HYBRID COAGULATION ULTRAFILTRATION FOR TENUN DYE WASTEWATER TREATMENT

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ABSTRACT

Hybrid Coagulation UF process has been studied to improve membrane performance and water quality for surface water treatment. Using coagulation before UF increases permeate quality; the extent of dissolved organic matter removal is controlled by the coagulation step. Efficient coagulation conditions for coagulation / settling process can be applied for the hybrid coagulation UF process. Floc cake resistance is lower than resistance due to the unsettled floc and the uncoagulated organics. For this research the hybrid process was applied in attempt to treating the effluent wastewater that discharged from the textile industries. The Hybrid Coagulation UF model was setup using the apparatus that already prepared at environmental laboratory. The waste water sample with addition of predetermined dosage of Aluminum Sulphate ($Al_2(SO_4)_3$) which has been left for 24 hours and 48 hours was filtered using the membrane filter with pore size 0.1 - 0.4 μ with the bar pressure used is between 3 – 4 bars. The filtered sample was taken to measure the parameters which are COD, BOD, TSS and Colour. Then the results were compared between the raw sample and after treatment sample. The application of the hybrid system, combining coagulation and ultrafiltration, offers better effects of the removal of organic pollution.

ABSTRAK

Gabungan hibrid diantara proses pemejatan cecair dan penapisan UF telah dikaji sejak dahulu lagi untuk meningkatkan prestasi membran dan kualit air untuk tujuan rawatan air permukaan. Dengan menggunakan proses pemejatan sebelum UF, ianya dapat meningkatkan kualiti serapan kerana penyingkiran bahan organik telah dibantu oleh proses pemejatan dan ianya boleh digunakan secara gabungan dengan proses penapisan UF. Rintangan bagi kek flok adalah lebih rendah daripada flok yang masih belum dirawat dan tidak mampu dipejatkan secara organik. Oleh itu proses gabungan hibrid ini telah digunakan dalam usaha untuk merawat air sisa pembuangan yang telah dilepaskan daripada industry tekstil. Dengan menggunakan model penapisan UF yang disediakan di dalam makmal alam sekitar, ujikaji rawatan dijalankan. Sampel air sisa dengan jumlah dos Aluminium Sulphate (Al2(SO4)3) yang telah ditetapkan telah dibiarkan supaya proses pemendakan berlaku untuk jangkamasa 24 jam dan juga 48 jam, kemudiannya telah ditapis menggunakan penapis membrane (UF) dengan saiz 0.1-0.4 μm dengan tekanan bar yang digunakan adalah diantara 3-4 bar. Sampel yang telah ditapis diambil untuk mengukur parameter bagi COD, BOD, TSS dan juga ADMI. Maka, keputusan dibandingkan antara sampel mentah dan sampel selepas rawatan. Penggunaan system gabungan yang menggabungkan proses pemejatan dan ultrafiltration, menawarkan kesan lebih baik dalam penyingkiran pencemaran berbanding yang tidak digabungkan.

TABLE OF CONTENT

		Page
SUPERVISOR'S DECLARATION		ii
STUDENT DECLARATION		iii
ACKNOWLEDGEMENTS		iv
ABSTRACT		v
ABSTRAK		vi
TABLE OF CONTENTS		vii
LIST OF TABLES		xi
LIST OF FIGURES		xii
LIST OF SYMBOLS		xiii
LIST OF ABBREVIATIONS		xiv
CHAPTER 1	**INTRODUCTION**	
1.1	Background of Study	1
1.2	Problem Statement	2
1.3	Objective of Study	3
1.4	Scope of Study	4
1.5	Research Significance	4
1.6	Expected Outcome	4
CHAPTER 2	**LITERATURE REVIEW**	
2.1	Wastewater from Textile Industry	5
2.2	Textile Wastewater Characteristic and Environmental Impact	6
2.3	Treatment of Textile Wastewater	8

