TREATABILITY STUDIES ON THE WASTEWATER FROM A DYE MANUFACTURING INDUSTRY

by

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Abstract

This study aimed to investigate the treatability options for wastewater generated from a dye manufacturing industry in Thailand. The industry generated wastewater ranging between 600 – 650 m^3/day. The wastewater characteristics was analyzed and compared with the Thailand Industrial effluent standards to determine the efficiency of the present treatment plant. The effluent characteristics were found to exceed the standard limits. In order to meet the standards, treatability study on the wastewater was performed to identify appropriate options to reduce the pollution. Options such as pretreatment through coagulation and membrane filtration were carried with the wastewater. Chemical coagulants such as Polyaluminium Chloride (PACl), Ferric Chloride ($FeCl_3$), and Ciba X-COL 7105 and Fenton's reagent method were investigated. Out of all the options for pretreatment, Fenton's method and Ciba X-COL 7105 was found to be highly effective in color removal of about 97% and Fenton's method was effective in COD removal. However, both of options are not economically viable. Therefore, the option with combination of 6000 ppm of $FeCl_3$ and 1000 ppm of Ciba X-COL 7105 was found to be effective with a removal efficiency of 87% color and 58% COD respectively and cost effective. On other hand, the volume of sludge produced from this option was high and possessed poor sludge volume index (SVI) necessitating coagulant aid to enhance settling. In the case of membrane filtration using, cross flow nanofiltration (NF) membrane and ultrafiltration (UF), NF was found to be efficient in the removal of color and heavy metals and less effective in the removal of TDS and COD. Thus, indicating need for further investigation on the permeate for TDS and COD. From the above study, modification of the existing treatment plant is proposed initiating with segregation of wastewater into low concentration high volume wastewater and high concentration low volume wastewater which can be diverted to the pretreatment unit following membrane filtration unit and sludge treatment.

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List of Abbreviations

ADMI	American Dye Manufactures Institute
AOX	Halogenated Organic Compounds
As	Arsenic
Ba	Barium
BOD	Biochemical Oxygen Demand
CA	Cellulose acetate, most often di- or tri- acetate
Ca	Calcium
Cd	Cadmium
cm	centimeter
Co	Cobalt
Cr	Chromium
CI	The Color Index
Cu	Copper
COD	Chemical Oxygen Demand
CP	Cleaner Production
DCOD	Dissolved Chemical Oxygen Demand
EA	Environmental Assessment
EMAS	Eco-Management and Audit Scheme (EU programme)
Fe	Iron
g	Gram
h	hour
HCl	Hydrogen Chloride
HCN	Hydrogen Cyanide (prussic acid, hydrocyanic acid)
Hg	Mercury
HMWC	High Molecular Weight Component such as a protein molecule
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen Sulfide
ISO	International Organization for Standardization
kg	Kilogram
L	Liter
Li	Lithium
LMWC	Low Molecular Weight Component such as NaCl
M	Molar
MF	Microfiltration
min.	Minute
MIGA	Multilateral Investment Guarantee Agency
Mg	Magnesium
mg	Miligram
mL	Mililiter
Mn	Manganese
Mo	Molybdenum
mS	miliSiemens
MSRL	Mild Steel Rubber Lined
MSRLTL	Mild Steel Rubber Lined Tile Lined
N/A	Not applicable
$NaBH_4$	Sodium tetrahydridobrate
NaOH	Sodium Hydroxide
NF	Nanofiltration

Ni	Nickel
NO_x	Oxides of Nitrogen
$OH^\bullet$	Hydroxyl Radical
P	Phosphorus
PAC	Powder Activated Carbon
PACl	Polyaluminium Chloride
Pb	Lead
PES	Polyethersulfone
PP	Polypropylene
ppm	part per million
PSO	Polysulfone (either polyethersulfone or polyarylethersulfone)
PVA	Polyvinyl Acetate
PVDF	Polyvinylidenendifluoride
PWA	Provincial Waterworks Authority
RO	Reverse Osmosis
rpm	round per minute
SBH	Sodium Borohydride
Se	Selenium
SME	Small and Medium-sized Enterprise
SO_x	Oxides of Sulfur
Sr	Strontium
SVI	Sludge Volume Index
TCOD	Total Chemical Oxygen Demand
TDS	Total Dissolved Solid
TKN	Total Kjedahl Nitrogen
TOC	Total Organic Carbon
TSS	Total Suspended Solid
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
VOCs	Volatile Organic Compounds
WW	Wastewater
Zn	Zinc

Chapter 1

Introduction

1.1 Background of the study

Dyes stuff are produced over 700,000 tons annually estimated from more than 100,000 commercially available dyes (Lee et al., 2006) and applied in many different industries, including the textiles, paper, cosmetic, leather, food and pharmaceutical industries. Dyes are soluble at some stage of the application process, whereas pigments in general retain essentially their particulate or crystalline form during application. A dye is used to impart color to materials of which it becomes an integral part. There are numerous types of dyes, which can be classified as acetate rayon dyes, acid dyes, azoic dyes, basic dyes, direct dyes, mordant or chrome dyes, lake or pigment dyes, sulfur or sulfide dyes and vat dyes. Mostly, correlation of chemical structure with color has been accomplished in the synthesis of dye using a chromogen–chromophore with auxochrome. Chromogen is the aromatic structure containing benzene, naphthalene, or anthracene rings. A chromophore group is a color giver and is represented by the following radicals, which form a basis for the chemical classification of dyes when coupled with the chromogen: azo (-N=N-); carbonyl (=C=O); carbon (=C=C=); carbon-nitrogen (>C=NH or -CH=N-); nitroso (-NO or N-OH); nitro (-NO_2 or =NO-OH); and sulfur (>C=S, and other carbon-sulfur groups). The chromogen–chromophore structure is often not sufficient to impart solubility and cause adherence of dye to fiber. The auxochrome or bonding affinity groups are amine, hydroxyl, carboxyl, and sulfonic radicals or their derivatives (MIGA, 2006).

Dyes are complex compounds with a big complicated molecular structure and toxic properties. Thus, it can affect aquatics life, human health and ecological system when dye wastewaters are extremely discharged wastewater into water sources. It eventually makes changes of ecological system and other serious pollution problems.

1.2 Statement of the Problem

Dye manufacturing processes generated high amount of wastewater and liquid effluents from cleaning equipment after each batch operation. Dye wastewaters can contain toxic organic residues with the major compounds of phenol derivatives, aniline derivatives, organic acid and benzene derivatives. The wastewater characteristics in dye–house can be highly variable from day to day and hour to hour depending on the type and color of dye (Kim et al., 2005). Their disposal is always a matter of great concern since they are considered as a quite dangerous source of environmental pollution. Despite, it is not only produce wastewater, air pollutions such as volatile organic compounds (VOCs), nitrogen oxides (NO_x), hydrogen chloride (HCl), and sulfur oxides (SO_x) are generated during dyes production process. Moreover, solid wastes are concerns that include filtration sludge, effluent treatment sludge, and container residue in dye manufacturing industry (MIGA, 2006).

Most of reactive dyes are toxic to some organisms and may cause direct destruction of aquatic life due to the presence of aromatic and metal chlorides. Moreover, colorant may interfere with light penetration and oxygen in water bodies. The dyes comprise likewise an aesthetic problem and color restricts which lead to conflict between upstream discharger and downstream user water. Methods for treating dye wastewaters consist of physical (carbon adsorption), chemical (chemical oxidation, coagulation and precipitation, electrochemical oxidation, Ozonation, and others), biological (aerobic and anaerobic biological processes), and advance treatment processes (membrane technology). Nevertheless, it is very difficult task for treating dye wastewater due to their high solubility, and complex molecular structure. However, each treatment processes has it's own limitation.

Although, many industries have traditionally treated the waste before discharging them to the environment this concept is called end–of–pipe. These include recycling off–site (i.e. within the different production sites), and dilution to reduce toxicity, etc., that have proven to be high costly and ultimately unsustainable (Abou-Elela et al., 2006; Cagno et al., 2005). Cleaner production is one option that provides an integrated approach both economic and environmental improvement. Furthermore, it deals with improving health, safety, outcome of process and the eco–efficiency of production systems. The term of cleaner production varies from the perspective in which it is used namely: Firstly for production processes, cleaner production includes conserving raw material and serving energy. Secondly, for products, its means reducing their environmental impacts during the entire life cycle from raw material extraction to disposal. Finally, for service, it is means incorporating environment concerns during designing and transporting services.

This study attempted to solve practical pollution problems of a dye manufacturing industry by using the concept of cleaner production (CP) focused on the production process. It includes identification of waste generation source, minimization waste and wastewater generation, and reduction the quantity of water consumption. In addition, it will able to utilize profits from successful pollution prevention.

1.3 Objectives of the study

The objectives of the study were:

- To evaluate wastewater quality by conducting physical and chemical analysis and assess the efficiency of existing treatment plant
- To identify possible in–plant modifications to conserve water and minimize the release of polluting substances in the wastewater
- To identify and recommend appropriate treatment based on the effluent quality standards as laid down by the Ministry of Industry, Thailand

1.4 Scope of the study

This study was focused on production process and wastewater treatment as mentioned below:

- An existing situation of dye stuff plant at Samut Prakan province
- Analyze the production process, water consumption and characteristic of wastewater generated at the Plant
- Suggest option for reducing water consumption and wastewater generation by laboratory–scale treatability studies was conducted to find out the method for improving original wastewater treatment processes of this Plant
- Technical and financial analysis for implementation of the proposed solutions.

Chapter 2

Literature Review

2.1 General information of synthetic dyes

The beginning of synthetic dyes, Mauveine was discovered by the Englishman, William Henry Perkin in 1856, by chance. Hence the dyestuffs industry can rightly be described as mature. Currently, all the dyes were discovered in the 1800s (Hunger, 2003).

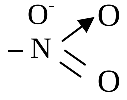
A dye or dyestuff is a colored compound that can be applied on a substrate. With few exceptions, all synthetic dyes are aromatic organic compounds. A substrate is the material to which a colorant is applied by one of the various processes of dyeing, printing, surface coating, and so on. Generally, the substrate includes textile fibers, polymers, foodstuffs, oils, leather, and many other similar materials (Rangnekar and Singh, 1980).

Not all colored compounds are dyestuffs because a colored compound may not have suitable application on a substrate. For example, a chemical such as copper sulphate, which is colored, finds no application on any substrate. If it is applied on a substrate, it will not have retaining power on the substrate and for this reason copper sulphate cannot be termed as a dye. On the other hand, congo red, a typical organic colored compound. When it applied to cotton under suitable conditions can be retained on this natural fibre and due to this finds useful application on this fibre. It is termed as a dyestuff (Rangnekar and Singh, 1980).

2.1.1 Chemistry of dyes

Chromophores and auxochromes are major component element of dye molecule. Dyes contain an unsaturated group basic responsible for color and designated it as chromophore (*"chroma"* means color and *"phore"* means bearer). Auxochromes (*"Auxo"* means augment) are the characteristic groups which intensify color and/or improve the dye affinity to substrate (Rangnekar and Singh, 1980).

Table 2.1 Chromophores structure

Structure	Linkage	Name
Chromophores	$-N=N-$	Azo
	$>C=S$	Thio
	$-N=O$	Nitroso
	$-N=\underset{O^-}{\underset{\vert}{N^+}}-$	Azoxy
	 $-N\begin{array}{l}\nearrow O \\ \diagdown\!\!\diagdown\, O\end{array}$	Nitro
	$-CH=N-$	Azomethine
	$>C=O$	Carbonyl
	$>C=C<$	Ethenyl

Source**:** Rangnekar and Singh (1980).

Table 2.2 Auxochromes structure

Structure	Group	Name
Chromophores	$–NH_2$ $–NHCH_3$ $–N(CH_3)_2$ $–SO_3H$ –OH –COOH –Cl $–CH_3$ $–OCH_3$ –CN $–COCH_3$ $–CONH_2$	Amino Methyl amino Dimethyl amino Sulphonic acid Hydroxy Carboxylic acid Chloro Methyl Methoxy Cyano Acetyl Amido

Source**:** Rangnekar and Singh (1980).

2.1.2 Classification systems for dyes

Hunger (2003) mentioned, dyes are classified in two methods. First of all, is the classification according to the chemical structure of dyes particularly considering the chromophoric structure presents in the dye molecule and the second classification is based on their usage or applying.

1) Classification of dyes by usage or application method

The classification of dyes by usage or application is the most important system adopted by the Color Index (CI), is summarized in Table 2.3 and 2.4

- ***Reactive dyes.*** These dyes form a covalent chemical bond with fiber is ether or ester linkage under suitable conditions. The major chemical classes of reactive dyes are azo that including metallized azo, triphendioxazine, phthalocyanine, formazan, and anthraquinone. These chemical classes are used for dyeing and printing of cotton, wool, etc. The molecules structures of reactive dyes have much simpler than direct dyes and the dyeing are brighter.

