 Effect of coagulant dosing on %COD removal with Copper sulphate as Coagulant at pH=6.

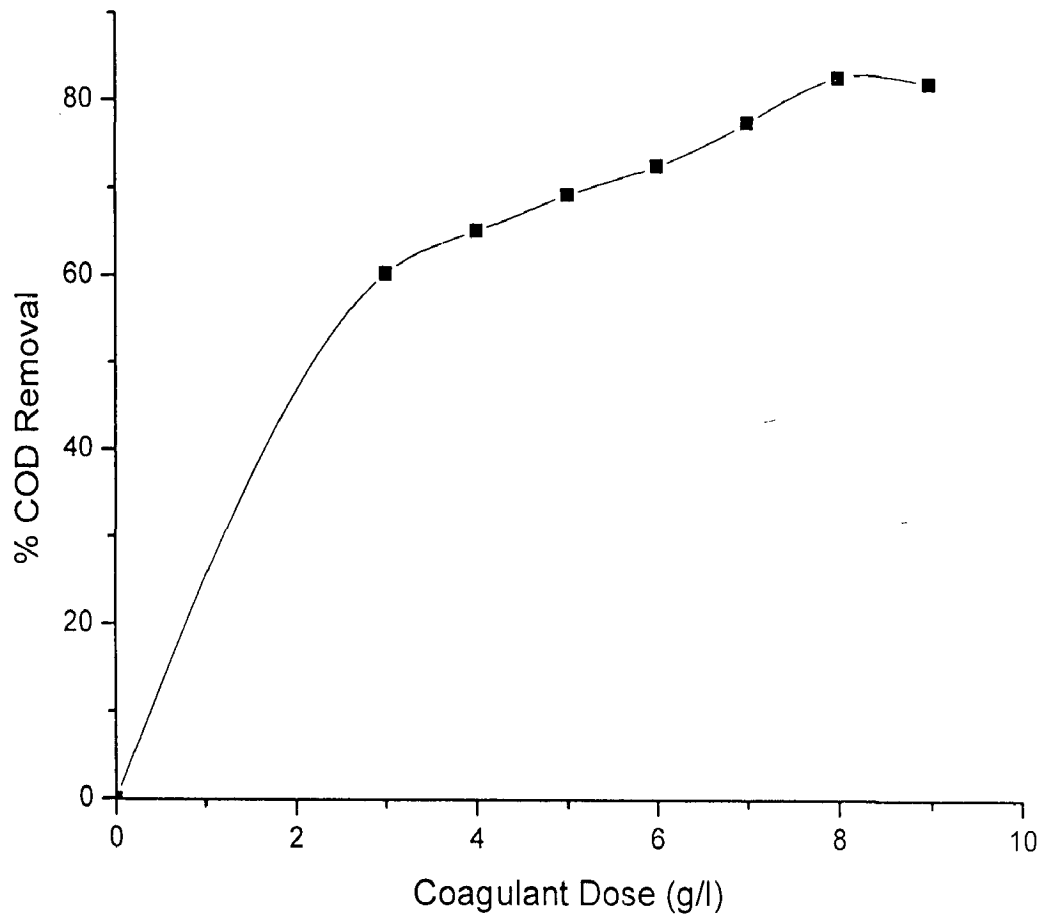


Fig.5.6 Effect of coagulant dosing on %COD removal with PAC as Coagulant at pH=5.

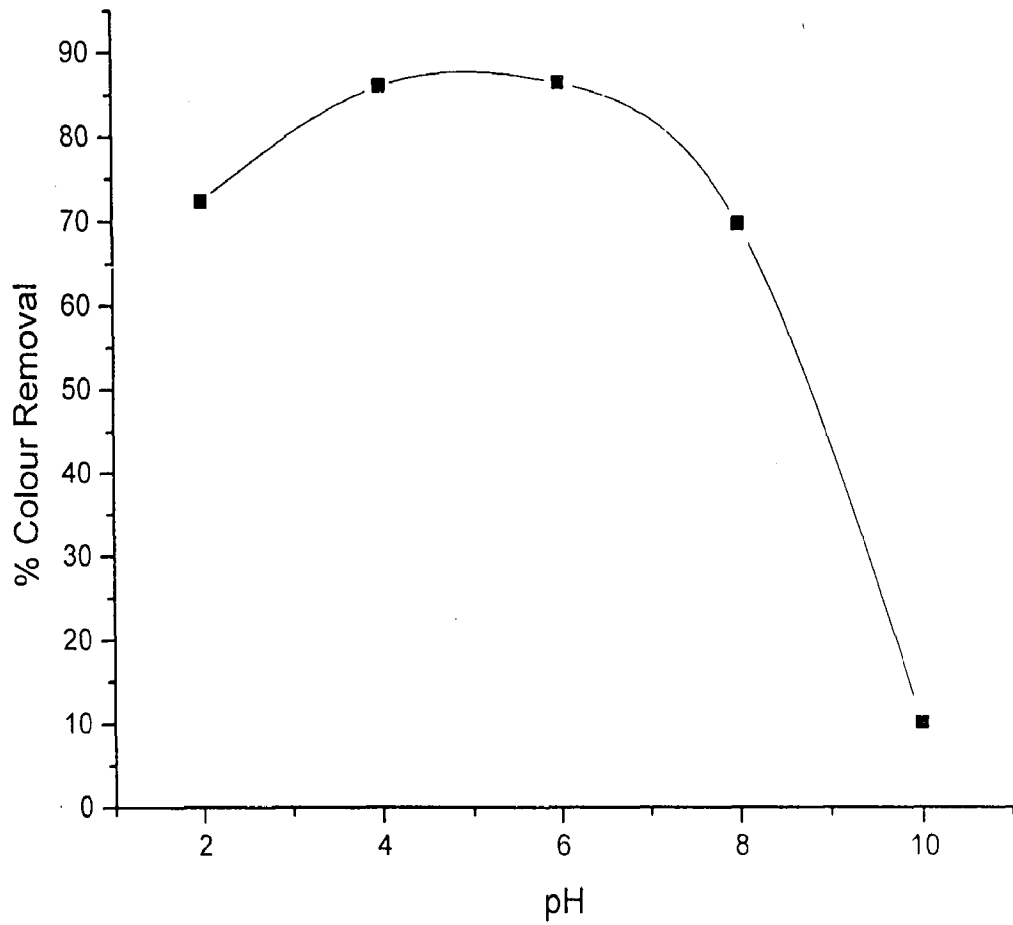


Fig.5.7 Effect of pH on %Colour removal with AlCl_3 as Coagulant
Dose of AlCl_3 = 5 g/l