2.4	Requirement of Wastewater Treatment	8
2.5	Hybrid Coagulation and Ultrafiltration in General	9
	2.5.1 Process description	9
	2.5.2 Fouling and chemical cleaning	10
2.6	Coagulation	12
2.7	Ultrafiltration VS Conventional Method	13
CHAPTER 3	**RESEARCH METHODOLOGY**	
3.1	Introduction	15
3.2	Flow Chart	15
3.3	Material Selection	16
	3.3.1 Wastewater Sampling	16
	3.3.2 Coagulant selected	17
3.4	Apparatus Preparation	18
3.5	Hybrid Coagulation UF Model	19
3.6	Experimental Set-up	21
3.7	Data Collection Method	21
	3.7.1 Jar Test	22
	3.7.2 Biochemical Oxygen Demand (BOD)	23
	3.7.3 Chemical Oxygen Demand (COD)	25

	3.7.4 Total Suspended Solids (TSS)	27
	3.7.5 Colourization (ADMI)	28
CHAPTER 4	**DATA ANALYSIS AND RESULTS**	
4.1	Introduction	30
4.2	Parameter Analysis	30
	4.2.1 Parameter Analysis Results	31
	4.2.2 Jar Test and Turbidity Analysis	31
	4.2.3 Chemical Oxygen Demand Analysis	32
	4.2.4 Biochemical Oxygen Demand Analysis	33
	4 2 5 Total Suspended Solid	34
	4.2.6 Colour (ADMI) Analysis	35
CHAPTER 5	**CONCLUSION AND RECOMMENDATION**	
5.1	Introduction	37
5.2	Conclusion	37
5.3	Recommendation	38

REFERENCES

APPENDICES

LIST OF TABLES

Table No.	Title	Page
2.1	Composite Textile Industry Wastewater Characteristics	8
3.1	Pressure Pump Characteristic	19
3.2	Membrane filter characteristic	19
3.3	The Bod Level In Wastewater Sample	25
3.4	The normal COD range in wastewater sample	27
4.1	Result of parameters analysis	31

LIST OF FIGURES

Figure No.	Title	Page
2.1	Coagulation process	12
2.2	Conventional method of filtration	13
3.1	Flow chart for methodology process	16
3.2	Picture of '*Pusat Tenun Diraja*' Pahang	17
3.3	Aluminum Sulphate	17
3.4 (a)	Pressure Pum	18
3.4 (b)	Pressure Meter	18
3.4 (c)	Membrane Filter	18
3.5	Hybrid Coagulation UF model	20
3.6	Experimental setup flow chart	21
3.7	Jar test experiment	22
3.8 (a)	Chart for Every Factors	24
3.8 (b)	BOD test process	24
3.9 (a)	COD Reactor	25
3.9 (b)	Sample	25
3.10 (a)	Filter Flask	28
3.10 (b)	Filtered Sample	28
3.11	Sample for ADMI test	29

4.1	Turbidity versus Coagulant dose	32
4.2	COD versus Settlements	33
4.3	BOD versus settlements	34
4.4	Tss versus Settlements	35
4.5	ADMI versus Settlements	36
5.1	Quality of water after treatment	38

LIST OF ABBREVIATIONS

UF	Ultrafiltration
COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
TSS	Total Suspended Solid
ADMI	American Die Manufacturer's Institute
PT / CO	Platinum-cobalt scale
NTU	Nephelometric Turbidity Units

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The industries of textile nowadays have becoming big and their existence can give harm to the public health and environment especially the aquatic ecological system. The use of a large variety of chemical in the dyes material during manufacturing of textiles products can created pollution. This is because their discharge water released into the environment worldwide annually.The main release of pollution during manufacturing occurs during the dyeing and finishing processes and is released by the manufacturer into their local waterways. The wastewater produced is not always biodegradable and often poses severe environmental and health hazards to the community they operate within.

The combination of the processes and products make the wastewater from textile plant contains various types of pollutants. The dyeing and finishing operations are such that the dyestuffs, chemicals and textile auxiliaries used can vary from day to day and sometimes even within several times a day (Lin and Chen, 1997). It contains various waste chemical pollutants such as sizing agents, wetting agents, complexing agents, dyes, pigments, softening agents, stiffening agents, fluorocarbon, surfactants, oils, wax and many other additives which are used throughout the processes. These pollutants contributes to high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, colour, acidity, basicity and other soluble substances (Ahn*et al.,* 1999).