- ***Disperse dyes.*** These are substantially water–insoluble nonionic dyes for application to hydrophobic fibers from microfine aqueous dispersion. They are used predominantly on polyester, polyamide, polyacrylonitrile, polypropylene fibers and a lesser on nylon, cellulose acetate, and acrylic fibers. Chemical classes of dyes mainly belong to azo and anthraquinonoid involving low molecular weight of structure and containing group which aid in forming stable aqueous dispersions.

- ***Direct dyes.*** These are water–soluble anionic dyes when dyed from aqueous solution in the presence of electrolytes, which are substantive to have high affinity for cellulose fibers. They are applied on cotton, cellulose, paper, leather, and nylon. Most of the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines, and oxazines. Commonly, chelations with salts of metals such as copper and chromium are applied to the dye material for improving wash fastness properties. Also, their treatment with formaldehyde or a cationic dye–complexing resin.

- ***Vat dyes.*** These are insoluble in water that can apply mainly to cellulose fiber by converting them to their leuco compounds by reduction and solubilization with sodium hydrosulphite and sodium hydroxide solution that is call as vatting process. The main chemical classes of vat dyes are anthraquinone and indigoid.

- ***Sulfur dyes.*** They are insoluble in water and are applied to cotton in the form of sodium salts by the reduction with sodium sulphide as reducing agent under alkaline conditions. The low cost and good wash fastness properties of the dyeing that cause important for an economic standpoint. However, they are under pressure from an environmental. Point of view, they are exposure to air to get the original dye after dyeing.

- ***Cationic (Basic dyes).*** These dyes are cationic dyes and water–soluble. They are applied on paper, polyacrylonitrile, modified nylons, and modified polyesters. In addition, they are used to apply with silk, wool, and tannin–mordant cotton when brightness shade was more necessary than fastness to light and washing. Mostly, the chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine, and acridine.

- ***Acid dyes.*** They are water–soluble anionic dyes that their can apply on nylon, wool, silk, and modified acrylics. Moreover, they are used to as dyeing for paper, leather, ink–jet printing, food, and cosmetics

- ***Solvent dyes.*** They are water–insoluble but solvent–soluble dyes are deficient polar solubility group for example sulfonic acid, carboxylic acid or quaternary ammonium. They are used for coloring plastics, gasoline, oils, and waxes. Azo and anthraquinone have predominantly to formation solvent dyes. In addition, phthalocyanine and triarylmethane dyes are used.

- ***Mordant dyes.*** These dyes have mordent dyeing property by good quality of the presence certain groupings in the dye molecule which are capable to hold metal residuals by formation of covalent and coordinate bonds involving a chelate compound. The salts of aluminium, chromium, copper, cobalt, nickel, iron, and tin are used as mordant that their metallic salts.

Aside from mentioned above, there are azoic dyes, ingrain dyes, pigment, and others which are any type of dyes also (Hunger, 2003; Rangnekar and Singh, 1980; Shenai, 1977)

Table 2.3 Usage classification of dyes

Class	Typical applied	Method of application	Chemical type	Characteristics
Acid	nylon, wool, silk, paper ink, and leather	usually from neutral to acidic dye–baths	Azo (including premetallized), anthraquinone, azine, triphenylmethane, xanthene, nitro and nitroso	- Anionic compounds; - Highly water soluble and; - Poor wet fastness.
Azoic and components (ingrain)	cotton, rayon, cellulose acetate, and polyester	fiber impregnated with coupling component and treated with a solution of stabilized diazonium salt	azo	- Contain azo group (and formic acid, caustic soda, Metallic compounds, and sodium nitrate)
Basic	leather, wool, silk paper, modified nylon, polyacrylonitrile, polyester, and inks	applied from acidic dye–baths	cyanine, azo, azine, hemicyanine, diazahemicyanine, triarylmethane, xanthen, acridine, oxazine, and anthraquinone	- Cationic; - Highly water soluble
Direct	cotton, paper, rayon, leather, and nylon	applied from neutral or slightly alkaline baths containing additional electrolyte	azo, phthalocyanine, stilbene, nitro, and benzodifuranone	- Anionic compounds; - Highly water soluble and; - Poor wet fastness.
Disperse	polyester, polyamide, acetate, acrylic, and plastics	fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermo fixed	azo, anthraquinone, styryl, nitro, and benzodifuranone	- Colloidal dispersion; - Very low water solubility and; - Good wet fastness
Mordant	wool, leather, and anodized aluminium	applied in conjunction with chromium salts	azo and anthraquinone	- Anionic compounds; - Water soluble and; - Good wet fastness
Reactive	cotton, wool, silk, and, nylon	reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and alkaline condition	azo, anthraquinone, phthalocyanine, formazan, oxazine, and basic	- Anionic compounds; - Highly water soluble and; - Good wet fastness.

Sources**:** Hunger (2003); Rangnekar and Singh (1980); Shenai (1977).

Table 2.4 Usage classification of dyes (con't)

Class	Typical applied	Method of application	Chemical type	Characteristics
Solvent	plastics, gasoline, varnishes, lacquers, stains inks, fats, oils, and waxes	dissolution in the appropriate solvent or medium	phthalocyanine, azo, anthraquinone and triphenylmethnae	- Water–insoluble
Sulfur	cotton and rayon	dissolved in water (with the addition of sodium sulfide for the in soluble types); exhausted with Glauber's salts	indeterminate structures	- Colloidal after reaction in fibre; - Water–insoluble and; - Wet fast
Vat	cotton, rayon, and wool	water–soluble dyes solubilization by reducing with sodium hydrogen sulfite, then exhausted on fiber and reoxidized	anthraquinone (including polycyclic quinones) and indigoids	- Water–insoluble and; - More chemically complex
Fluorescent brighteners (white dyes)	soaps and detergents, all fibers, oils, paints, and plastics	from aqueous solution, dispersion or by incorporation in a mass	stilbene, pyrazoles, coumarin, and dibenzothiophenes	- absorb ultraviolet light; - visible light and; - brighten
Food, drug, and cosmetic	Foods, drugs, and cosmetics		azo, anthraquinone, carotenoid and triarylmethane	
Oxidation bases	hair, fur, and cotton	aromatic amines and phenols oxidized on the substrate	aniline black and indeterminate structures	- like azoic dyes

Sources**:** Hunger (2003); Rangnekar and Singh (1980); Shenai (1977).

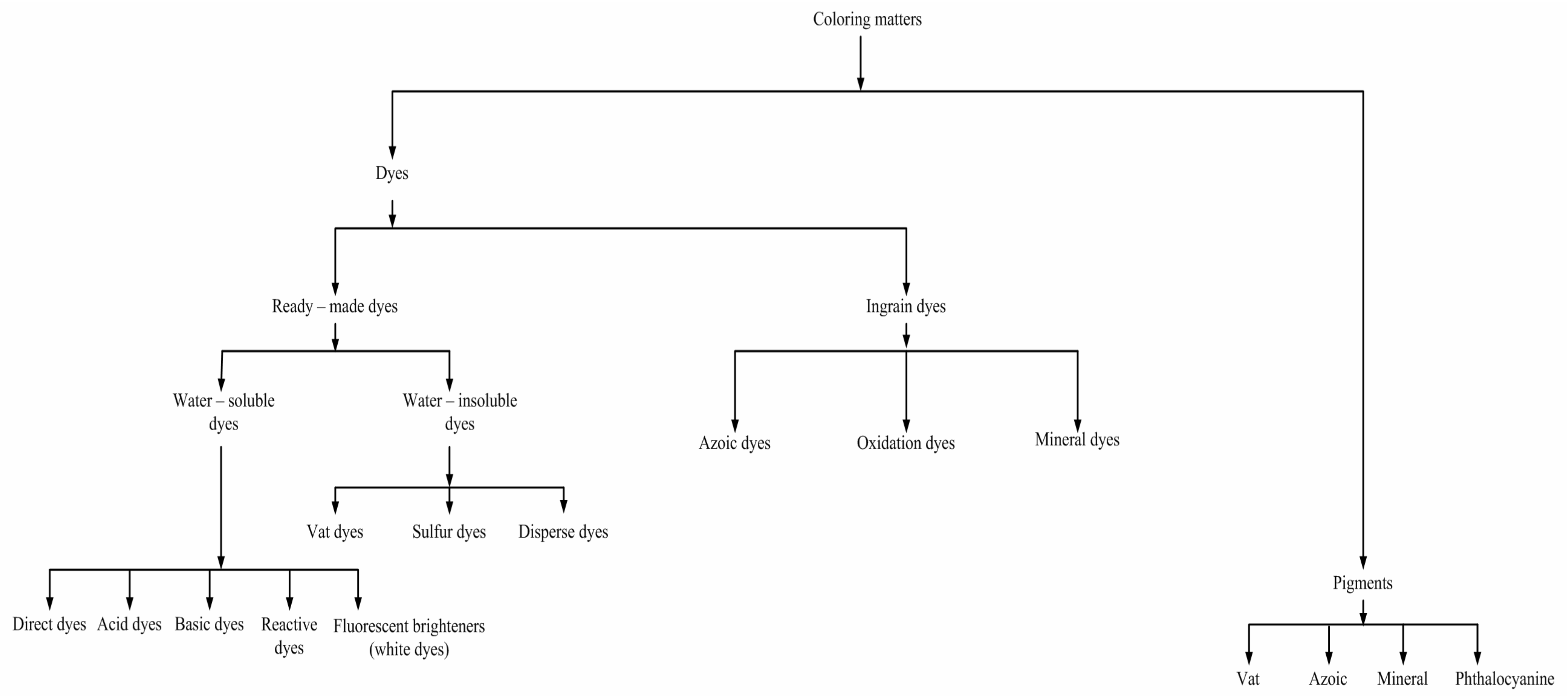


Figure 2.1 Dyes classification for application (Shenai, 1977)**.**

2.1.3 Production process of dyes manufacturing industry

- **Basic steps of synthetic dyes**

Traditional, the basic steps of dye manufacturing industry are shown in Figure 2.2. Normally, there are several reaction steps or unit processes consist of synthesize, filtered, dryed and blended with other additives. At the synthesis step, involves reactions such as sulfonation, halogenation, amination, diazotization, and coupling, followed by separation processes that include distillation, precipitation, and crystallization. In general, organic compounds such as naphthalene are reacted with an acid or an alkali along with an intermediate (namely: a nitrating or a sulfonating compound) and solvent to form a dye mixture and purified. To success the dye manufacturing, finishing operations such as drying, grinding, and standardization are performed. They are important for maintenance consistent product quality (MIGA, 2006). In addition, salt (NaCl), small molecular weight intermediates and residual compounds are produced from the synthesis process which must be removed before the dyes are dried for sale as powder because they reduce purity of the dyes (Kim et al., 2005). Dye is precipitated from an aqueous solution using salt. The slurry is passed through a fliter press. The filter retains the dye then the filtrate contains salt. After that, small molecular–weight residual products from chemical reactions are disposed. The retained dye is collected in trays and dried in ovens. Afterward, dried dye is grinded and blended become powder dyes. The final stage is brought for packaging process to sale further. However, Yu et al. (2001) reported the purity of the final dye product from the conventional process is low because it remains salt content around 30%.