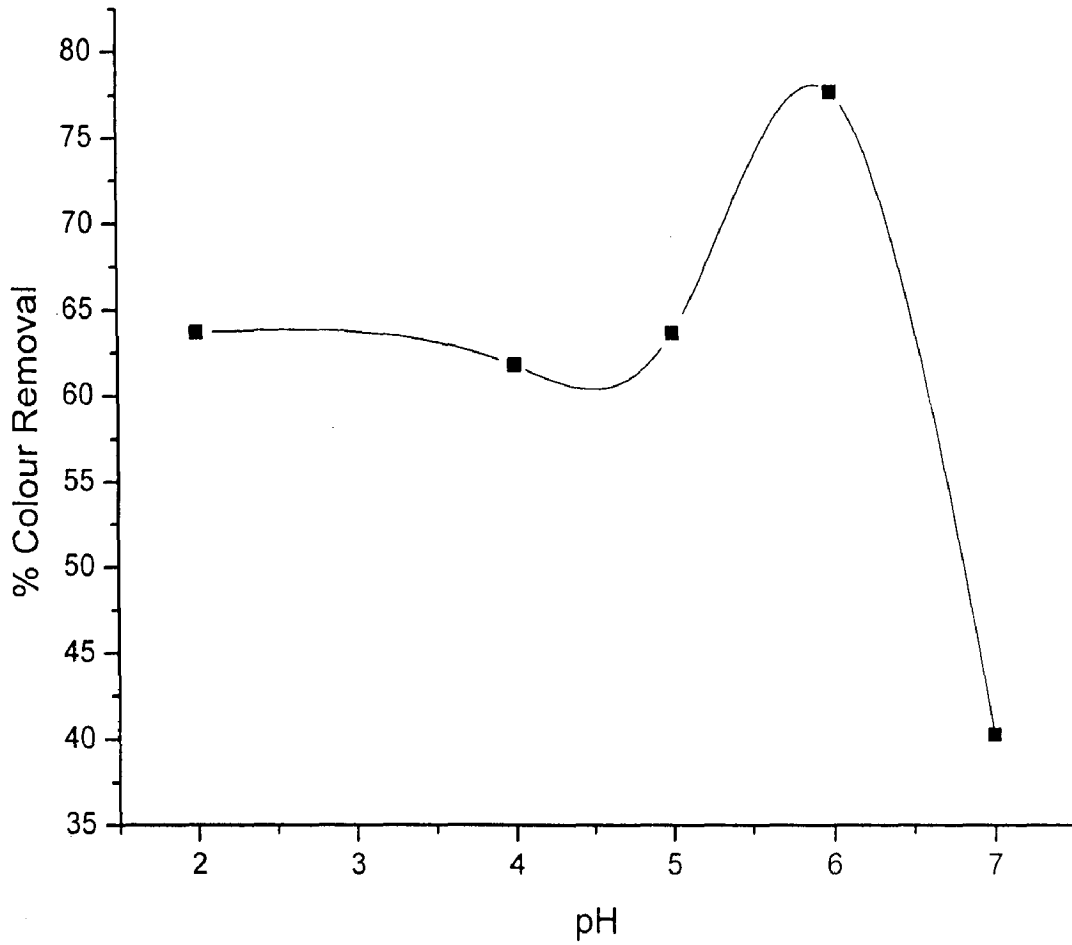


Fig.5.8 Effect of pH on %Colour removal with Copper sulphate as Coagulant.

Dose of Copper sulphate = 5 g/l

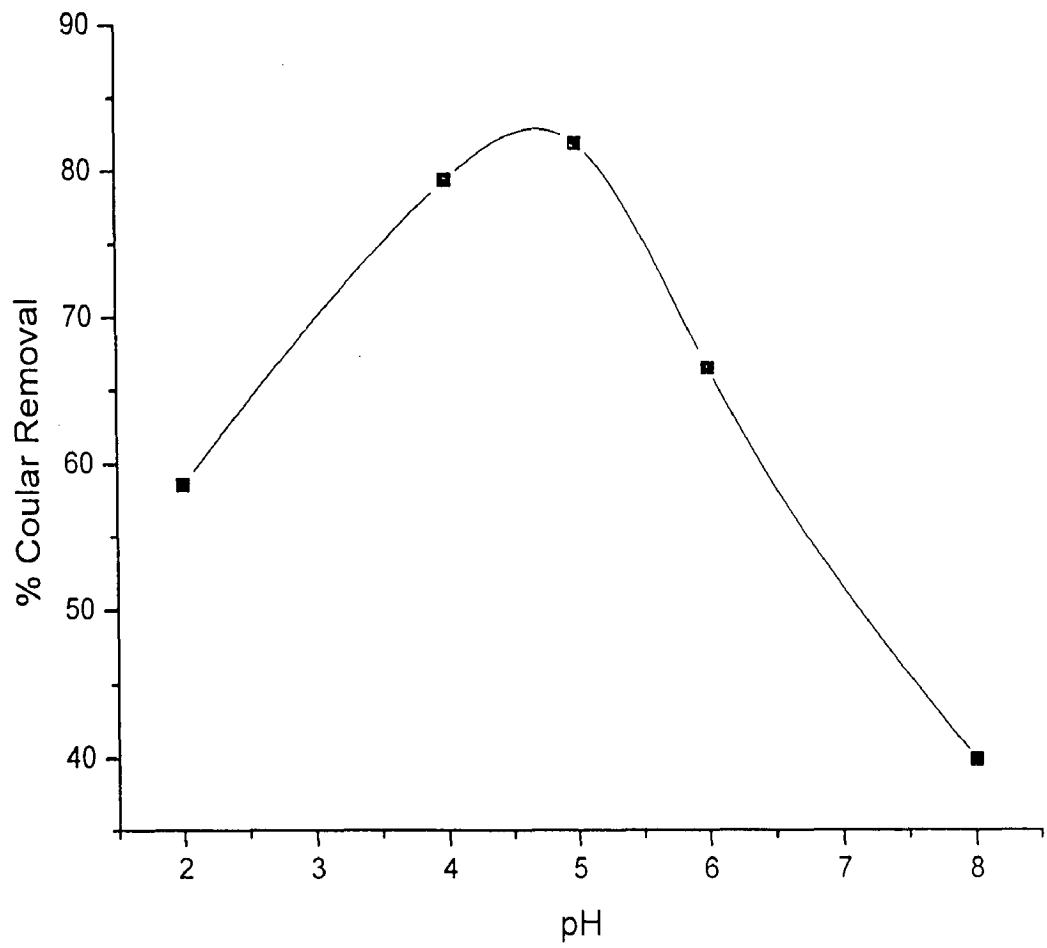


Fig.5.9 Effect of pH on %Colour removal with PAC as Coagulant.