Price competition, demand in high quality products, new and innovative products that are highly durable put further pressure to the industry as they have to use more dosage of chemicals and continually change to new chemicals to suit the market demand. This will finally result in the complication in the wastewater that is being discharged. Stringent legislation on discharge as per the requirement of Environmental Quality Act of Malaysia and other developed countries give further challenges to the industry. Thus there is a need for continues study and research on the waste water treatment to find new methods of treatment in order to sustain this industry. (ArumaiDhas J. P., 2008)

1.2 Problem Statement

Textile processes produce multi component wastewater which can be difficult to treat (O'Neill *et al.,* 2000). This wastewater can cause serious environmental problems due to their high colour, large amount of suspended solids, and high chemical oxygen demand (Kim *et al.,* 2004). Standard discharge limits of textile effluent are becoming more stringent in recent days creating continuous problems for industries to comply with. The conventional treatment of wastewater containing dyestuffs includes biological oxidation, chemical oxidation and adsorption. Biological methods are generally cheap and simple to apply and are currently used to remove organics and colour from dyeing and textile wastewater. However this wastewater cannot be readily degraded by conventional biological processes e.g. activated sludge process because the structure of most commercial dye compounds are generally complex and many dyes are non-biodegradable due to the chemical nature and molecular size (Kim *et al.,* 2004).

At present, several methods have been developed to treat textile wastewater but they cannot be used individually because this wastewater has high salinity, colour and non-biodegradable organics. In coagulation process, large amount of sludge is created which may become a pollutant itself and increase the treatment cost. Oxidation process such as ozonation effectively decolorizes almost all dyes except disperse dyes but does not remove COD effectively (Ahn*et al.,* 1999). Electrochemical oxidation produce pollutants which increases the treatment cost (Kim *et al.*, 2003). There is no single process capable of adequate treatment mainly due to. the complex nature of these effluents. The use of combined processes has been suggested recently to overcome the disadvantage of individual unit processes (Kim *et al.,* 2003).

The use of coagulants in wastewater treatment, in spite of being efficient in the removal of most contaminants, is not able to generate water of high portability standards, which leads to the necessity of the simultaneous use of other techniques. Membrane filtration technique is already widely recognized and can be implemented in combination with coagulation processes. In this study, Ultrafiltration (UF) process is an alternative method to know the feasibility to apply for textile industries wastewater treatment. This process employs the pressure-driven force to separate the colloidal and high molecule from the liquid mainly by sieving mechanism and some possible chemical interaction with membrane surface. UF membranes are physical barriers that are able to efficiently remove suspended particles and colloids, turbidity, bacteria, algae, parasites, and viruses for clarification and disinfection purposes.

Normally, ultrafiltration process has been used for separation of proteins and preparation of ultra-pure water. This research aims to propose the optimum operating conditions on the previous treatment of textile industries wastewater in order to determine the effectiveness of ultrafiltration process as a clean technology for wastewater treatment when implemented in combination with coagulation process.

1.3 Objectives of Study

1. To characterize the PusatTenun Pahang dye wastewater.
2. To determine the effectiveness of hybrid coagulation-ultrafiltration in treating tenun dye wastewater.

3. To determine the optimum dosage of coagulant needed in tenun dye wastewater.

1.4 Scopes of Study

The case study is on the wastewater from the textile millknown as PusatTenun Pahang in Pekan, Pahang that have discharged their wastewater on the near river that contains chemical and any other particle and colloids. The productions of these tenun's product consist of desizing, scouring, bleaching, mercerization, dyeing and finishing.Thus, after characterized the wastewater sample, the effective treatment process must be applied to that wastewater to ensure that it is free from any pathogens and chemicals that pose health risk whenflow to the water intake location for water supply purposes.

1.5 Research Significance

In optimizing the performance of the combine process for the wastewater treatment, the interfacial zones between percent of coagulant added and the ultrafiltration process are a key concern. Understand the characteristic of this interfacial region as a function of material properties in thus crucial. This research is about to understanding the congeniality of the coagulation and the UF process in the wastewater treatment. Through this study, we can know the outcome of the process as applied in the treatment of Tenun dye wastewater.

1.6 Expected Outcome

The findings of this project are believed to be beneficial in the textile wastewater treatment process. Because there is many improvements can be done for the previous treatment to get a better result and also to decrease cost involved.