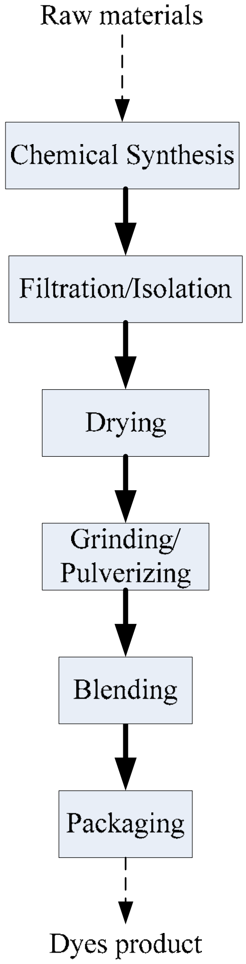
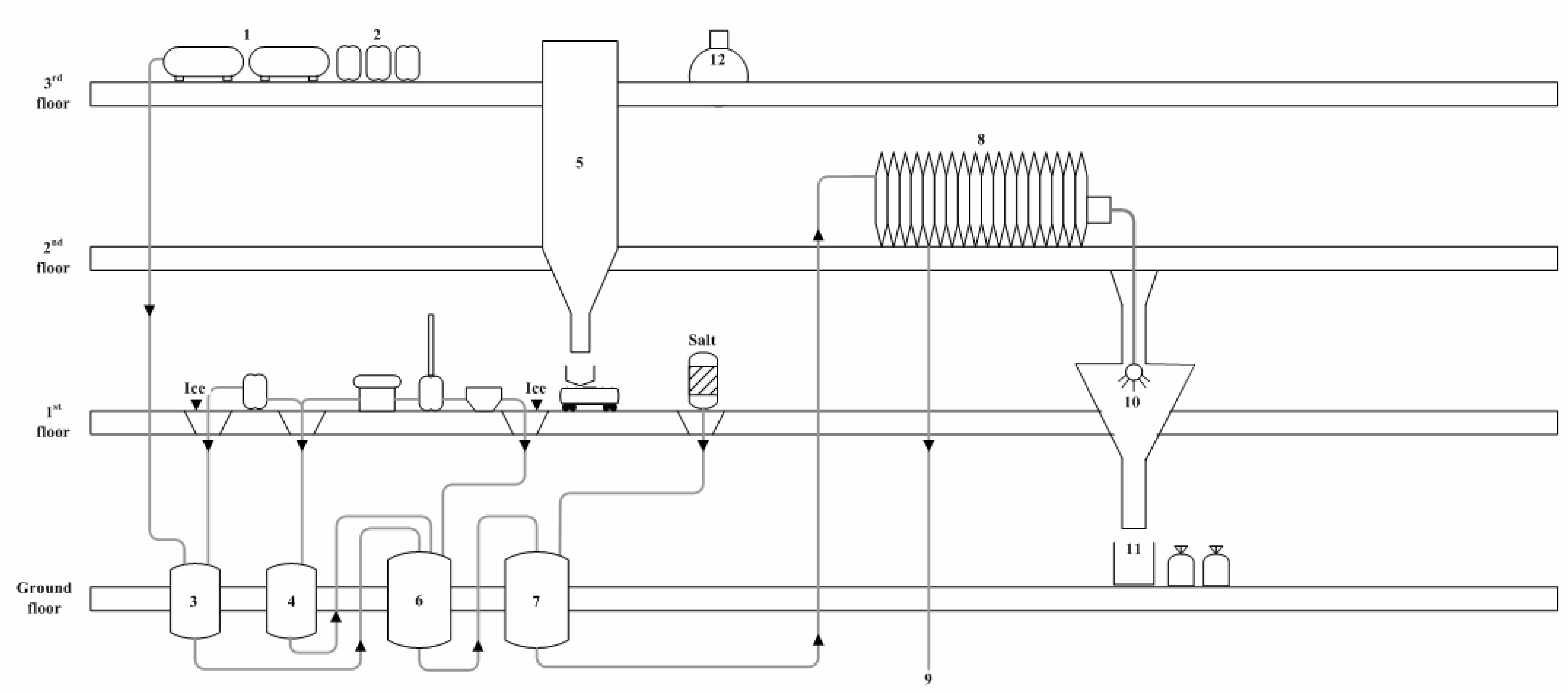


Figure 2.2 Operation sequence in dye manufacture



1 = Storage tanks for liquid starting materials
2 = Storage drums for solid starting materials
3 = Diazotization vessel
4 = Coupling component vessel
5 = Ice machine
6 = Coupling vessel

7 = Isolation vessel
8 = Filter presses
9 = Filtrate to waste liquor treatment plant
10 = Spray dryers
11 = Emptying of dyes for feeding to the mill
12 = Exhaustion air to purification Plant

Figure 2.3 Layout of azo dye manufacturing industry (Hunger, 2003).

The batch processes for the production of dyes are accomplished in the reaction vessels made from cast iron, stainless, or steel lined with rubber, glass, brick, or carbon blocks. These vessels have capacities around 2 – 40 m^3 (500 – 10000 gallons) and there are agitators, thermometers or temperature recorders, condensers, pH probe, and others depending on the type of the operation in each Plant. Normally, the reaction vessels cover two or more floors in a Plant to facilitate of operation. For example, raw materials are transferred by gravity flow, pumping or blowing with air or inert gas. In another word, process operators and instruments are required in a typical dye manufacturing industry as shown in figure 2.3.

2.2 Assessment waste of the dye production process (USEPA, 1991).

1) Raw material receiving and charging/Material transfer

A major source of waste is generated from transferring of raw material or shipping container to the production equipment that wastes are empty containers and vapors or dust during material transportation.

2) Synthesis

Dye synthesis is a critical step in process because it is the primary operation that determines the volume and type of chemicals used in the process and chemical characteristics of the effluent.

3) Isolation/Filtration

Normally, it can be excessive the source of wastewater generation, lost product, and spent processing aids. Various pollution prevention opportunities have been identified that will reduce operation costs associated with isolation and filtration will minimize the volume of waste generated from the process.

4) Drying

Drying wet filter consumed more energy for operating. This section should optimize dryer operation. Optimization of drying conditions will reduce energy consumption, save operational costs and help reaching pollution prevention goal.

5) Grinding

Pollution prevention in the area of grinding has been identified in four major areas. There are waste material (products, raw materials and byproducts), wastewater, air emission, and energy.

6) Blending

Mostly, blending operations generated large quantities of waste consisting of spilled material, dust collector waste, packaging material, and material containers.

7) Packaging

Large amount of the solid waste disposed at landfill that industries should identify way to use less packaging and to substitute material that cannot be recycled with recyclable material.

2.3 Sources of waste and its characteristic

2.3.1 Air pollutants

Mostly, in dye manufacturing emitted volatile organic compounds (VOCs), nitrogen oxides (NO_x), hydrogen chloride (HCl), and sulfur oxides (SO_x) (MIGA, 2006). Moreover, air pollution caused by emission of particulate for example dust during material transport grinding material or result from open dumping while dry material such as spray dryer.

2.3.2 Liquid waste

The main liquid effluents generated from equipment washing after batch operation. Mostly, wastewaters from dye manufacturing are highly variable in composition that wastewater contain a large number of different compounds such as raw materials (e.g. anilines, solutes, etc.), intermediate products, and even the dyes themselves. They are considered as a more dangerous source of environmental problem. High chemical oxygen demands (COD), biochemical oxygen demands (BOD), suspended solids and intense color due to dye intermediates or residues and auxiliary chemicals are normal their wastewaters characterize from the dye production process. Kornaros and Lyberatos (2006) presented wastewater characteristics in Table 2.5. They conducted by grabbing two samples of mixed wastewater was taken at two different operation periods of the dye manufacturing industry.

Table 2.5 Characteristics of wastewater

Parameter	Unit	Sample 1	Sample 2	Average sample
TCOD	mg/L	10970	16430	13320
DCOD	mg/L	7410	13580	11830
BOD_5	mg/L	660	570	610
TSS	mg/L	749	3243	2000
pH	-	4.40	1.71	2.22
Total unfiltered P	mg/L	15.4	78.7	46.8
Total filtered P	mg/L	12.6	79.4	46.1
TKN	mg/L	N/A	N/A	68.5
Fe	mg/L	2.94	9.93	N/A
Mn	mg/L	0.23	0.52	N/A
Cu	mg/L	0.34	1.17	N/A
Pb	mg/L	0.80	1.23	N/A
Zn	mg/L	4.57	20.83	N/A
Cr	mg/L	0.15	0.30	N/A

Note: TCOD = Total Chemical Oxygen Demand TSS = Total Suspended Solid
DCOD = Dissolved Chemical Oxygen Demand

Source: Kornaros and Lyberatos (2006).

Dye manufacturing industry consumed high amount of water for cleaning equipments, cooling tower; boiler and raw material that causes high amount of wastewater generation. From studying of development alternative technologies for pollution control in vinyl sulphone industry by Central Pollution Control Board (CPCB) in association with National Chemical Laboratory (NCL) was found approximately water consumption per ton of vinyl sulphone production is given in Table 2.6.

Table 2.6 Water consumption per ton of vinyl sulphone producing

Sources	Quantity (kg/ton)
Wash water	5,070
Production process ice	12,500
Make up water in utilities steam, Cooling tower water, chilled water	1,600
Process water (Raw material)	2,434
Total	21,604

Source: CPCB (2007).

2.3.3 Solid waste

Major solid wastes such as sludges that are generated from effluent treatment process and container residues. In conventional wastewater effluent treatment process produced sludge after sludge is treated, it becomes sludge cake that is mainly contained gypsum. Some industries will sell it to cement manufacturers or disposed at landfill.

2.4 Emission guidelines by Multilateral Investment Guarantee Agency (MIGA)

2.4.1 Liquid effluents

The following effluent levels should be achieved as Table 2.7:

Table 2.7 Effluents level discharging of dye manufacturing industry

Parameter	Unit	Maximum value
pH	-	6 – 9
BOD_5	mg/L	30
COD	mg/L	150
TSS	mg/L	50
Oil and grease	mg/L	10
Phenol	mg/L	0.5
Chromium (hexavalent)	mg/L	0.1
Copper	mg/L	0.5
Zinc	mg/L	2
Halogenated Organic Compounds (AOX)	mg/L	1
Color	hazen	400
Toxic organics such as benzidine etc.	mg/L	0.05

Source: MIGA (2006); CPCB (2006).

2.4.2 Air emissions

Emission level from dye manufacturing the maximum value should be achieve as Chlorine (or Chloride) equal 10 mg/Nm^3 and VOCs is 20 mg/Nm^3.

2.5 Industrial effluent quality standards in Thailand

Table 2.8 Industrial effluent standards in Thailand

Parameter	Unit	Standard value	Method for examination
pH	-	5.5 – 9.0	Using pH meter
TDS	mg/L	≤ 3,000 or 5,000*	Dried at 103 -105 °C, 1 hours
TSS	mg/L	≤ 50 or 150*	Filtering pass thought Glass Fiber Filter Disc
Temperature	°C	≤ 40	Using temperature meter measure at sampling point immediately
Color and odor	-	Not objectionable	Not specified
Sulfide as H_2S	mg/L	≤ 1.0	Titrate
Cyanide as HCN	mg/L	≤ 0.2	Distillation and follow by Pyridine Barbituric Acid method
Fat, oil and Grease	mg/L	≤ 5.0 or 15*	Extraction with solvent
Formaldehyde	mg/L	≤ 1.0	Spectrophotometry
Phenols	mg/L	≤ 1.0	Distillation and follow by 4 – Aminoantipyrine method
Free Chlorine	mg/L	≤ 1.0	Iodometric Method
Pesticide	mg/L	non detected	Gas–Chromatography
BOD_5	mg/L	≤ 20 or 60*	Azide Modification incubate at 20 °C, 5 day
TKN	mg/L	≤ 100 or 200*	Kjeldahl
COD	mg/L	≤ 120 or 400*	Potassium Dichromate Digestion
Zn	mg/L	≤ 5.0	Atomic Absorption Spectro Photometry: Direct Aspiration or Plasma Emission Spectroscopy: Inductively Coupled Plasma (ICP)
Hexavalent Chromium	mg/L	≤ 0.25	
Trivalent Chromium	mg/L	≤ 0.75	
Cu	mg/L	≤ 2.0	
Cd	mg/L	≤ 0.03	
Pb	mg/L	≤ 0.2	
Ba	mg/L	≤ 1.0	
Ni	mg/L	≤ 1.0	
Mn	mg/L	≤ 5.0	
As	mg/L	≤ 0.25	Atomic Absorption Spectrophotometry: Hydride Generation or Plasma Emission Spectroscopy: Inductively Coupled Plasma (ICP)
Se	mg/L	≤ 0.02	
Hg	mg/L	≤ 0.005	Atomic Absorption Cold Vapor Technique

Source**:** PCD (2004).* Depending on receiving water or type of industry under consideration of PCC

2.6 Wastewater treatment methods

Variation of component in dyes wastewater is high, contains a large number of different compounds arise from raw material (Sarasa et al., 1998). The compound structure of dyes can be complex and influence to degradability. Several methods have been studied for treating dye wastewater. However, these effluent treatments have different advantages and disadvantages as shown in Table 2.9.