Dose of PAC = 5 g/l

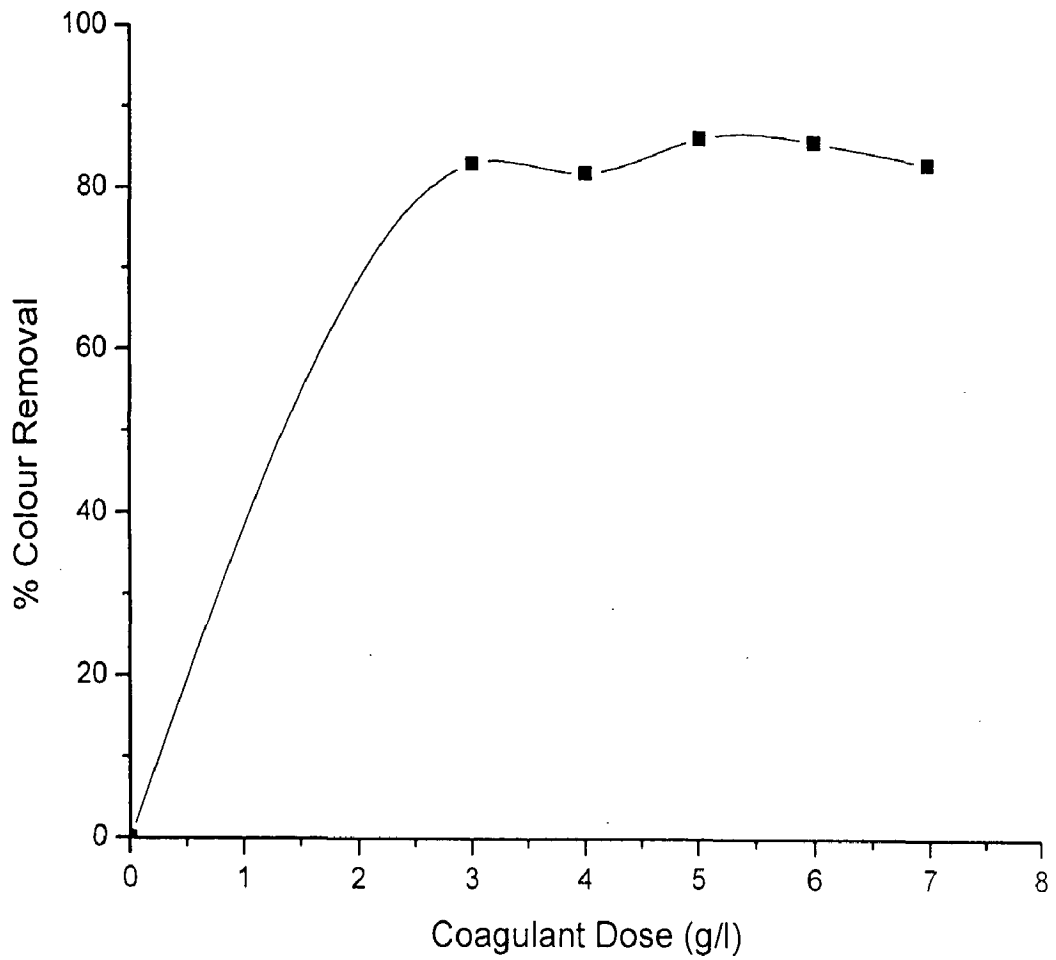


Fig.5.10. Effect of coagulant dosing on %Colour removal with AlCl₃ as Coagulant at pH=4

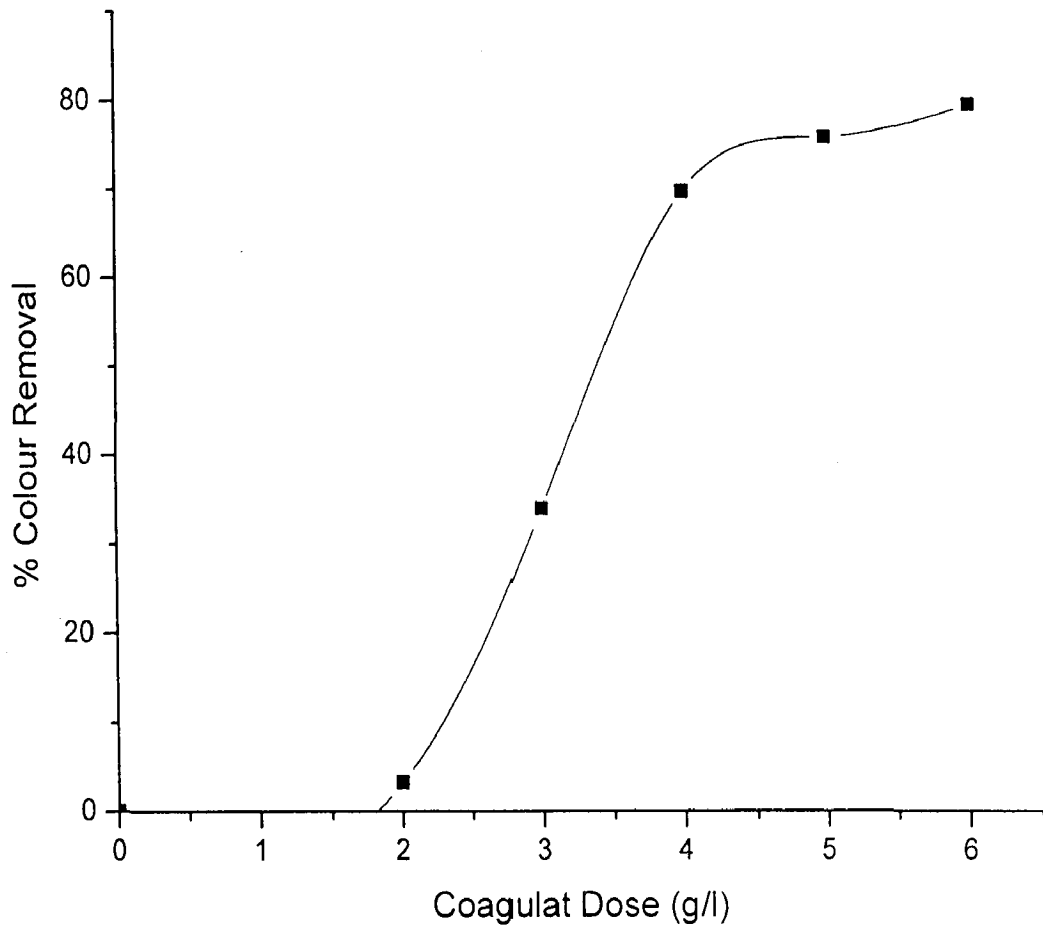


Fig.5.11 Effect of coagulant dosing on %Colour removal with Copper sulphate as Coagulant at pH=6

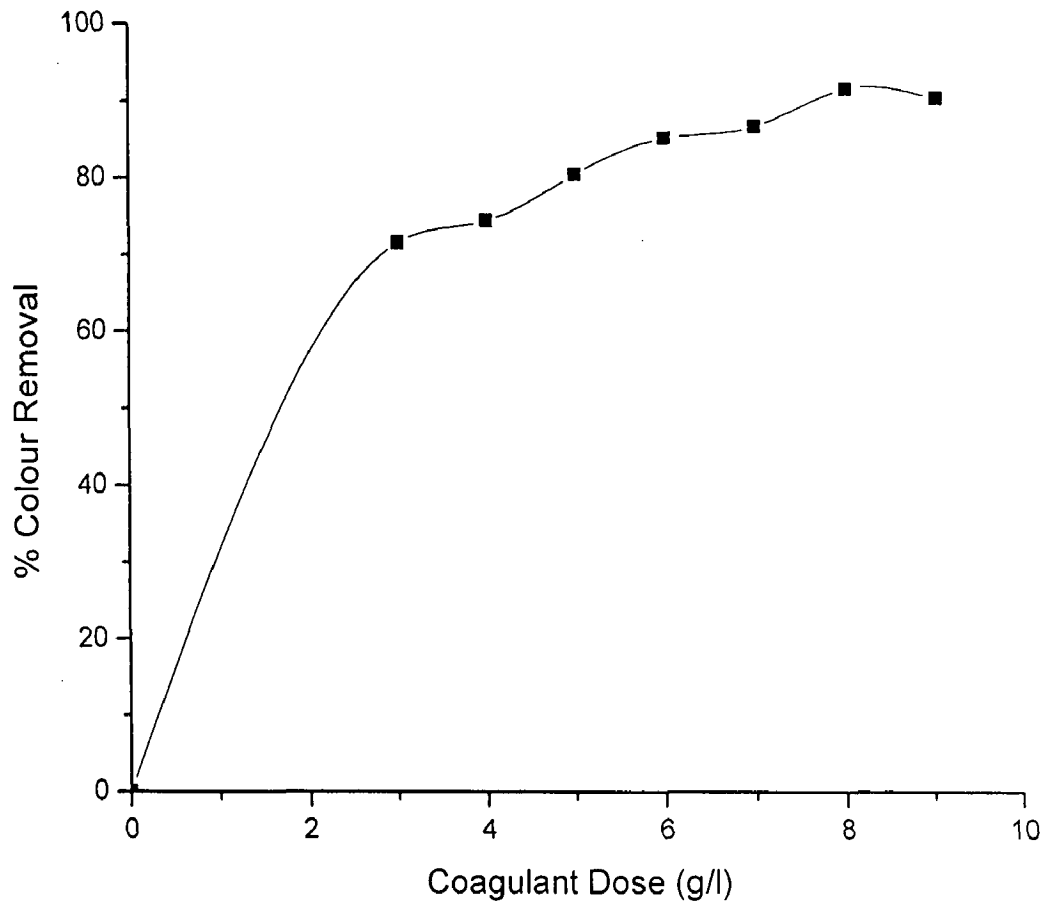


Fig.5.12 Effect of coagulant dosing on %COD removal with PAC as Coagulant at pH=5