CHAPTER 2

LITERATURE REVIEW

2.1 WASTEWATER FROM TEXTILE INDUSTRY

Textile industry is one of the most complicated industries among manufacturing industry (Selcuk, 2005). The main sources of wastewater normally come from cleaning water, pretreatment, dyeing and finishing process water non-contact cooling water and others (Kim *et al.,* 2003). The amount of wastewater varies widely depending on the type of process operated at the mill. Various toxic chemicals such as complexing agents, sizing, wetting, softening, anti-felting and finishing agents, wetting agents, biocides, carriers, halogenated benzene, surfactants, phenols, pesticides dyes and many other additive are used in wet processing, which are mainly called washing scouring, bleaching, mercerizing, dyeing, finishing (Selcuk, 2005).

The water employed in the process eventually ends up as wastewater (Lin and Chen, 1997). Main pollutants from dyeing and finishing units include high suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, colour, acidity, basicity, and other organic pollutants (Ahn*et al.,* 1999; Karim*et al.,* 2006). Government legislation is becoming more stringent in most developed countries regarding the removal of dyes from industrial effluent. This creates problems for the textile industries to comply with. Environmental protection in Europe is promoting prevention of transferal of pollution problems from one part of the environment to another. This means that most textile industry is developing on site or in-plant facilities to treat their own effluent before discharge (Banat *et al.,* 1996).

2.2 TEXTILE WASTEWATER CHARACTERISTIC &ENVIRONMENTAL IMPACT

Composite textile wastewater is characterized mainly by measurements of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS) and dissolved solids (DS). Typical characteristics of textile industry wastewater are presented in Table below. (Al-Kdasi etal. 2005)

Table 2.1: Composite textile industry wastewater characteristics

Parameters	**Values**
pH	7.0-9.0
Biochemical Oxygen Demand (mg/L)	80 - 6,000
Chemical Oxygen Demand (mg/L)	150 - 12,000
Total Suspended Solids (mg/L)	15 - 8,000
Total Dissolved Solids (mg/L)	2,900 -3,100
Chloride (mg/L)	1,000 – 1,600
Colour (Pt-co)	50 – 2,500

Dyes and dyestuffs find use in a wide range of industries but are of primary importance to textile manufacturing. Increasingly, the environmental and subsequent health effects of dyes released in textile industry wastewater are becoming subject to scientific scrutiny. Wastewater from the textile industry is a complex mixture of many polluting substances ranging from organ chlorine-based pesticides to heavy metals associated with dyes and the dyeing process. Inefficiencies in dyeing result in large amounts of the dyestuff being directly lost to the wastewater, during textile processing, which ultimately finds its way into the environment.

Enormous volumes of effluent are generated at different stages of textile manufacturing, due to the usage of copious amounts of chemicals and dyes. Wastewaters from textile industries are a complex mixture of many polluting substances like salts, acids, heavy metals, pigments, dyes etc. Several tons of textiles required to meet up with societal demands are produced daily in this industry. Lot of effluent is derived from the textile and dyestuff activities. This can provoke serious environmental impact in the neighbouring receptor water bodies because of the presence of toxic reactive dyes and dark coloration.. Textile dyeing industries are facing problems to safe discharge of wastewater due to complex nature and hard-to-treat by conventional methods. In recent years, biological decolourization using potential microorganisms capable of decolourizing and detoxifying the synthetic dyes has been considered as a promising and eco-friendly method.

The textile industries produce effluents that contain several types of chemicals such as dispersants, acids, levelling agents, carriers, alkalis and various dyes. The textile factories daily discharge millions of litres of untreated effluents in the forms of wastewater into public drains that eventually empty into rivers. This alters the pH, increases the biochemical oxygen demand (BOD) and chemical oxygen demand (COD), and releases intense colourations in the river. The use of these water resources is limited and the ecosystem is affected. Many procedures are used in the treatment of textile effluents to achieve decolourization. These include physiochemical methods such as filtration, use of activated carbon, chemical flocculation and specific coagulation. Some of these methods are effective but quite expensive. The ubiquitous nature of bacteria makes them invaluable tools in effluent biotreatment. Biotreatment offers a cheaper and environmentally friendlier alternative for colour removal in textile effluents.