Table 2.9 Summary the advantages and disadvantages of methods for treating dye wastewater

Method	Advantages	Disadvantages
Activated carbon adsorption	- Suspended solids and organic substances well reduced.	- Blocking filter
Coagulation–Flocculation	- Effective for all dyes - Elimination of insoluble–water dyes	- High cost - High sludge production
Advanced chemical oxidation	- Non–hazardous end products	- High cost
Electrochemical oxidation	- Removes small colloidal particles - Low sludge production - Breakdown compounds are non–hazardous - No chemicals use	- High cost - Iron hydroxide sludge - Not effective for all dyes
Photo–oxidation	- No sludge production	- Releases aromatic amines
Ozonation	- No sludge production - No alteration of volume	- High cost - Short half life
Supported liquid membrane	- Minimal loss of extractants - Simple to operate - Low energy consumption - Easy to scale up - Low cost	- Emulsification may occurs
Liquid – liquid extraction	- Low cost - Low energy consumption - Variety of solvents available - Easy to scale up	- Emulsification may occur - Effluent must be treated
Biological process	- Environmentally friendly - Rates of elimination by oxidizable substances about 90% - Economically attractive	- Low biodegradability of dyes - Needs adequate nutrients - Narrow operating temperature range - Cost
Nanofiltration	- Removes all dye types - High effluent quality - Easy to scale up	- High investment costs membrane fouling - Influent must be pre-treated
Reverse osmosis	- Removal of all mineral salts, hydrolyzes reactive dyes and chemical auxiliaries	- High pressure
Ultrafiltration–Microfiltration	- Low pressure	- Insufficiency quality of treated wastewater

Source: Mahmoud et al. (2007); Allegre et al. (2006)

2.6.1. Carbon adsorption of dyes

Adsorption is an effective method for reducing the concentration of dissolved organics in an effluent. For instance, bentonite, powder activated carbon and granule activated carbon that their capability adsorption is different due to their properties. Reife and Freeman (1996) referred, activated carbon has been evaluated extensively for the waste treatment of the different classes of dyes such as acid, disperse, direct, basic, reactive and others. The most widely adsorbent is used for treating dyes wastewater. The feasibility of adsorption on carbon for the removal of dissolve organic pollutants has been demonstrated by adsorption isotherms. Carbon adsorption isotherms are generated by conducting a fixed quality of dye wastewater with different amounts of activated carbon for fixing length of time in order to remove impurities. Temperature and polar of dyes have an influence adsorption onto carbon. Therefore, adsorption on activated carbon without pretreatment is impossible for dye removal, combination of physical and chemical or biological treatments are recommended. However, carbon adsorption of dyes is neither very efficient nor economical.

Lee et al. (2006) investigated the efficiency of combined processes of adsorption and coagulation of complete removal dyes. They found that coagulation followed by adsorption was more efficient than having adsorption before coagulation. In additional, combined coagulation–adsorption process has the capability of complete dye removal and due to decolorization, reduction in coagulation and adsorption amounts. Due to this the amount of sludge is less produce.

2.6.2 Chemical coagulation

Coagulation is employed for the removal of pollutants in suspended or colloidal form. Various chemicals was used to eliminate compounds present in wastewater from dye manufacturing industry such as alum, lime, ferric sulfate, ferric chloride, Polyaluminium chloride(PACl), polymer, etc. Chemicals used for coagulation in water or wastewater treatment not only should be cost effective for coagulating impurities but should not leave toxic or other undesirable residues in the water. The chemical coagulant application is presented in Table 2.10 and 2.11.

Table 2.10 Chemical coagulant applications

Chemical	pH	Comments
Alum	4.5 – 7.0	For colloid coagulation and phosphate removal Basic reactions: $Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4$
Lime	9.0 – 11.0	For colloid coagulation and phosphate removal Basic reactions: $Ca(OH)_2 + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + 2H_2O$ $MgCO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCO_3$
$FeCl_3$, $FeCl_2$	4.0 – 7.0	For colloid coagulation and phosphate removal Basic reactions: $FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$
$FeSO_4$	4.0 – 7.0	For colloid coagulation and phosphate removal Basic reactions: $FeSO_4 + 3H_2O \longrightarrow Fe(OH)_3 + 3HSO_4$

Source: Eckenfelder (2000).

Table 2.11 Chemical coagulant applications (con't)

Chemical	pH	Comments
Cationic polymer	No change	For colloid coagulation or to aid coagulation with a metal
Anionic and Some nonionic polymers	No change	Use as a flocculation aid to speed flocculation and settling

Source: Eckenfelder (2000).

1) Mechanism of coagulation

Coagulation arises from two basic mechanism: perikinetic (or electrokinetic) coagulation, in which the zeta potential is reduced by ions or colloids of opposite charge to a level below the van–der–waals attractive forces, and orthokinetic coagulation, in which the micelles aggregate and form clumps that agglomerate the colloidal particles. There are a number of successive or simultaneous stages involved in the agglomeration of particle as presented in the Table 2.12.

In addition high-valence of cations depresses the particle charge and the effective distance of the double layer, thereby reducing the zeta potential. As the coagulant dissolves, the cations serve to neutralize the negative charge on the colloid. This occurs before noticeable floc formation, and rapid mixing which "coats" the colloid is effective in this stage. Micro–flocs are then formed which retain a positive charge in the acid range because of the adsorption of H^+. These micro–flocs also serve to neutralize and coat the colloidal particle. Flocculation agglomerates the colloids with a hydrous oxide (OH^-) floc. In this stage, surface adsorption is also active. Colloids not initially adsorbed are removed by enmeshment in the floc. The mechanism of the coagulation process is shown in Figure 2.4 (Eckenfelder, 2000).

Table 2.12 Stage of agglomeration

Stage	Factor	Term
Addition of coagulant	➢ Reaction with water, ionization, hydrolysis, polymerization	Hydrolysis
Destabilization	➢ Double layer compression ➢ Specific absorption of ions from the coagulant on the surface of the particle ➢ Specific linkage between ions or species on the surface of the particle ➢ Inclusion of the colloid in a hydroxide precipitate ➢ Interpaticular linkage by polymeric species of coagulant	Coagulation
Transport	➢ Brownian movement	Preikinetic flocculation
	➢ Dissipated energy (velocity gradient)	Orthokinetic flocculation

Source: Degremont (1991).

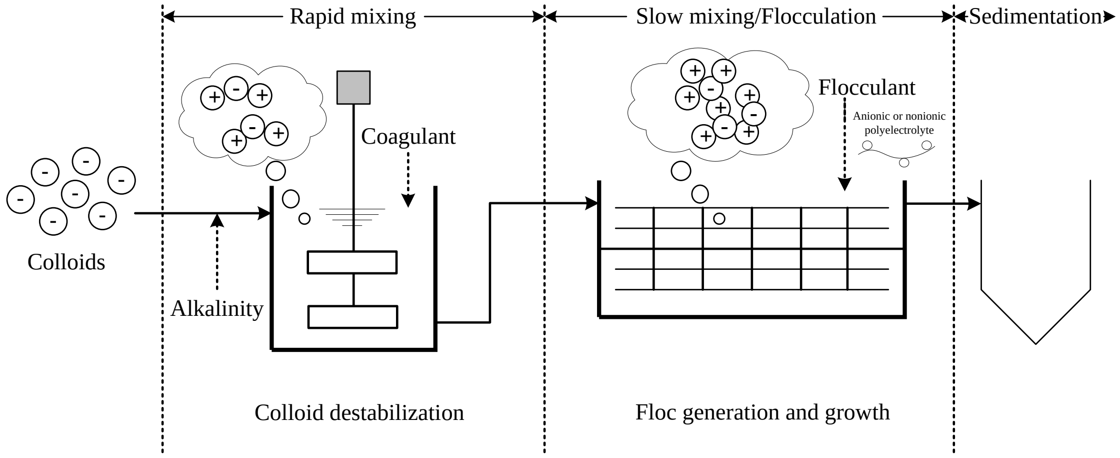


Figure 2.4 Mechanisms of coagulation

2) Sodium Borohydride dye reduction in wastewater

Sodium Borohydride is strong water–soluble reducing reagents commercially available. They can remove the dissolved various metal cations for example Cu^{2+}, Ni^{2+}, Pb^{4+}, Hg^{2+}, and Ag^{2+} contained in wastewater (Reife and Freeman, 1996). However, Sodium borohydride has not widely used in dye wastewater decolorization because it is rapid reacts with water at pH less than 8. Thus, bisulfite is added into borohydride to improve efficiency of decolorization (Reife and Freeman, 1996).

Prachumyat (2002) research was conducted, by using a stable aqueous solution of sodium-borohydride (SBH) containing 1.2 % $NaBH_4$ and 4 % NaOH to remove colors from reactive dye wastewater. It was found that suitable conditions for wastewater treatment are at pH 10 and 7 times the chemical dosage. The effective of color removal was found to be 94.08%, 93.85%, and 99.03% for C.I. Reactive Black 5, C.I. Reactive Red 180 and C.I. Reactive blue 171 respectively at 200 mg/L their concentration. Conversely, the efficiency dye removal of C.I. Reactive red 180 is lower than sodium hydrosulphite for all concentrations.

2.6.3 Fenton's method

Fenton's method consists of ferrous salts combined with hydrogen peroxide (H_2O_2) under acidic condition that is used to treat a variety of industrial wastewaters containing toxic and non–biodegradable organic compounds. Especially, complex wastes derived from dyes, phenols, formaldehyde, plastic additives, and rubber chemicals. The reaction of Fenton's reagent as showed in Figure 2.5 (Martinez et al., 2003). At the beginning of reaction, hydroxyl radicals and $Fe^{3+}$are produced, and then Fe^{3+} will react with H_2O_2 and hydroperoxyl radical, which leads to regenerating $Fe^{2+}$of the so–called Fenton–like reaction. Thus, Fe^{2+} reacted with organic radical intermediates that will able to degrade organic pollutants in wastewater. The advantages of Fenton's reagent are COD and BOD reduction, color removal, organic pollutants destruction, biodegradability improvement, and toxicity reduction. A widely application this method for wastewater treatment with many industries such as textile, pharmaceutical, pulp and paper manufacturing, and others. In generally, these industries contain high COD value and low BOD value, which it is impossible to achieve for treatment wastewater by biological process (Szpyrkowicz et al., 2001).

Reaction 1 $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^{\bullet}$

Reaction 2 $Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^+$

Reaction 3 $Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + O_2 + H^+$

Reaction 4 $Fe^{3+} + R^{\bullet} \longrightarrow Fe^{2+} + R^+$

Figure 2.5 Fenton's reagent reaction

2.6.4 Ozonation

The reaction of dyes with ozone is important from the viewpoint of ozone fading colorants in dye wastewater treatment. Although, the structures of dyes are very complicate, ozone can be attack dye molecule. Normally, using ozone alone is not always accompanied by reduction of the COD. Thus, Oguz and Keskinler (2007) investigated combination with other treatments such as HCO^{3-}, H_2O_2 or PAC. Moreover, Sarasa et al. (1998) determined, efficiency of treatment wastewater from azo dyes manufacturing by combination ozone and chemical coagulation that calcium hydroxide was used coagulant. The results are COD, total organic carbon (TOC) and color reduced 50%, 42%, and 62% respectively.

2.6.5 Membrane Technology

From reviewing the articles found membrane technology is used by many process in industries for product purification and wastewater treatment to reduce water usage by recycling wastewater is treated into the Plant. The membrane made from a long chain organic molecule, called a polymer. This polymer must be hydrophilic. Membrane can be helpful in areas such as color removal, BOD reduction, salt reduction, polyvinyl acetate (PVA) recovery, and latex recovery (Naveed and Bhatti, 2006). The four common types of membrane namely: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The principle for the different separation systems depends on the pore size of the membrane and the size of the particle that is to be separated. The membrane classification based on size and molecular weight of particles that can be penetrated as shown in Figure 2.6 and 2.7. In addition, the membrane characteristics are presented in Table 2.13.

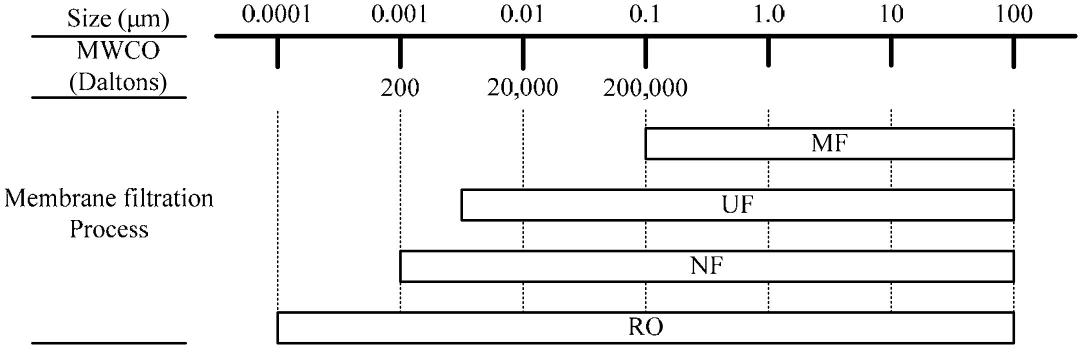


Figure 2.6 Membrane filtration application guide (USEPA, 2005)