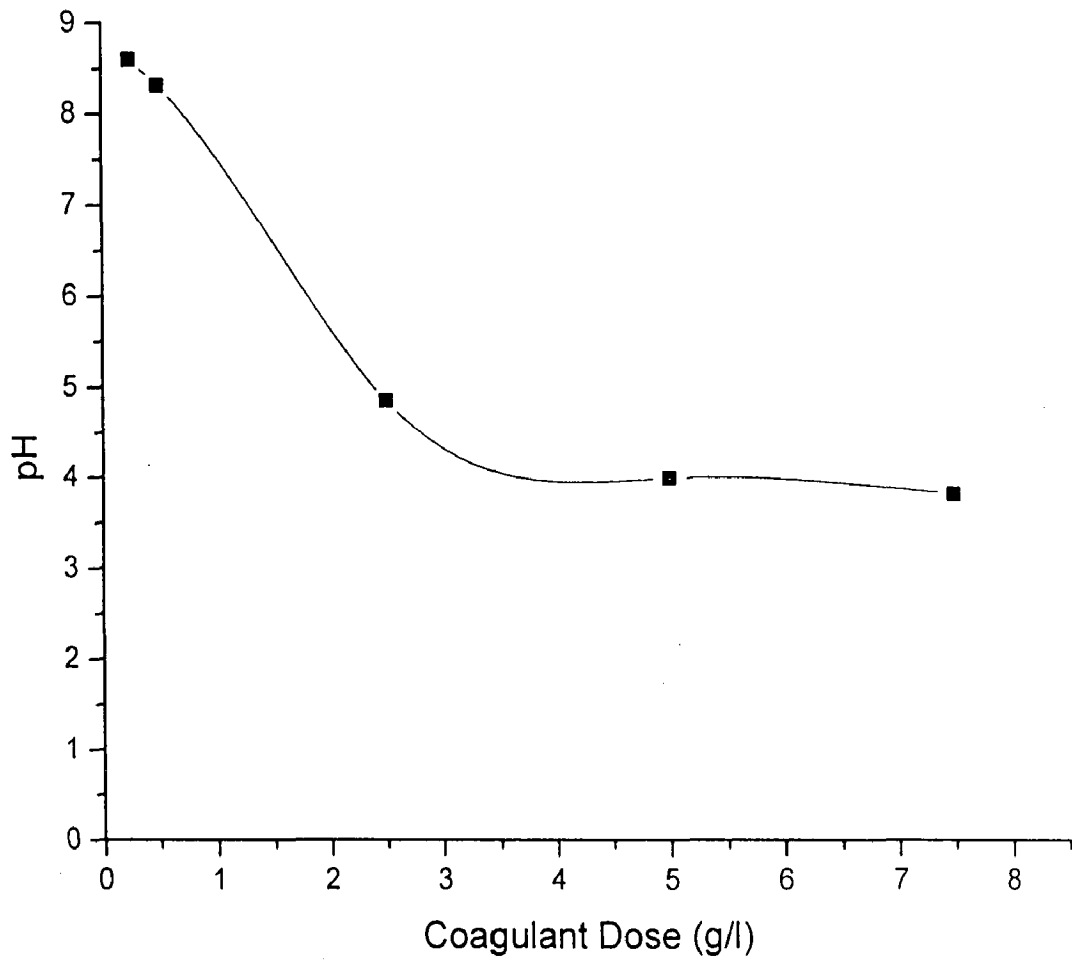


Fig.5.13 Effect of coagulant dosing on pH with AlCl_3 as Coagulant

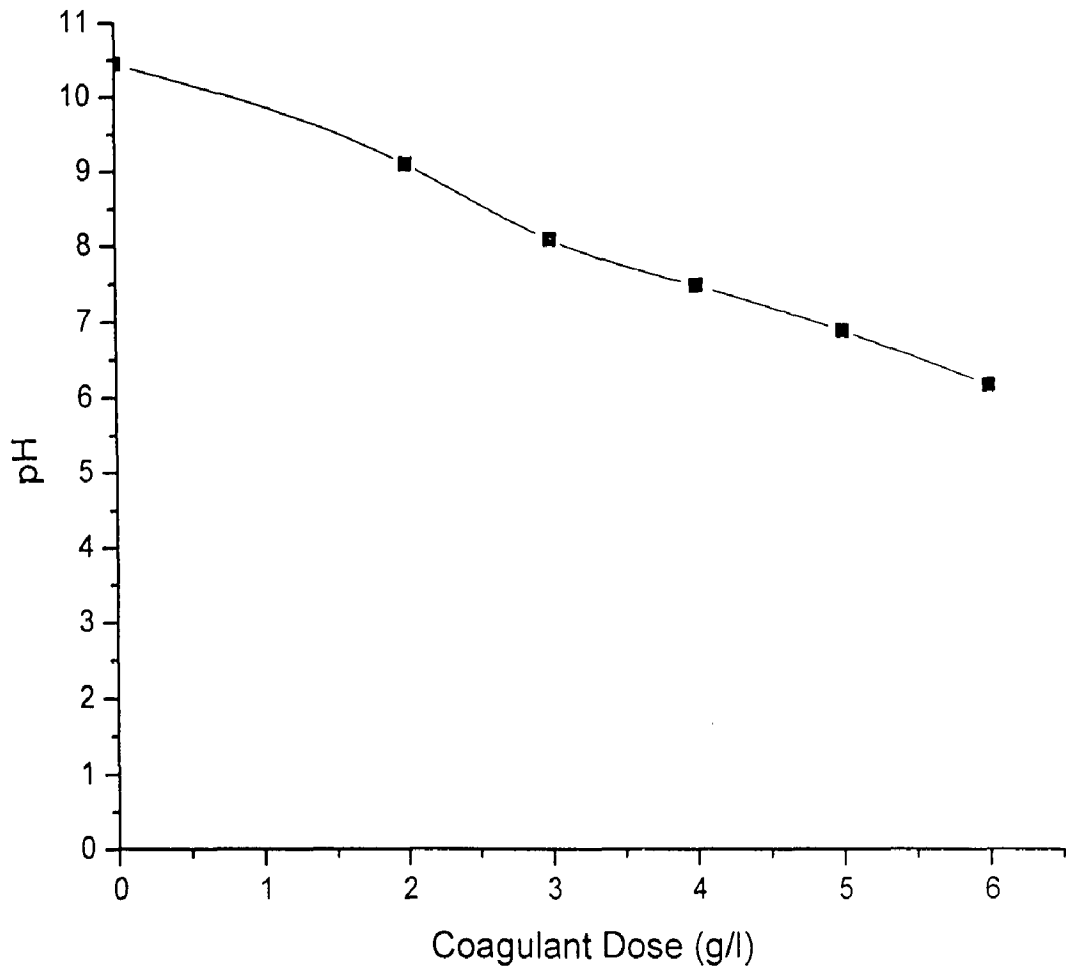


Fig.5.14 Effect of coagulant dosing on pH with Copper sulphate as Coagulant

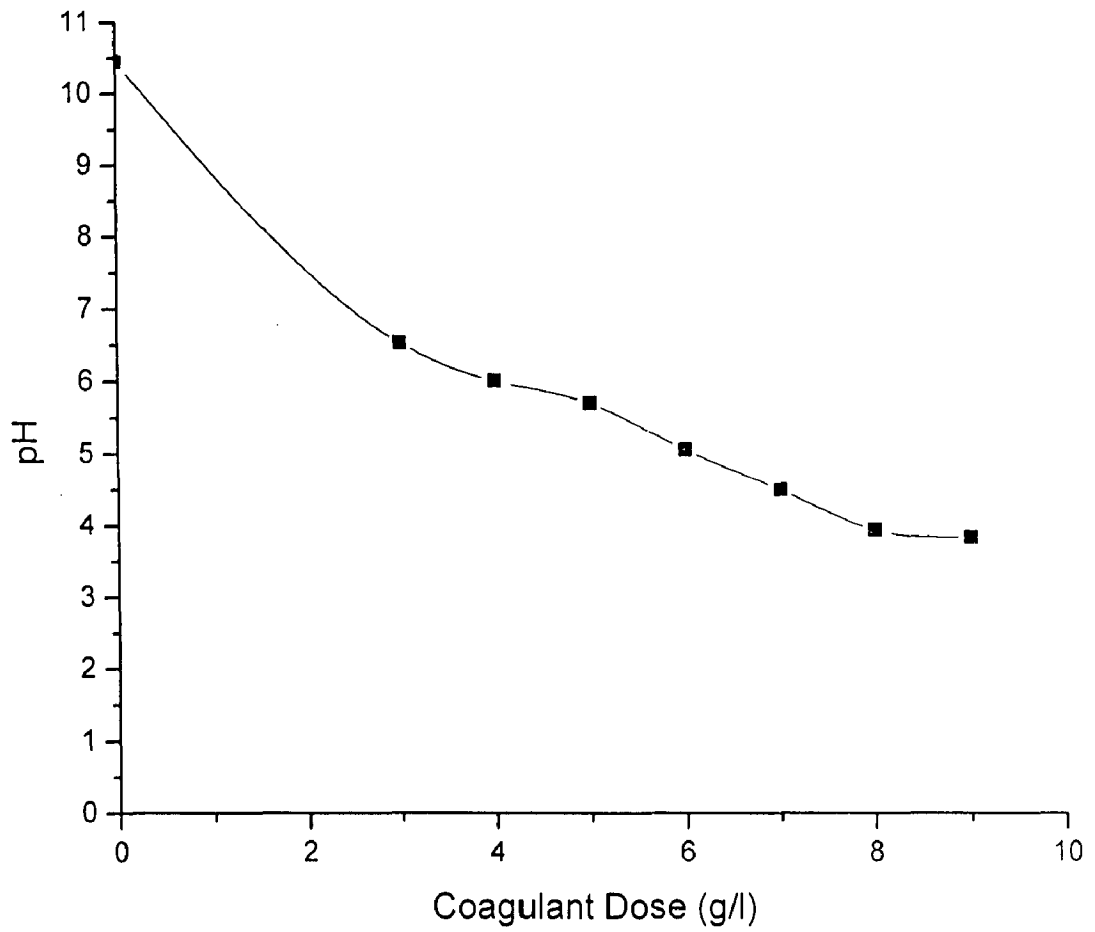


Fig.5.15 Effect of coagulant dosing on pH with PAC as Coagulant

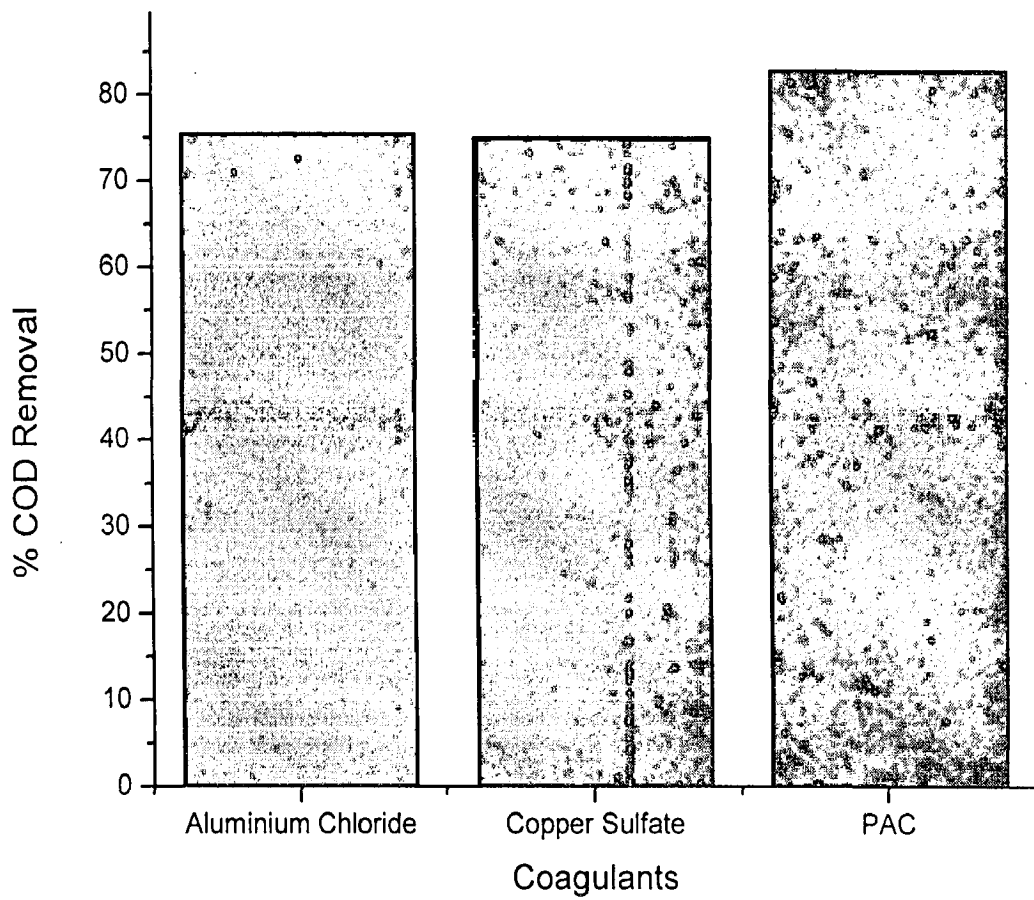


Fig.5.16 Comparison of different coagulant for maximum COD removal (corresponding to optimum pH & optimum dose)