Textiles effluent contains dyestuffs, which are visible, even at low concentration (Prado *et al.,* 2004). These coloured effluents are aesthetically displeasing as colours are normally related to untreated wastewater. Dyes even in low concentration can affect the aquatic life and food web. Since many of the organic dyes are harmful to human being, the removal of colour from processes on waste effluent becomes environmentally important (Malik, 2003). The discharge of coloured wastewater is not only damaging the aesthetic nature of receiving streams but also it may be toxic to the aquatic life. In addition, colour interferes with the transmission of sunlight in a stream and therefore reduces photosynthetic action (Kadirvelu*et al.*, 2000). This disturbs the natural equilibrium by affecting the aquatic life and food chain.

2.3 TREATMENT OF TEXTILE WASTEWATER

Generally, it is rather difficult to treat textile effluent because the industry produces multi-component wastewater. The dye contained in the effluent can vary daily and even hourly. The hot and strongly coloured wastewater contains large amount of suspended solids, high chemical oxygen demand concentration and greatly fluctuating pH which can be difficult to be treated. Hundreds of small scale dyeing industries is facing closure since they are not treating their effluent as it is not economical (Rao and Rao, 2006).

Textile wastewater includes a large variety of dyes andchemical additions that make the environmental challengefor textile industry not only as liquid waste but also in its chemical composition. Main pollution in textile wastewater comes from dyeingandfinishing processes. These processes require the input of a wide range ofchemicals and dyestuffs, which generally are organic compounds of complex structure. Water is used as the principal medium to apply dyes and various chemicals for finishes. Because all of them are not contained in the final product,became waste and caused disposal problems. Major pollutants in textile wastewaters are high suspendedsolids, chemical oxygen demand, heat, colour, acidity, and other soluble substances. Substances which need to be removed from textilewastewater are mainly COD, BOD, nitrogen, heavy metalsand dyestuffs (Tripathi V., 2013).

2.4 REQUIREMENT OF WASTEWATER TREATMENT

When dealing with wastewater treatment, there are several requirements of effluent standards for industrial wastes that need to be followed. This requirement somehow depends on each country.

In Malaysia, the discharge standard is stipulated in the Third Schedule Environmental Quality Act, 1974. Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979 is shown in Table 1 (Appendix A). After every effort of reduce waste strength and volume by conservation and good housekeeping there are still problems of disposing the effluent without affecting the receiving stream. Governmental agencies, non-governmental agencies and also the public are becoming more and more concern over environmental issues. There are many ways for treating the textile effluent. The best combination of methods differs from plant to plant depending on the size, type of waste and degree of treatment needed.

2.5 HYBRID COAGULATION ULTRAFILTRATION IN GENERAL

The hybrid method involving the addition of a coagulant (aluminium sulphate or ferric chloride) prior to the ultrafiltration or microfiltration process can increase the removal of natural and anthropogenic organic substances, also the disinfection of by-products. Such an approach can also contribute to a better yield of the membranes, both polymer and ceramic ones but the permeate flux during UF is most favourable when the coagulation conditions bring about the formation of floccules of the zeta potential close to zero.

2.5.1 Process Description

Coagulants with charges opposite those of the suspended solids are added to the water to neutralize the negative charges on dispersed non-settable solids such as clay and colour-producing organic substances. Once the charge is neutralized, the small suspended particles are capable of sticking together. The slightly larger particles formed through this process and called microflocs, are not visible to the naked eye. The water surrounding the newly formed microflocs should be clear. If it is not, all the particles' charges have not been neutralized, and coagulation has not been carried to completion. More coagulant may need to be added.

A high-energy, rapid-mix to properly disperse the coagulant and promote particle collisions is needed to achieve good coagulation. Over-mixing does not affect coagulation, but insufficient mixing will leave this step incomplete. Coagulants should be added where sufficient mixing will occur. Proper contact time in the rapid-mix chamber is typically 1 to 3 minutes.

Meanwhile, the ultrafiltration is a separation process using membranes with pore sizes in the range of 0.1 to 0.001 micron. Typically, ultrafiltration will remove high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules. Low molecular-weight organics and ions such as sodium, calcium, magnesium chloride, and sulphate are not removed. Because only high-molecular weight species are removed, the osmotic pressure differential across the membrane surface is negligible. Low applied pressures are therefore sufficient to achieve high flux rates from an ultrafiltration membrane. Flux of a membrane is defined as the amount of permeate produced per unit area of membrane surface per unit time. Generally flux is expressed as gallons per square foot per day (GFD) or as cubic meters per square meters per day.