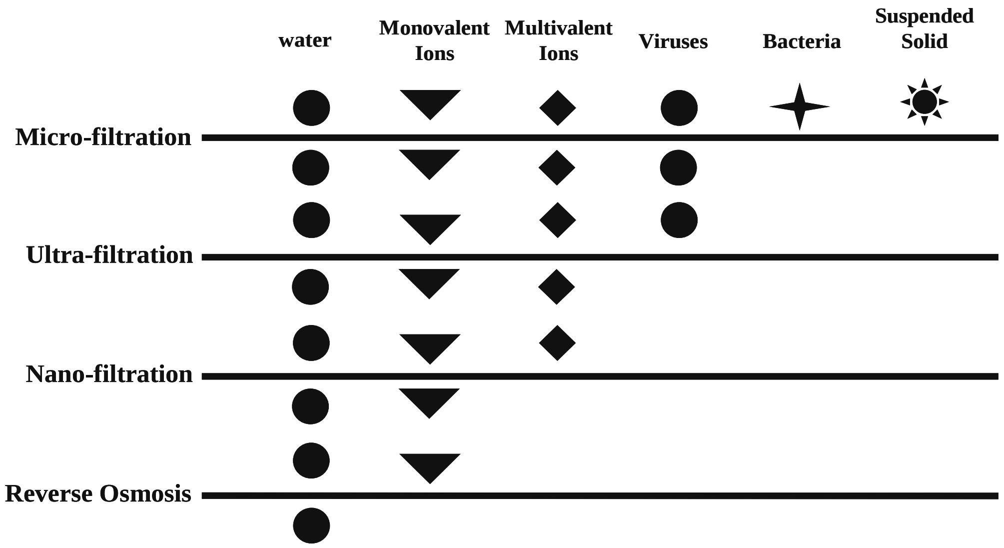


Figure 2.7 Separation scheme for different membrane systems
(Koch Membrane System, 2006)

Table 2.13 Membranes characteristics

Properties	Membrane process			
	Reverse Osmosis (RO)	**Nanofiltration (NF)**	**Ultrafiltration (UF)**	**Microfiltration (MF)**
Membrane	Asymmetrical	Asymmetrical	Asymmetrical	Symmetrical, Asymmetrical
Thickness	150 μm	150 μm	150 – 250 μm	10 – 150 μm
Pore size	< 0.002 μm	< 0.002 μm	0.2 – 0.02 μm	4 – 0.02 μm
Rejection of	HMWC, LMWC Sodium chloride glucose Amino acids	HMWC mono-, di- and oligosaccharides polyvalent ions	Macro molecules, proteins, polysaccharides, virus	Particles, Clay, Bacteria
Membrane material	CA, Thin film	CA, Thin film	Ceramic, PSO, PVDF, CA, Thin film	Ceramic, PP, PSO, PVDF
Membrane module	Tubular, Spiral wound, Plate–and–Frame	Tubular, Spiral wound, Plate–and–Frame	Tubular, Spiral wound, Plate–and–Frame, Hollow fiber	Tubular, Hollow fiber
Pressure	15 – 150 bar	5 – 35 bar	1 – 10 bar	< 2 bar

Source: Wagner (2001).

Yu et al. (2001) achieved, using the NF technology for the desalting and concentrating of aqueous dye. This membrane system produced dye solution having more than 25% dye and less than 1% salt content. A spray dryer continuously dried the aqueous dye desalted and concentrated by NF. Therefore, the NF membrane process followed by spray drying provided a continuous process, operating automatically and producing dye of high purity and consistency.

Kim et al. (2005) reported, the nanofiltration and reverse osmosis membrane combined in process of reactive dye production was found to be suitable for the removal of residual organics, color, salt and the water recycling from waste stream arising from reactive dye manufacturing process. This combination can remove COD and color more than 98.4% and 99.6% respectively and permeate can recycle into the production process that offers economical benefits by reducing the water consumption and wastewater treatment cost. Moreover, the type of membrane and dye solution had a significant effect on both permeate flux and rejection efficiencies. Also, variation of pressure affected the COD, color and salt rejections that increased with increasing pressure.

2.6.5.1 Membrane configuration

Membrane configurations used in waste treatment including spiral elements, hollow fiber cartridges, and tubular modules as showed in Table 2.14. Normally, selection membranes depend on the type of waste stream, final concentration factor or yield, and final concentrate solid. On the other hand, its comparative cost where pretreatment requirements, capital and operating costs are taken into consideration (Brady, 2006).

Table 2.14 Feature and application of different membrane configurations

Membrane configurations	Feature of membrane configurations	Application
Hollow fiber cartridges	Thin channel membrane	Potable water processing, Cooling tower
Spiral elements	Flat sheet that is rolled around a central permeate collection tube	Food, dairy and seawater desalination to wastewater treatment
Tubular modules	Open channel membrane	Suitable process stream which have very high solid levels

Source: Brady (2006).

2.6.5.2 Factors of supporting membrane system for waste treatment

The major factors of supporting membrane system for waste treatment include:

- Lower operating costs
- A positive barrier between the waste concentrate and the discharged permeate
- Simple operation
- Reduced labor for waste treatment
- Reliability
- Consistent and high quality effluent
- Minimal chemical treatment

2.7 Cleaner production (CP)

Cleaner production is a general term that describes a preventative approach to industrial activities. The concept is straightforward to minimize waste and emissions at their sources instead of treat them after these have generated or it is the continuous application of an integrated preventive environmental strategy applied to processes, products and service to increase eco–efficiency and reduce human risks, cost for production and the environment. In spite of cleaner production, conceptual simplicity for it has become recognized in practice as a valuable approach for achieving of environmental improvement and industrial development (Pagan et al, 2006).

2.7.1 Cleaner production hierarchy

The Cleaner production hierarchy is a good tool to assist cleaner production option in an operation and to focus on eliminating or reducing waste at source as presented in Figure 2.8. In adopting a cleaner production philosophy, try to consider how wastes were created rather than how they can be treated. Typically, strategies higher up the hierarchy are more cost effective (Pagan et al, 2006).

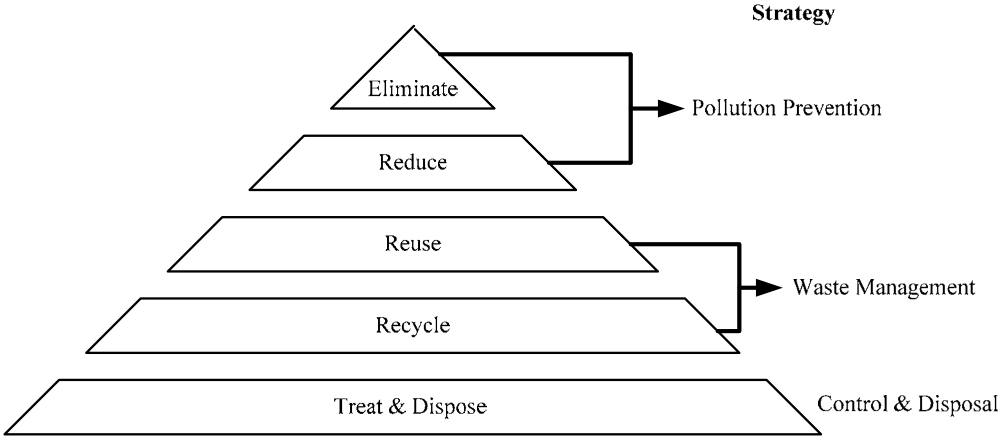


Figure 2.8 Integrated approach of cleaner production (Pagan et al, 2006).

The cleaner production is considered in numerous elements namely as showed in Figure 2.9:

- Raw material substitution
  By reducing and eliminating hazardous materials that enter the production process. For instance, Vigneswaran et al. (1999) mention in textiles industries can be reduced phosphate–containing chemicals. In painting of electrical light components, which powder paints can be used instead of organic solvent based on paints.

- Changing technology
  These consist of changes in the production process, equipment, layout or piping changes and changing process condition such as flow rates, temperature, pressures and residence times (USEPA, 1996). Applying new technologies can reduce resource consumption and minimize waste generation throughout improved operation efficiencies. However, these options are highly capital cost, but payback periods may be quite short.

- Good housekeeping
  Good housekeeping in an industry implies that the management and employees of the company are diligent in ensuring that they comply with all environmental regulations and looking for ways in which the waste they generate and the resources they use are kept to a minimum. Housekeeping practices can lead to significant waste minimization.

- Changing product
  Changing products, which can perform by product substitution such as in case of batteries from non–rechargeable becomes rechargeable, spray can also change to water–soluble formulation instead of using volatile chemicals, and others. (Vigneswaran et al., 1999)

- On-site reuse
  It is recycling or reuses a waste material each of originating process that is substituted input material or another process within the same production site

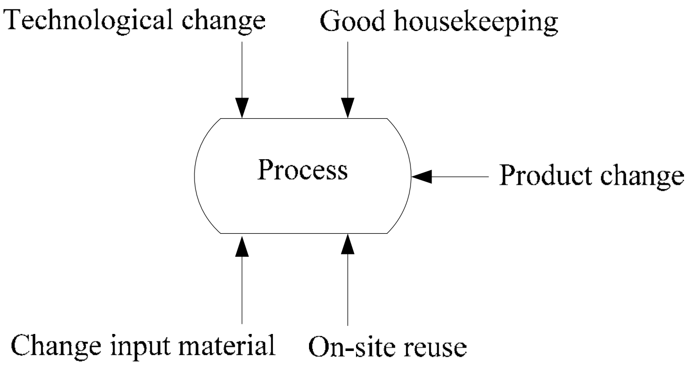


Figure 2.9 Process elements for cleaner production (UNEP, 1996)

2.7.2 Present situation of cleaner production (CP) in Thailand

The Cleaner Technology Information Center (CTIC) was established in 1997 at the Thailand Environment Institute to promote CP. The cleaner production movement in Thailand is at a critical turning point, as one of national agenda for sustainable development. At this point, ongoing field level cleaner production activities such as capacity building, training, awareness, and cleaner production audits; and a national level muti–stakeholder effort is being initialed to institutionalize the cleaner production through national polices and plans. Therefore, there is a rapid develop the cleaner production from industrial sector to other sectors such as service sector namely: hospital, schools, agriculture, tourism, finance, academic, and research and development (ICETT, 1998).

2.8 Waste audit

A waste audit (or waste assessment) is the systematic gathering of information and a through consider of the waste from industries and unit operation to determine options for reducing or eliminating waste by following process as Figure 2.10 (UNEP, 1996). The audit is the most probably important particular item in the accomplishment of a pollution prevention program. It allows the identification and quantification of individual waste streams and allows the identification of practices, procedures, and processes that lead to waste generation. A waste audit is essential initial points for identifying areas where waste can be reduce into an existing Plant's process or equipment. The information collected in the waste audit can be used to select and evaluate appropriate waste reduction and management techniques (USEPA, 1996). In order to go further, it is often helpful conceptually divide the process into several essential elements as shown in Figure 2.10**.**

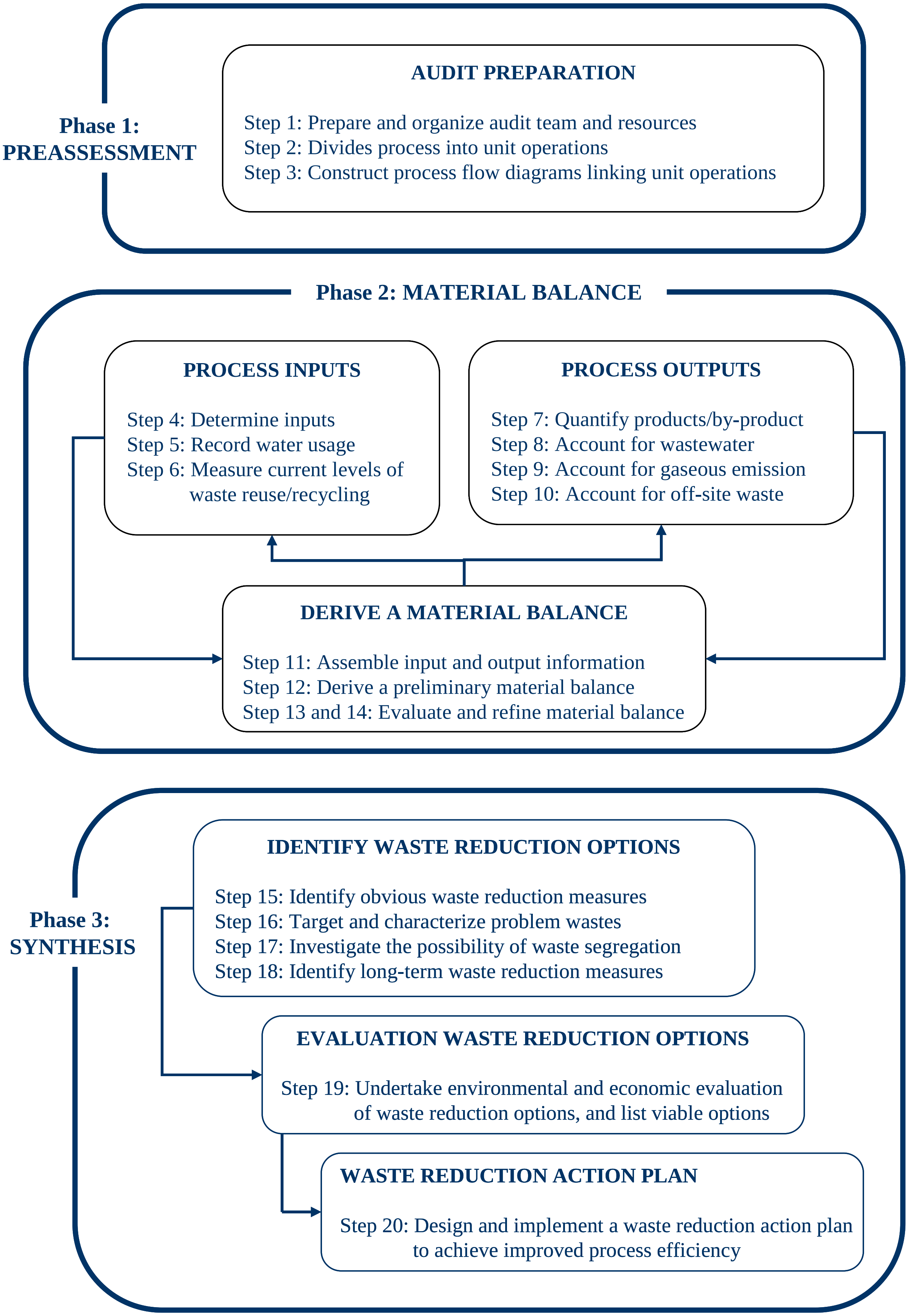


Figure 2.10 Waste audit procedures (UNEP, 1996).