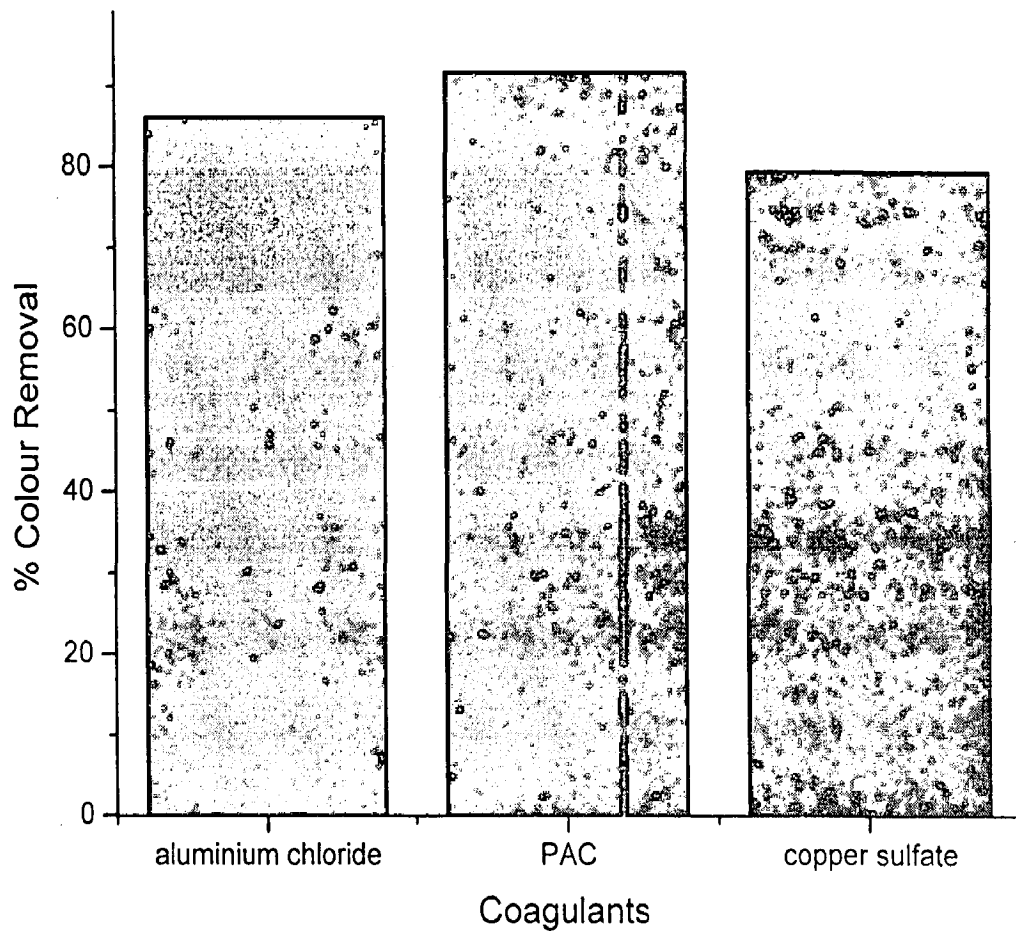


Fig.5.17 Comparison of different coagulant for maximum Colour removal
(corresponding to optimum pH & optimum dose)