Ultrafiltration, like reverse osmosis, is a cross-flow separation process. Here liquid stream to be treated (feed) flows tangentially along the membrane surface, thereby producing two streams. The stream of liquid that comes through the membrane is called permeate. The type and amount of species left in the permeate will depend on the characteristics of the membrane, the operating conditions, and the quality of feed. The other liquid stream is called concentrate and gets progressively concentrated in those species removed by the membrane. In cross-flow separation, therefore, the membrane itself does not act as a collector of ions, molecules, or colloids but merely as a barrier to these species.

2.5.2 Fouling and Chemical Cleaning

Fouling and subsequent chemical cleaning of nanofiltration (NF) membranes used in water quality control applications are often inevitable. To unravel the mechanisms of organic fouling and chemical cleaning, it is critical to understand the foulant-membrane, foulant-foulant, and foulant-cleaning agent interactions at the molecular level.

Membranefouling is determined by the coupled influenceof physical and chemical interactions. These interactionsand the resulting properties of the fouling layer arecontrolled by the foulant characteristics, feedwater solutionchemistry (pH, ionic strength, divalent cation concentration),membrane properties (surface charge, hydrophobicity, roughness),and hydrodynamic conditions (permeate flux, cross flow velocity). The physicochemical characteristics of thefoulant, such as charge and molecular conformation, directlycontrol the rate of foulant accumulation and the propertiesof the fouling layer and, therefore, have significant impactonmembranepermeate flux

Despite the vast efforts to reduce membrane fouling, for instance, by improving membrane properties, optimizing operational conditions and pretreatment of feedwater, fouling is still inevitable. Indeed, several pretreatment processes designed to solve specific fouling problems may lead to other problems. As a result, chemical cleaning is a necessary process to ensure sustainable operation of membrane systems. Membrane cleaning is often applied when a significant decrease in permeate flux or salt rejection is observed or when the transmembrane pressure has to be raised significantly to maintain the designed water flux.

For chemical cleaning of fouled membranes, five categories of cleaning agents are commonly used: alkalines, acids, metal chelating agents, surfactants, and enzymes. Commercial cleaning products are usually mixtures of these compounds, but the actual composition is often unknown. Consequently, all chemical cleaning studies conducted so far were not able to provide useful information to elucidate the mechanisms of chemical cleaning. Chemical cleaning of fouled membranes is realized through chemical reactions between the chemical agents and the foulants. A cleaning agent cleans the membrane by removing the foulants, changing the morphology of the foulants, or altering the surface chemistry of the fouling layer. Consequently, proper selection of chemical cleaning agents relies on our mechanistic understanding of the foulants particularly the chemical reactions between the foulant and the cleaning chemicals. To date, mechanistic studies on chemical cleaning of polymeric membranes are rather scarce. Most reported work utilized commercial membrane cleaning products, and the cleaning procedures followed were specified by the membrane manufacturers. The effectiveness of chemical cleaning was found to depend on various factors, including temperature, pH, concentration of the cleaning chemicals, contact time with the cleaning solution, and operating conditions, such as cross flow velocity and pressure.

However, the test conditions used in these studies were very specific in terms of raw water quality, membrane properties, and operating conditions. The results obtained from such studies often disagree and are therefore not applicable for other situations. This further points out to the need for more controlled and fundamental studies on chemical cleaning of NF (and other) membranes. (Li Q. &Elimelech M., 2004)

2.6 COAGULATION

The coagulation treatment influenced by raw water characteristic, temperature, pH, coagulant typeand dose, and also rapid mix intensity and the duration. Most of the work in this field was concerned with water turbidity removal by coagulation to obtain drinkable water, (Amirtharajah and Mills, 1982) and (Johnson and Amirtharajah, 1983) published design and operation diagrams for aluminium and iron coagulation which suggested the correct dose and pH for optimal coagulation.