2.9 Eco–mapping

Engel (2002) reported, Eco–mapping is a creative tool that helps companies to implement environmental management, ISO 14001 and EMAS. This visual and practical tool helps SME managers and employees to analyze and manage the environmental performance of small companies.

The aim of eco–mapping is to provide small companies and organization with a free, visual, simple and practical tool to analyze and manage their environmental behavior. It consists of making a map to create a perceptive environment situation of an organization's current. However, eco-mapping is not a goal in itself, but a process framework that helps to describe and priorities environmental problems and issues to act upon.

2.9.1 Functions of eco–mapping

- An inventory of environmental practices and problems;
- A systematic method of conducting an on–site environmental analysis and audit;
- A tool that allows employee involvement and participation;
- A support for training and awareness, and to assist with internal and external communication;
- An easy way to document and track environmental improvements and;
- A catalogue of immediate small positive actions.

2.9.1 Benefits of eco–mapping

- Eco-mapping allows an organization to easily visualize the origins of environmental impacts at its premises.
- The tool is free and can be used economically.
- It can be used to encourage all employees to participate in embedding environmental changes and thinking across the organization's personnel and on–site activities. Anyone in the organization can use this tool to support their work and training.
- Raises awareness, by providing an easy visual symbol for understanding of the seriousness and geographical impact of environmental behavior and management.
- Provides a systematic review for wide ranging environmental issues.
- It can be used regularly to motivate continuous improvement.
- It can provide a method for communicating environmental assurance to stakeholders.
- Eco–mapping can provide depending on which to seek other environmental standards such as ISO 14000 and the Eco–Management Audit Scheme (EMAS) regulation or other environmental management system.

Chapter 3

Methodology

3.1 Introduction

The overall work approach is summarized in Figure 3.1 in order to achieve the objectives.

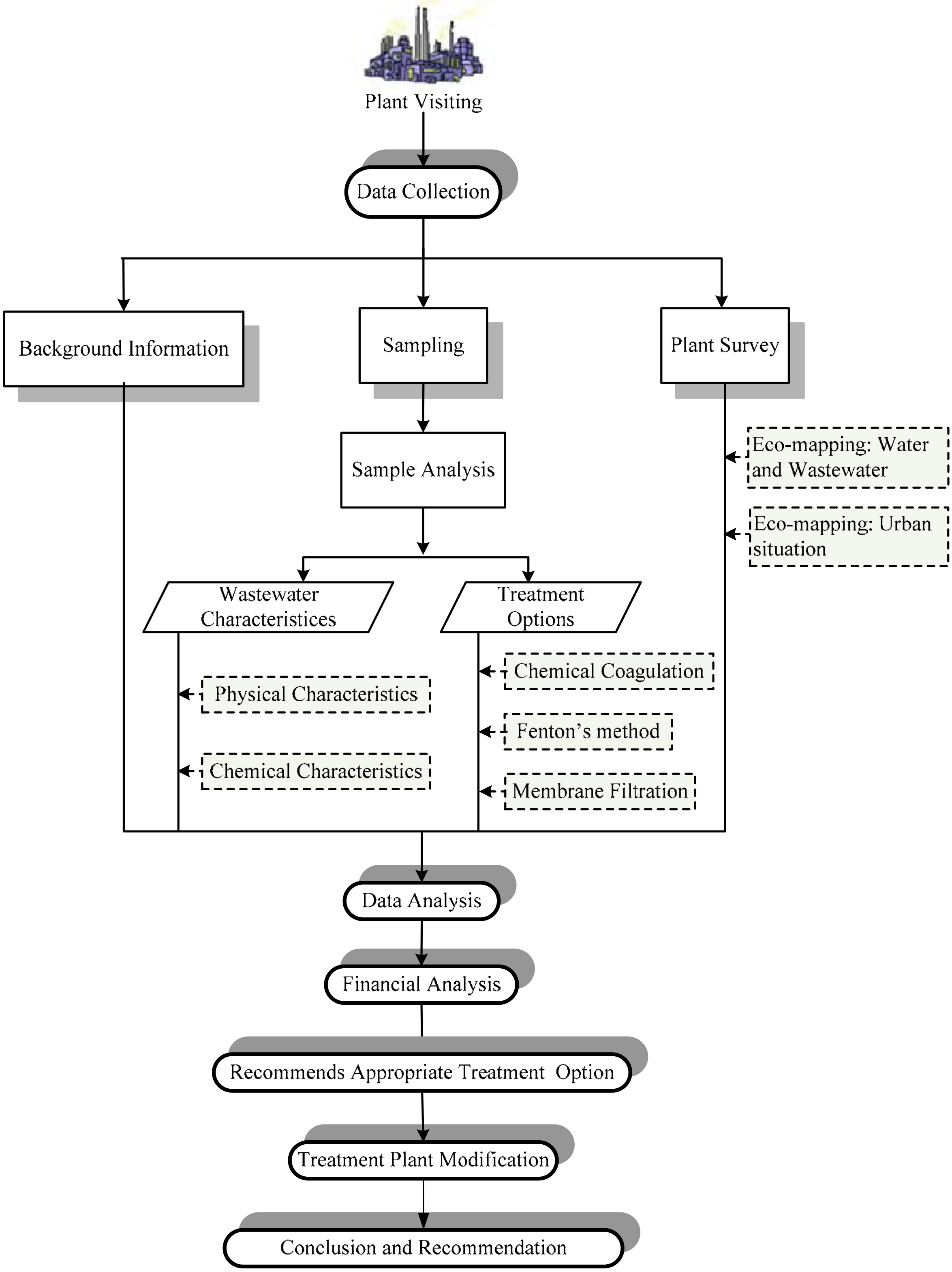


Figure 3.1 Study framework

3.2 Data collection

This study was conducted on a dye manufacturing industry located at Samut Prakan, Thailand. The process of data collection involved three steps that include background information, sampling and Plant survey. Background information was obtained from Plant visits and interviews with production manager, and staff of the Plant. Sampling was done at different locations of the wastewater treatment plant and in production units. The Plant survey was focused on water consumption and wastewater generation.

3.2.1 Background information

This includes information on production processes, Plant layout, water consumption, raw material, products, waste streams, and others presented in Figure 3.2. This background information was further used to structure the layout for Plant survey and locating the sampling points required for analysis.

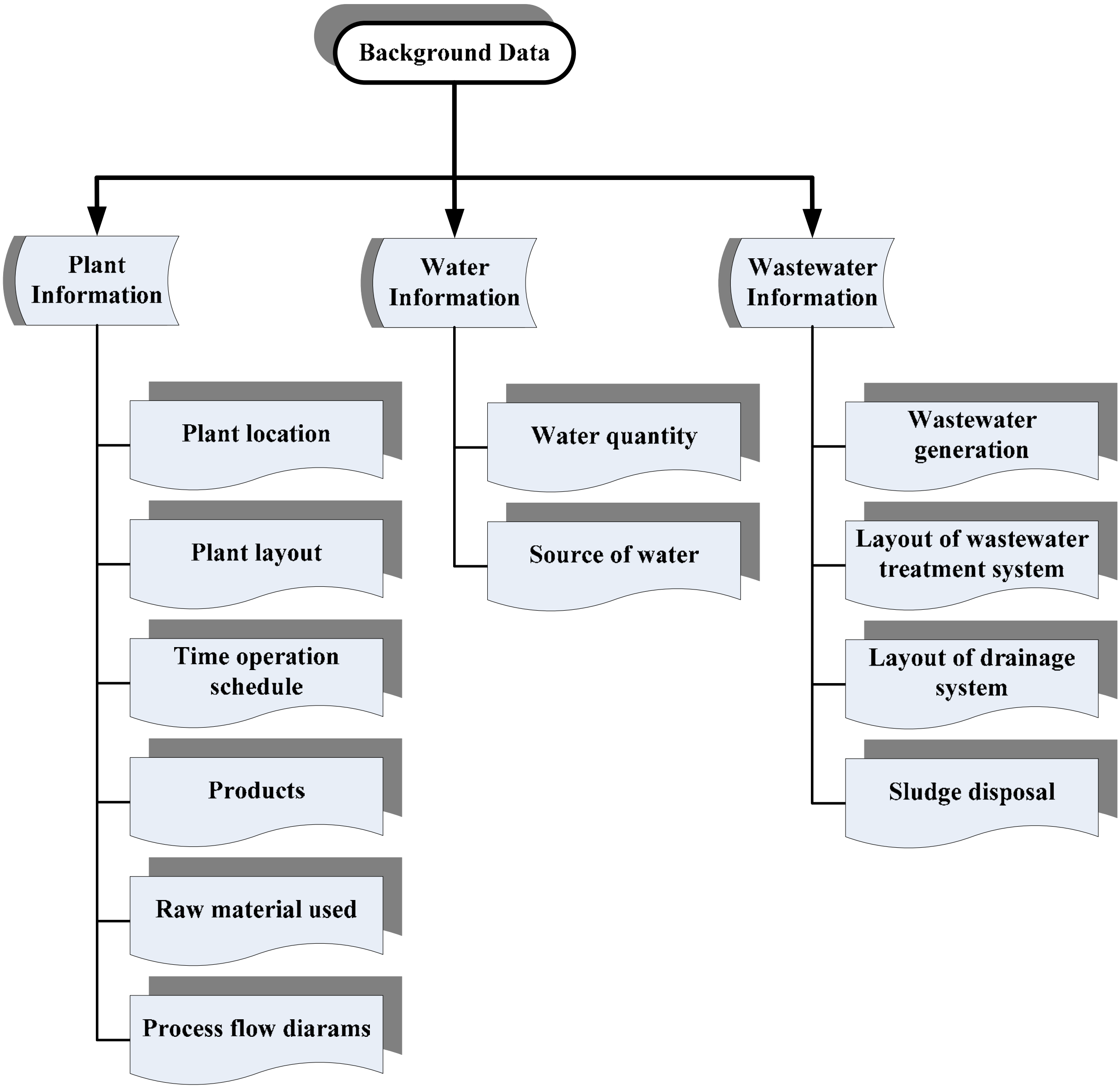


Figure 3.2 Background information of a dye manufacturing industry

3.2.2 Plant survey

The Plant survey aided information on each steps involved in production process, from raw material to final product and wastewater treatment plant. Eco–mapping was used as a tool as a process framework that helped to define and prioritize environmental problems and issues to act upon. Even though, it can be presented in several themes, this research focused on urban situation, and water consumption and wastewater generation.

The first step involved drawing a map of industry site. This includes access areas, roads and the immediate surrounding environment. These map copies reflect:

- **Eco–map: Urban situation**
  This map looks at areas of inter action between company and neighbors.

- **Eco–map: Water consumption and wastewater generation**
  This map looks at consumption of water and discharge of wastewater

For each eco–map framework, three symbols were used to map the issues: An ellipse with different hatched lines to indicate small, moderate and high level of water consumption and wastewater discharge.

3.2.3 Sampling

Grab samples were collected from some unit of production process and each point of wastewater treatment plant. The collected samples were preserved with ice and then transported to the Environment Engineering Laboratory of Asian Institute of Technology (AIT) and stored in 5°C room temperature prior to use. The wastewater samples were separated into two portions. One portion was used for identifying the wastewater characteristics (physical and chemical). Another portion was used for experimental treatability studies.