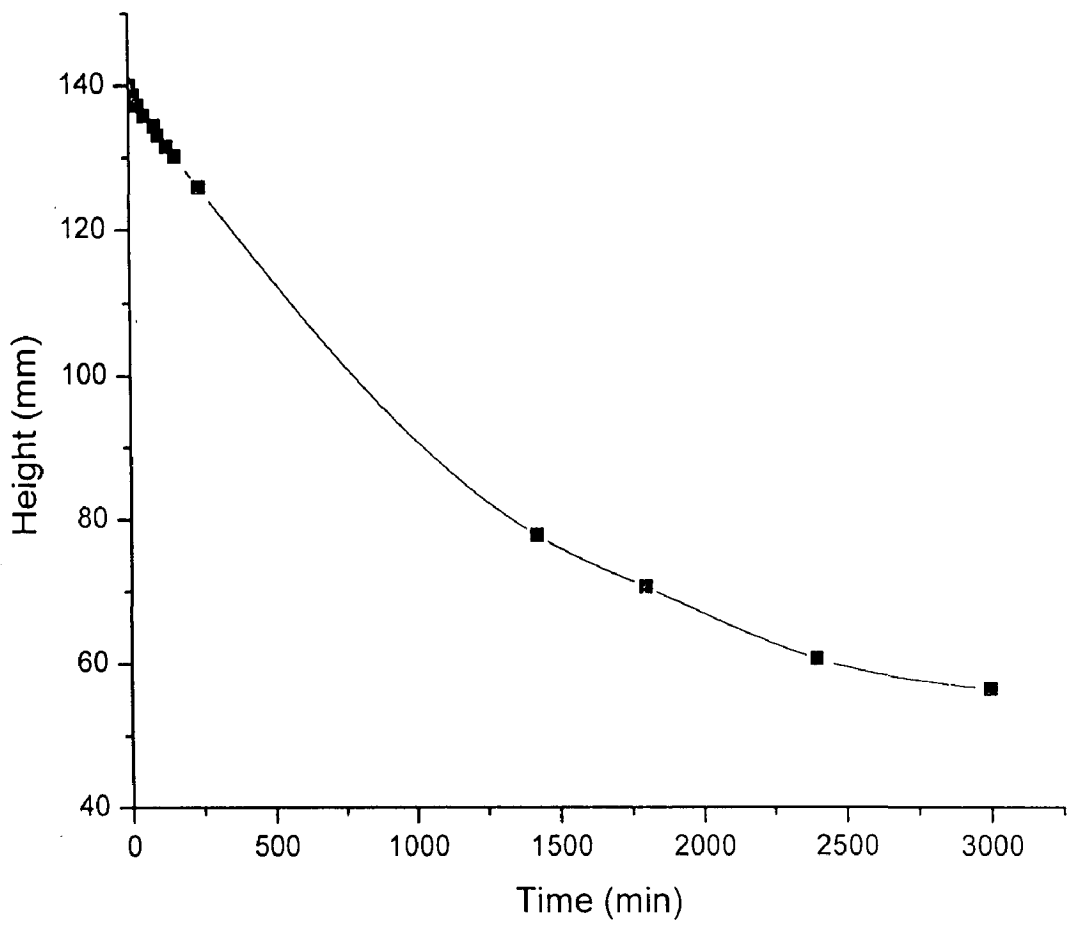


Fig.5.18 Settling of paper mill effluent after treating with $AlCl_3$

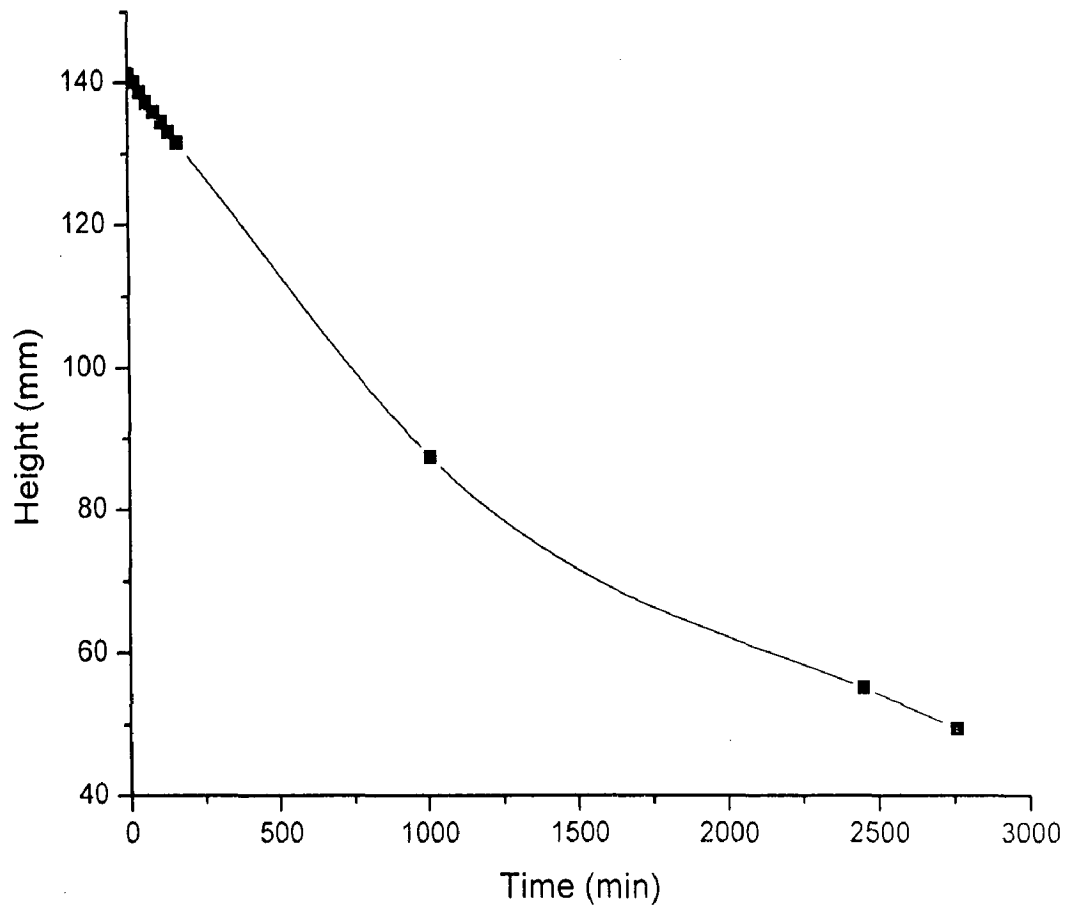


Fig.5.19 Settling of paper mill effluent after treating with copper sulphate

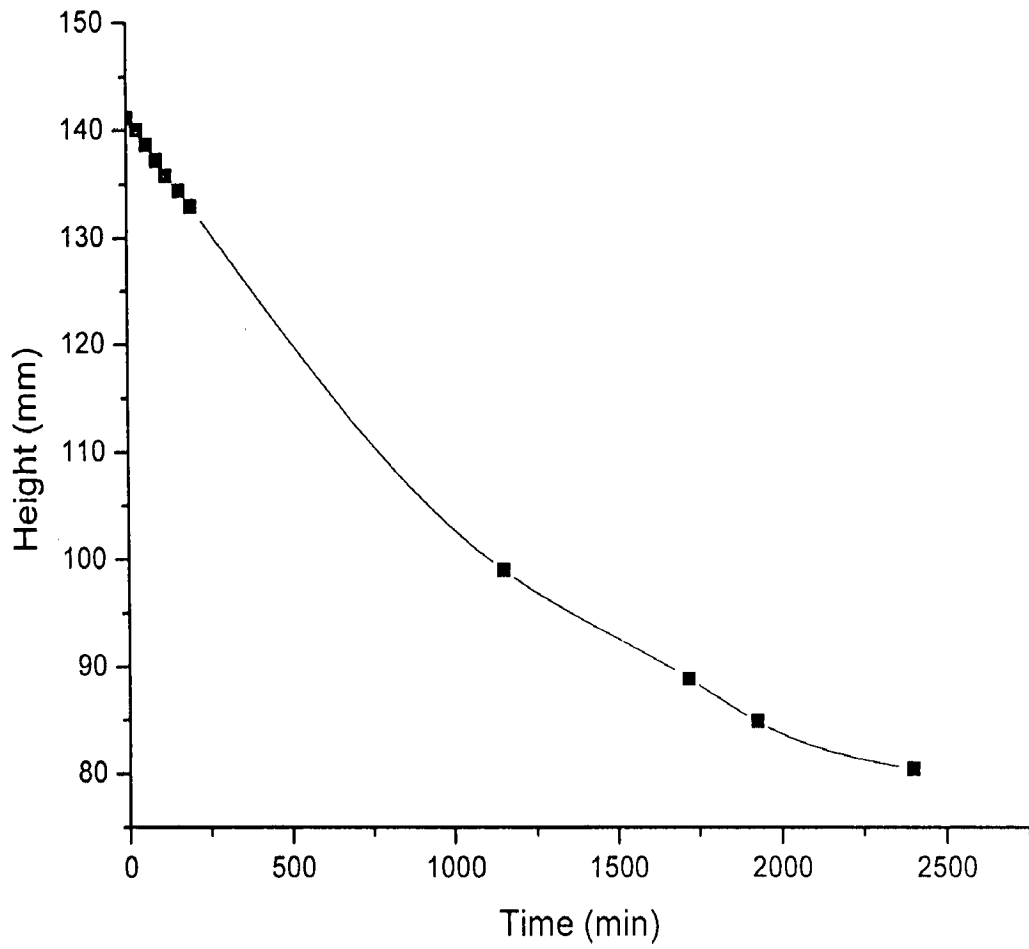


Fig.5.20 settling of paper mill effluent after treating with PAC

CHAPTER 6

CONCLUSIONS & RECOMMENDATIONS

6.1 Conclusions:

For the treatment of paper mill effluent by coagulation, experiments were performed and results were discussed with the help of figures in previous chapter. Effluent was treated with different coagulants like aluminium chloride, copper sulphate, poly aluminium chloride (PAC). Results indicate:

1. The maximum COD and colour removal of 82.85% and 91.81% respectively were obtained using PAC as compared to 75.5% and 83.18% for aluminium chloride and 75.00% and 75.96% for copper sulphate.
2. The dose for maximum COD removal and maximum colour removal were not same, as for copper sulphate and aluminium chloride. The maximum COD removal (75%) was found at coagulant dosing of 5 g/l but maximum colour removal (79.64%) was found at 6 g/l copper sulphate coagulant dosing. For aluminium chloride, the maximum COD removal (75.5%) was found at coagulant dosing of 7 g/l but maximum colour removal (86.30%) was found at 5 g/l.
3. The aluminium chloride treated effluent settled faster in comparison to other two studied coagulants. So, for better settling aluminium chloride may be suggested.
4. PAC is better as coagulant in comparison to other two coagulants. However, copper sulphate may be considered better coagulant where wet air oxidation is being used as secondary treatment since copper ion act as a catalyst for wet air oxidation.

6.2 Recommendations:

- 1) It was observed by this work that poly-coagulants have potential for better removal of COD and colour. Hence, other polyelectrolyte (as poly iron sulphate, poly alumino-iron chloride or other synthesized poly salts) may be studied for better removal.
- 2) Two-stage treatment may also be done by coagulation.

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**Table.A-1 Effect of pH on Colour and COD removal after addition of AlCl₃
(At constant coagulant loading= 5 g/l)**

S. No.	pH (after coagulant addition)	pH (adjusted)	COD (after treatment)	%COD Removal	CU (after treatment)	%Colour Removal
1	3.17	2	2143.75	69.37	1421.8	72.43
2	3.17	4	1837.5	73.75	714	86.15
3	3.17	6	2327.5	66.75	691.2	86.59
4	3.17	8	3797.5	45.75	1552.8	69.89
5	3.17	10	4042.5	42.25	4629.4	10.24

Table.A-2 Effect of AlCl₃ dosing at optimum pH=4.00

S. No.	Coagulant dosing (g/l)	pH (after coagulant addition)	COD (after treatment)	% COD Removal	CU (after treatment)	%Colour Removal
1	3	4.34	2633.75	62.37	869.2	83.14
2	4	4	2266.25	67.62	930.2	81.96
3	5	3.72	1837.5	73.75	706.2	86.30
4	6	3.65	2021.25	71.12	729.6	85.85
5	7	3.47	1715	75.5	867.4	83.18

Table.A-3 Effect of pH on Colour and COD removal after addition of Copper sulphate (at constant coagulant dose= 5 g/l)

S. No.	pH(after coagulant addition)	pH (adjusted)	COD (after treatment)	%COD Removal	CU (after treatment)	%Colour Removal
1	6.81	2	3375	51.78	1872.6	63.69
2	6.81	4	2687.5	61.60	1967.4	61.85
3	6.81	5	2562.5	63.39	1869.8	63.74
4	6.81	6	1750	75.00	1145.6	77.78
5	6.81	7	4375	37.5	3044.28	40.28

Table.A-4 Effect of Copper sulphate dosing at optimum pH=6.00

S. No.	Coagulant dosing (g/l)	pH(after coagulant addition)	COD (after treatment)	% COD Removal	CU (after treatment)	%Colour Removal
1	2	9.1	6000	14.28	4993.2	3.18
2	3	8.1	4125	41.07	3404.6	33.98
3	4	7.49	2750	60.71	1560.8	69.73
4	5	6.89	1750	75	1239.4	75.96
5	6	6.18	1937.5	72.32	1049.8	79.64

Table.A-5 Effect of pH on Colour and COD removal after addition of PAC (at constant coagulant dose= 5 g/l)