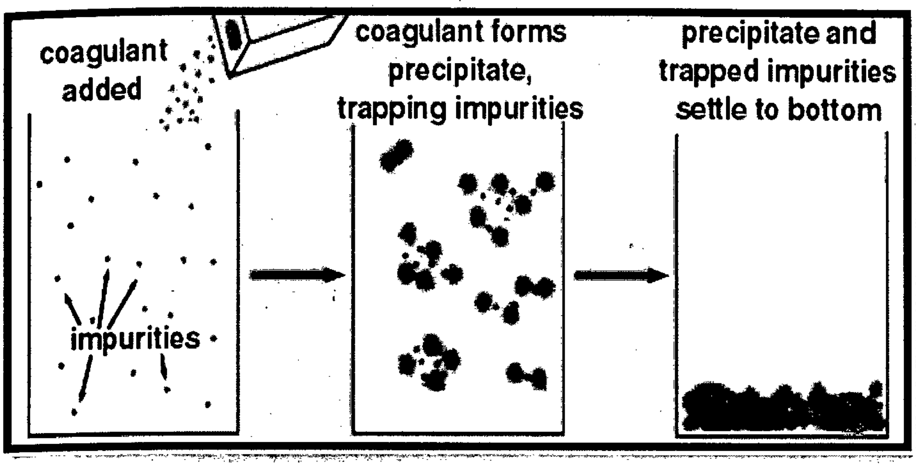

Figure 2.1: Coagulation process (source: water.me.eccs.edu)

Coagulation is a chemical (e.g alum or iron salts) used to form a floc; used in the clarification of turbid or coloured water, as an aid in removing particles is suspended or colloidal form. These particles do not settle out on standing and cannot be remove by conventional physical treatment process.

2.7 ULTRAFILTRATION VS CONVENTIONAL METHOD

Ultrafiltration, like reverse osmosis, is a cross-flow separation process. Here liquid stream to be treated (feed) flows tangentially along the membrane surface, thereby producing two streams. The stream of liquid that comes through the membrane is called permeate. The type and amount of species left in the permeate will depend on the characteristic of the membrane, the operating conditions, and the quality of feed. The other liquid stream is called concentrate and gets progressively concentrated in those species remove by the membrane. In cross-flow separation, therefore, the membrane itself does not act as a collector of ions, molecules, or colloids but merely as a barrier to these species.

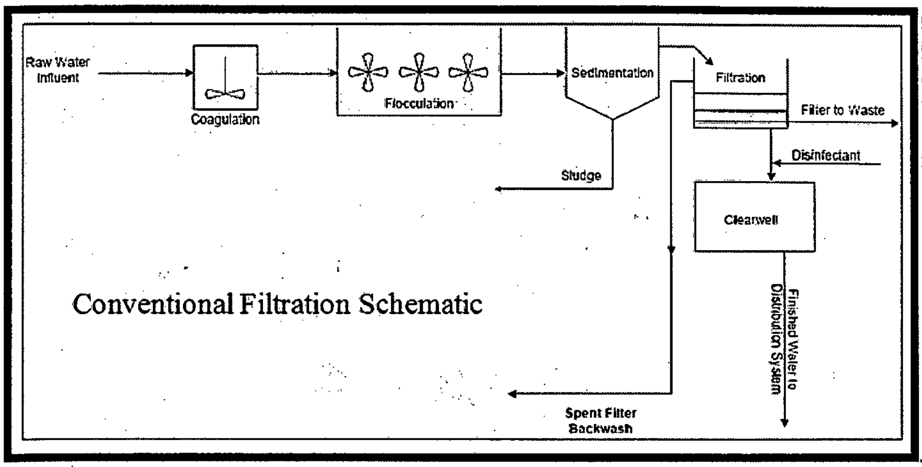

Figure 2.2: Conventional method of filtration (source: public.health.oregon.gov)

Conventional filters such as media filters or cartridge filters, on the other hand, only remove suspended solids by trapping these in the pores of the filter-media. These filters therefore act as depositories of suspended solids and have to be cleaned or replaced frequently. Conventional filters are used upstream from the membrane system to remove relatively large suspended solids and to let the membrane do the job of removing fine particles and dissolved solids. In ultrafiltration, for many applications, no pre-filters are used and ultrafiltration modules concentrate all of the suspended and emulsified materials.