1) Wastewater characteristics

The physical and chemical characteristics of the wastewater samples were determined. Physical characteristics such as color, conductivity, temperature, total solid (TS), total suspended solids (TSS) and total dissolved solid (TDS) were determined. Chemical characteristics of wastewater such as pH, Chemical Oxygen Demand (COD), total nitrogen, and heavy metals such as calcium (Ca), cobalt (Co), chromium (Cr), copper (Cu), lithium (Li), manganese (Mn), molybdenum (Mo), Nickel (Ni), Lead (Pb), Strontium (Sr), Magnesium (Mg), Cadmium (Cd), Iron (Fe) and Zinc (Zn) were determined. Summary of sampling, handling, analytical method and interference and limitations requirement are presented in Table 3.1.

Table 3.1 Summary of sample handling requirements and method of analysis

Determination	Container	Minimum Sample size (mL)	Preservation	Maximum Storage Recommended	Unit	Analytical Method	Interference and Limitations
COD	P,G	100	Analyze as soon as possible, or add H_2SO_4 to pH<2; refrigerate	7 Days	mg/L	Closed Reflux Method	Chloride ion (Cl^-), Bromide, iodide, Ammonia, Nitrite(NO_2^-)
TSS	P,G	200	Refrigerate	7 Days	mg/L	Dry in oven at 103 - 105°C about 1 hour	-
TDS	P,G	200	Refrigerate	7 Days	mg/L	Heat at 180 ± 2 °C about 1 hour	-
Heavy Metals	P,G	1000	Refrigerate and add Nitric acid (HNO_3) to pH<2	6 months	mg/L	Inductivity Coupled Plasma (ICP) Method	-
Color	P,G	500	Refrigerate	48 hour	ADMI	Spectrophotometric method	Turbidity
pH	P,G	50	Analyze immediately	6 hour	-	pH meter	-
Conductivity	P,G	-	Refrigerate	-	mS/cm	Conductivity meter	-

Source: APHA et al. (1998).

Note: P = Plastic G = Glass

Refrigerate = storage at 4°C± 2°C in the dark

2) Treatability study experiments

After understanding wastewater characteristics, treatability study were performed to identify an appropriate wastewater treatment option to improve the existing wastewater treatment process. Among many options, chemical coagulation, Fenton's method and membrane filtration were investigated. The details of each method are described as below:

- **Chemical coagulation**

Jar test apparatus was used to determine the optimum dosage of coagulant. The coagulants used in this study were Polyaluminium chloride (PACl) 10% solution, ferric chloride ($FeCl_3$); commercial grade, Ciba X-COL 7105. The Jar test apparatus set up is presented in Figure 3.3. The procedure for a jar test involved using a 1,000 mL of beaker, adding 800 mL of wastewater samples to be coagulated to each of the jar test beakers. A coagulant stock solution was prepared using selected coagulants and was dosed in each beaker with increasing amounts of solution. After dosing each beaker, the stirrers were initially operated at a speed of 130 rpm for 2 min. that is known as rapid mixing. Following that, stirrers speed was slowed down to 30 rpm for 20 min., which is known as slow mixing. After slow mixing, the wastewater with coagulant was left undisturbed for 60 minutes allowing the flocs formed to settle down. The pH, Color, and COD was determined. In addition, sludge volume index (SVI) was determined as shown in Figure 3.4 for the option proposed. The sludge volume index (SVI) is the volume in milliliters occupied by 1 g of a suspension after 30 min. settling. Equation used to calculate SVI is given below:

$$\text{SVI (mL/g)} = \frac{\text{Settled sludge volume (mL/L) X 1000}}{\text{Suspended solids (mg/L)}} \qquad \textbf{Eq. 3.1}$$

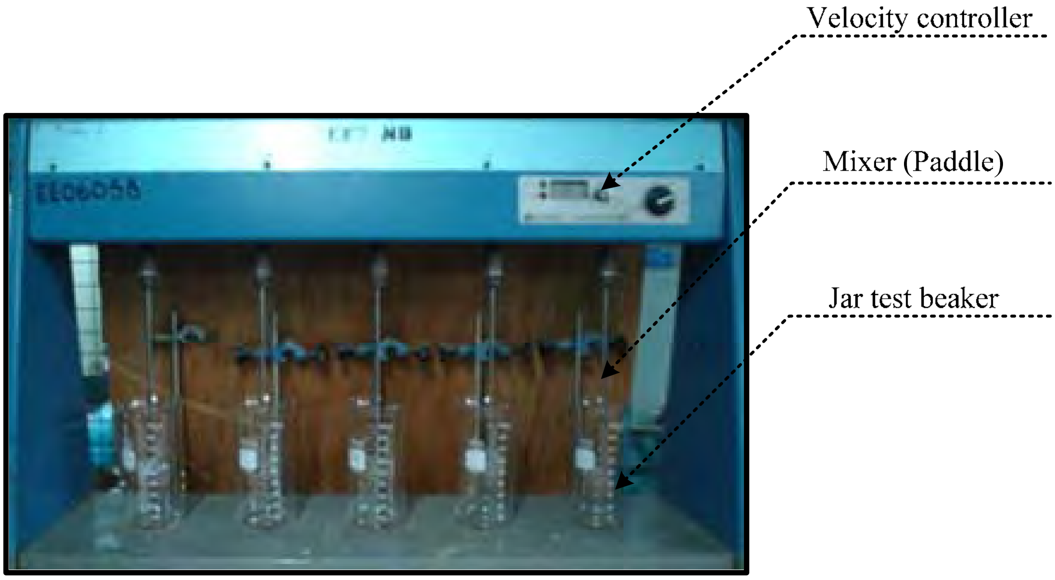


Figure 3.3 Jar test apparatus

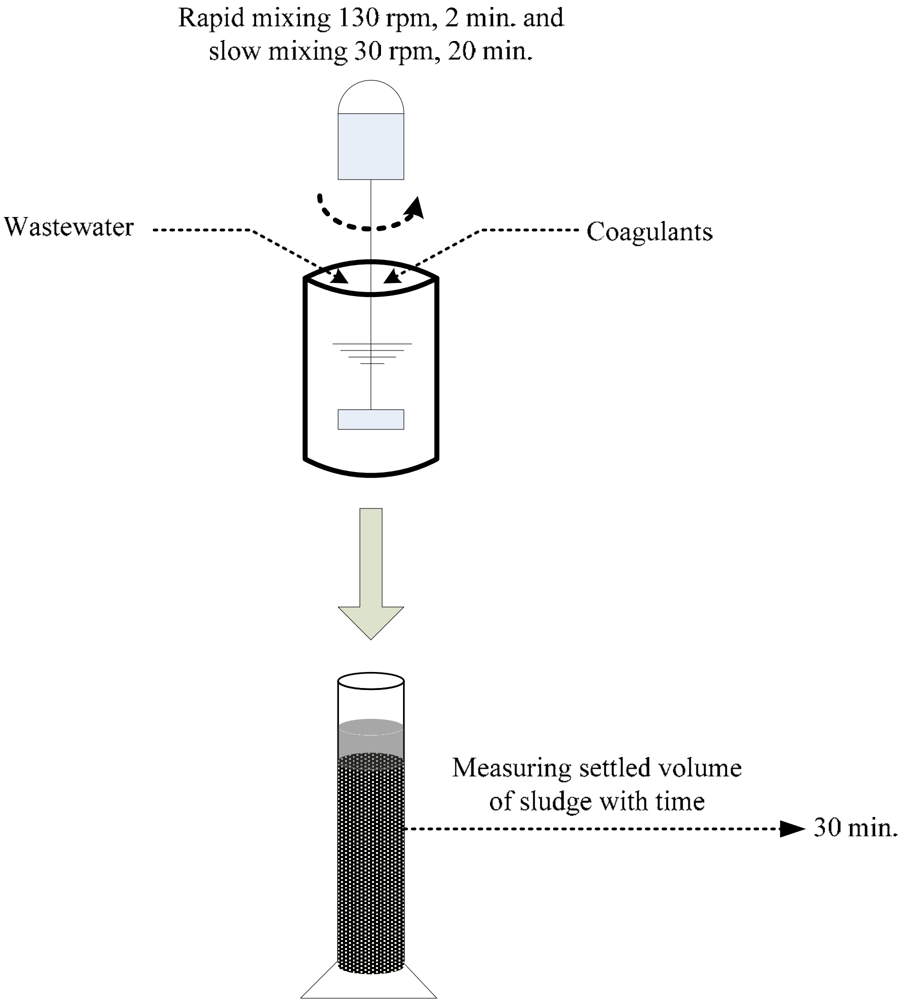


Figure 3.4 Procedure of Sludge Volume Index (SVI) analysis

- **Fenton's method**

Fenton's method was conducted by following the procedure in Figure 3.5 (Martian et al., 2003; Szpyrkowicz et al., 2000). Fenton's reagent is a mixture of hydrogen peroxide and ferrous ion. This reagent was investigated by adding ferric sulfate ($FeSO_4$); commercial grade to provide $Fe^{2+}$and following by hydrogen peroxide (H_2O_2) 30% solution; analytical grade that is oxidizing agent. One of the main factors affecting Fenton's reagent is pH of the wastewater. The oxidizing efficiency of the Fenton reagent is the high for pH ranging from 3 – 5. At high pH, iron precipitates as $Fe(OH)_3$ and catalytically decompose H_2O_2 to oxygen which is hazardous. The following steps were followed to prevent the effect of H_2O_2 on COD value.

- Parameter analysis were performed after 30 minutes reaction time
- pH was to 12 by adding 1M of NaOH solution and the parameter was analyzed. The main purpose of this step is to remove the residual H_2O_2 which interferes and increases the actual COD value.

In order to optimize the dosage of H_2O_2 and Fe^{2+}, the first set of analysis was performed by fixing H_2O_2 concentration at 1M and Fe^{2+}at varying concentrations (0.1M, 0.2M, 0.3M, and 0.4M).

In the second set of analysis, Fe^{2+}concentration was fixed at 0.1 M and applied in combination with different H_2O_2 concentrations such as 0.2M, 0.4M, 0.6M, and 0.8M.

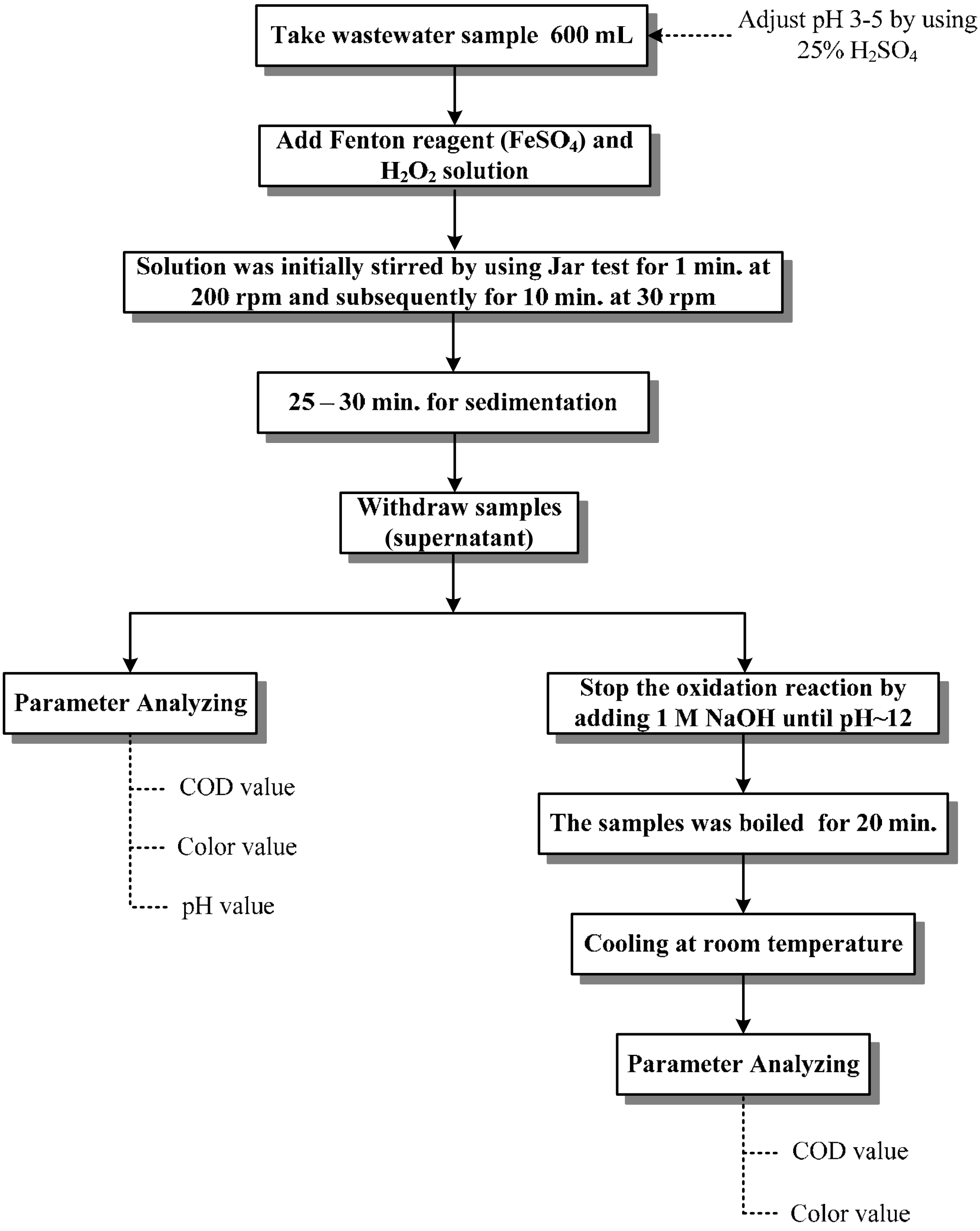


Figure 3.5 Fenton's reagent process

- **Membrane filtration**

The membrane test involved investigating permeates flux and pollutant removal efficiency. Permeate (or Filtrate) obtained from membrane test was tested for parameters COD, conductivity, salt and color and heavy metals. The experimental set up for membrane test is cross flow system (Model: NITTO DENKO make in Japan) as presented in Figure 3.6 and 3.10. There are two type of membrane that used in this experiment is that ultrafiltration (PES 10) and nanofiltration (XN 45).