S. No.	pH(after coagulant addition)	pH (adjusted)	COD (after treatment)	%COD Removal	CU (after treatment)	%Colour Removal
1	5.45	2	3240.74	53.70	2136.6	58.57
2	5.45	4	2199.04	68.58	1063.8	79.37
3	5.45	5	2141.20	69.41	934	81.89
4	5.45	6	2546.29	63.62	1725	66.55
5	5.45	8	3587.96	48.74	3100.2	39.89

Table.A-6 Effect of PAC dosing at optimum pH=5.00

S. No.	Mass loading(g/l)	pH(after coagulant addition)	COD (after treatment)	% COD Removal	CU (after treatment)	%Colour Removal
1	3	6.53	2777.7	60.31	1462	71.65
2	4	6.01	2430.55	65.27	1311.8	74.56
3	5	5.70	2141.21	69.41	998.8	80.63
4	6	5.05	1909.72	72.71	750.6	85.44
5	7	4.5	1562.4	77.67	672.2	86.96
6	8	3.94	1200	82.85	422	91.81
7	9	3.84	1250	82.17	482.6	90.64

Platinum-Cobalt standard curve:

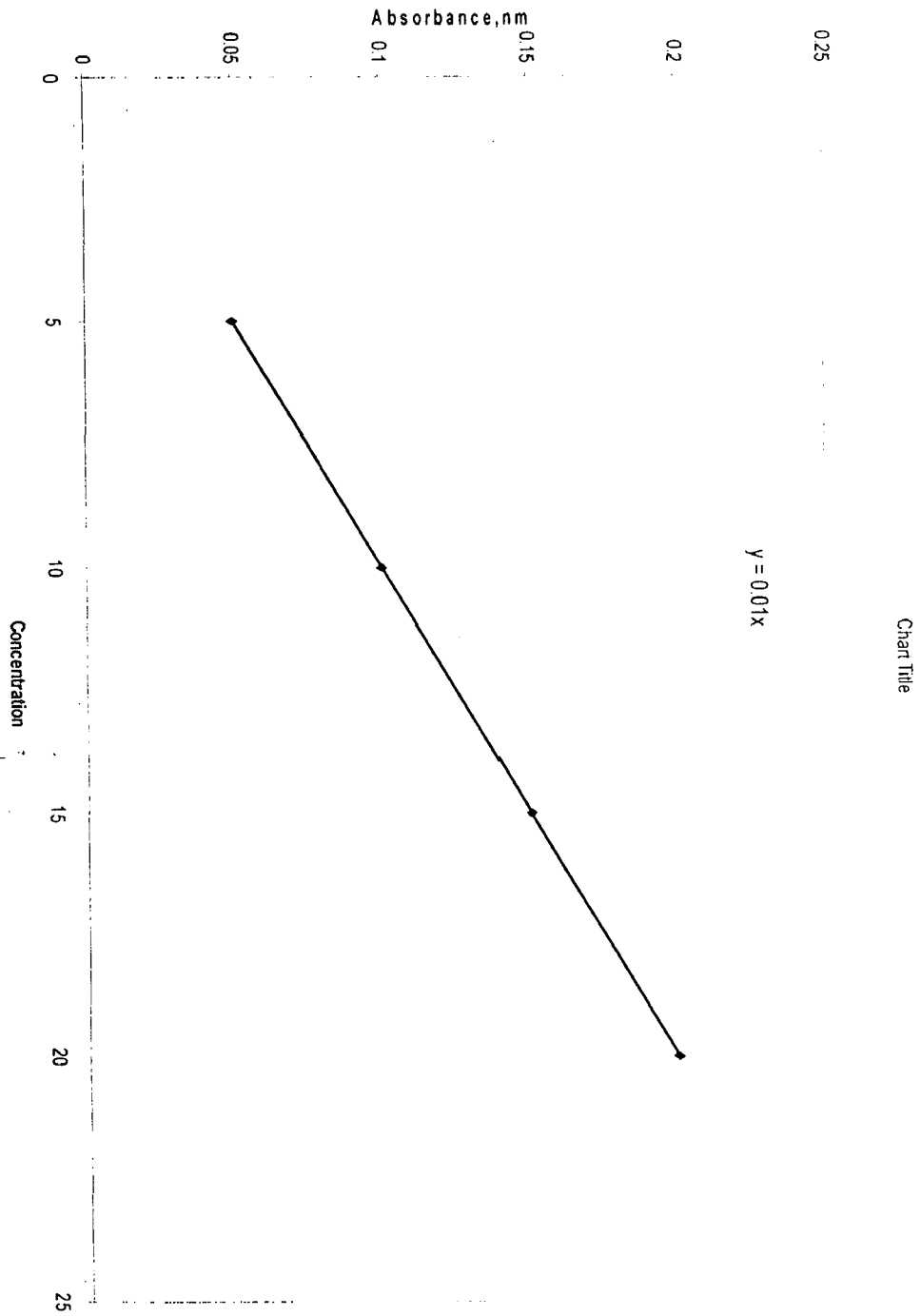


Table 2: Volume of effluent discharged by various pulp, paper & board mills^[11]

S. No.	Type of mill	Product	Production tonne/day	Volume of effluent per day (m ³)	Volume of effluent per tonne of product (m ³)
1	Sulfate mills				
	No. 1	White printing, writing & kraft paper	200	44400	222
	No. 2	White printing, writing & 45% kraft unbleached paper	200	70000	350
	No. 3	White printing, writing & kraft unbleached paper	200	61000	305
	No. 4	White printing, writing & kraft unbleached paper	110	34100	310
	No. 5	White printing, writing & speciality board paper (25%)	100	34300	343
	No. 6	Bleached pulp	80	16000	200
2	Sulfite mill	White printing, writing & paper	55	13200	240
3	Newsprint mill (sulfate & ground wood)	Newsprint	130	34000	262
4	Packing paper mill (soda lime)	Packing paper	15	2040	136

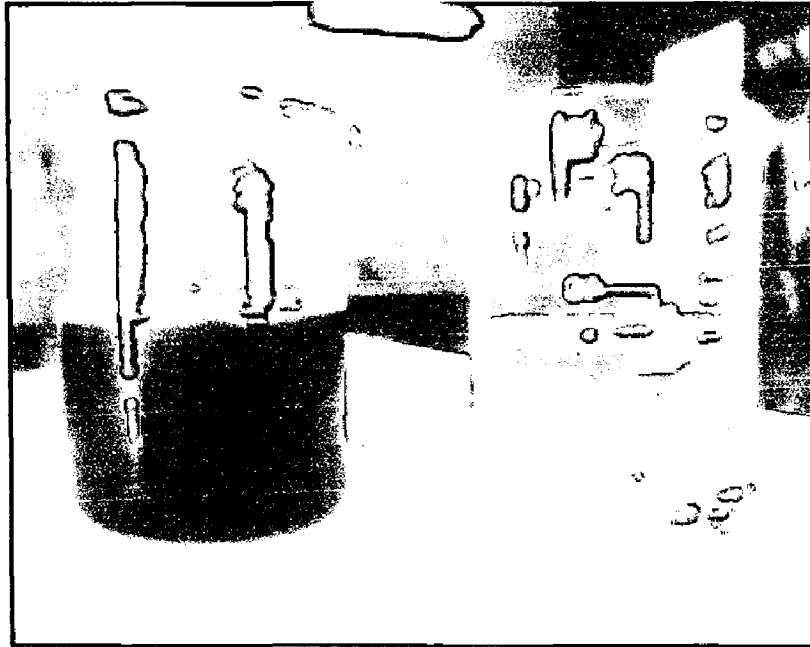


Fig.B-1. Treated (with PAC at pH = 5 and dose =8 g/l) and untreated sample