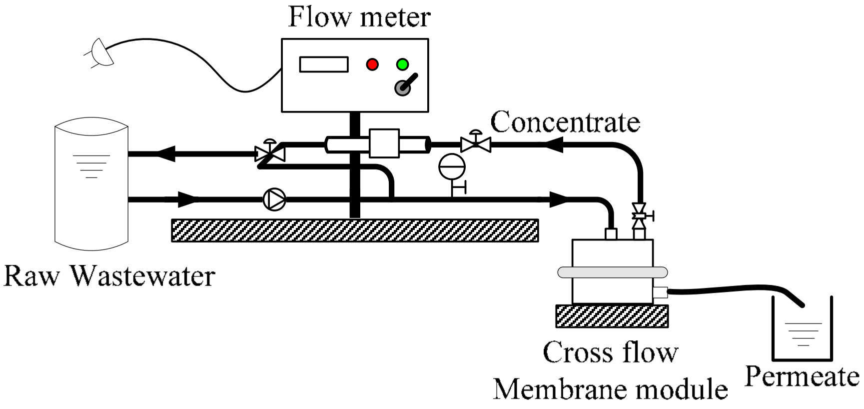


Figure 3.6 Membrane cross flow system diagram

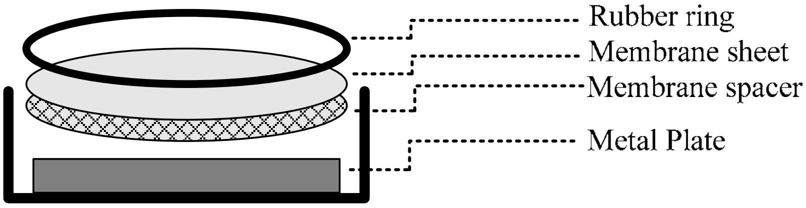


Figure 3.7 Membrane cross flow configurations

The equations permeate flux calculating as below:

$$\text{Permeate Flux (L/m}^2\text{.h)} = \frac{Q_p}{A} \qquad \textbf{Eq. 3.2}$$

Where,

Q_p = Permeate flow rate (L/hr.)
A = Membrane Area (m^2)

3.3 Financial analysis

The cost of chemical required for the treatment per unit volume of wastewater was determined based on price of chemicals available in Thailand. The calculations were done using the following equations.

$$\text{Mass of chemical (kg)} = \left[\text{Chemical Dosage (mg/L) x volume of WW (L)}\right]/10^6 \qquad \textbf{Eq. 3.3}$$

$$\text{Cost of chemical (Baht)} = \text{Mass of chemical (kg) x Chemical price (Baht/kg)} \qquad \textbf{Eq. 3.4}$$

Chapter 4

Results and Discussions

4.1 Present status of the research site

The dye manufacturing industry under study was established in 1982 at Samut Prakan province, Thailand. The location of the Plant is shown in Figure 4.1.

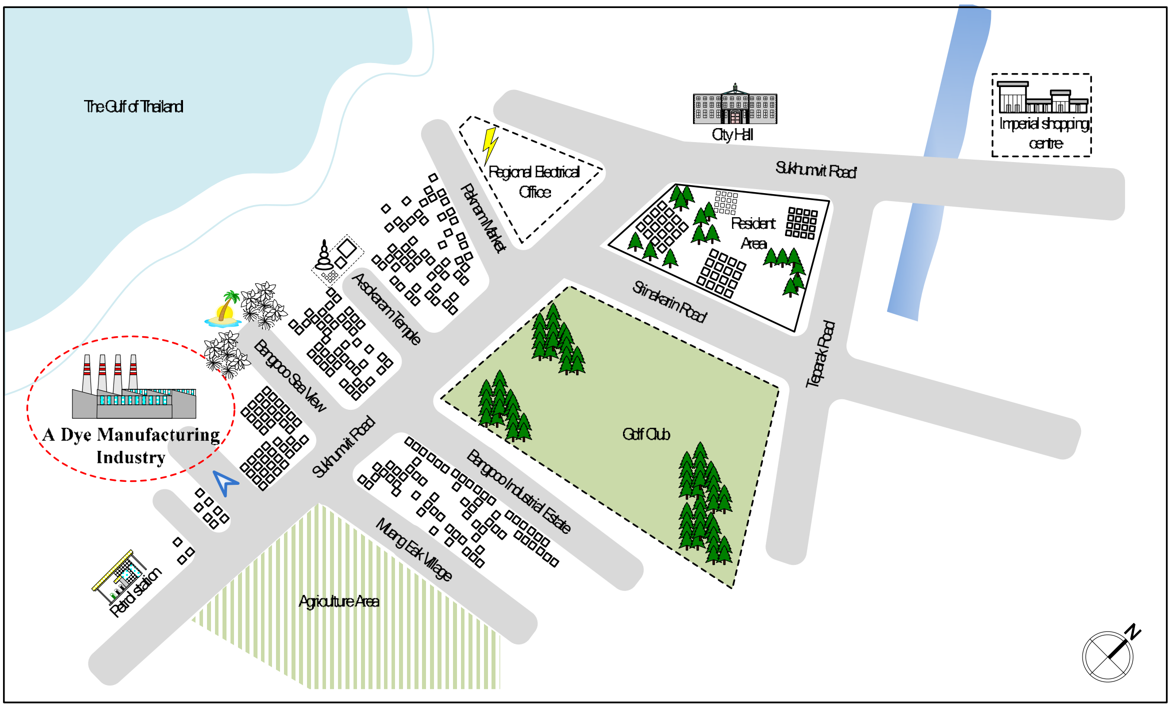


Figure 4.1 Plant location

4.1.1 General plant information

The production process in this industry is carried out is three shifts per day (08.00–16.00, 16.00–24.00, and 24.00–08.00 hours). The production of dyes can be classified under four main category such as acidic, reactive, direct and disperse dyes. More than 200 types of dyes are manufactured based on the market needs and production capacity. The duration of dyes production in each batch takes about 2 – 3 days depending on the type of dyes manufactured. Moreover, the factory has a maximum capacity to handle ten batches simultaneously and the consumption of raw material is based on the number of batch operation in one slot of production. Approximately 7 – 8 tons of raw materials are required per day per slot which produces about 9 – 10 tons of final dyes products per day. The daily water consumption is about 700 m^3 and wastewater discharge is around 600-650 m^3 while around 40 m^3 of wastewater is recycled into Plant for washing vessel, but currently not used due to high COD value. Overall production process is carried out in four Plants namely: Plant A, B, C and D as shown in Figure 4.2. Eco–mapping of urban is presented in Appendix B.

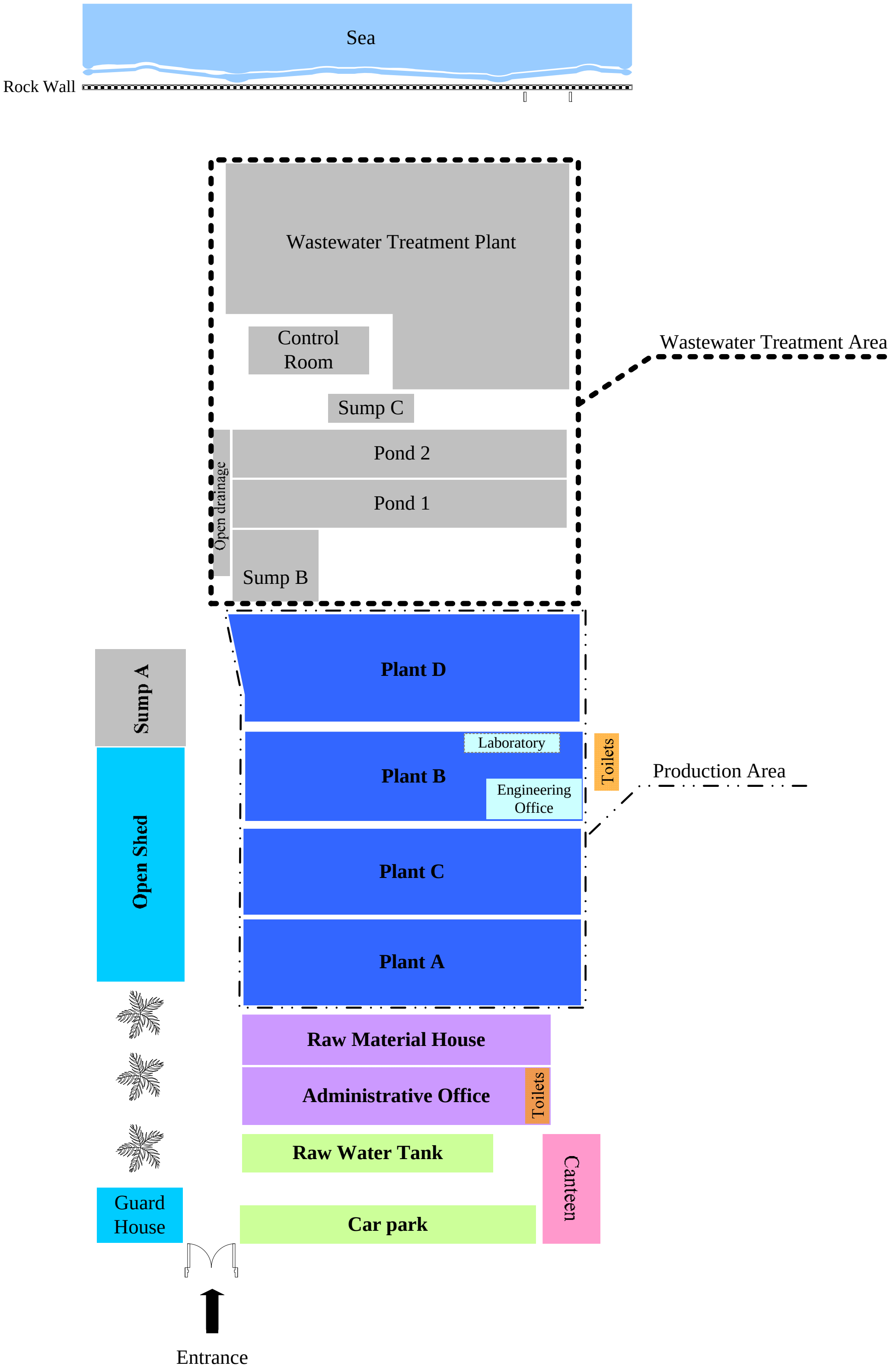


Figure 4.2 Plant layout

4.1.2 Operation in Plants

Unit operation taking place in Plant A, B, C and D is presented in Table 4.1. The major types of dyes produced in this Plant are reactive dye, acid dye and direct dye. The information of production processes are presented in Appendix A.

Table 4.1 Production unit in different Plants

Plant	Unit operation
A	Packing and storing products
B	Synthesis–dye processing, filter pressing, Sand milling, Stirrer, Spray drying, Nauta mixing and packing
C	Sand milling, Spray drying, Nauta mixing and packing
D	Synthesis-dye processing and filter pressing

4.1.2.1 General production process in Plants

The dye production processes involves five major stages. Initially, charging of raw material in the reactors that are specially designed for the synthesis of dye. Next, is shifting to filter press to make dye in wet cake form. After filter pressing and acquiring compressed wet cakes, the obtained wet cake is processed in cooking vessels. Wet cake, which contains big particles of dye are passed into sand mill for reducing size of the particles before sending to cooking vessels. In addition, the water–soluble dye is sent to stirrer and then it is transferred directly to spray dryer for making dye powder. In some cases, completely processed dye in cooking vessel is directly sent to spray dryer. Then, dye powder is passed to Nauta mixer for standardization and finally, it is packed into the containers as showed in Figure 4.3. Almost all processes are carried out in gravity flow and dye materials are transported by pumping.

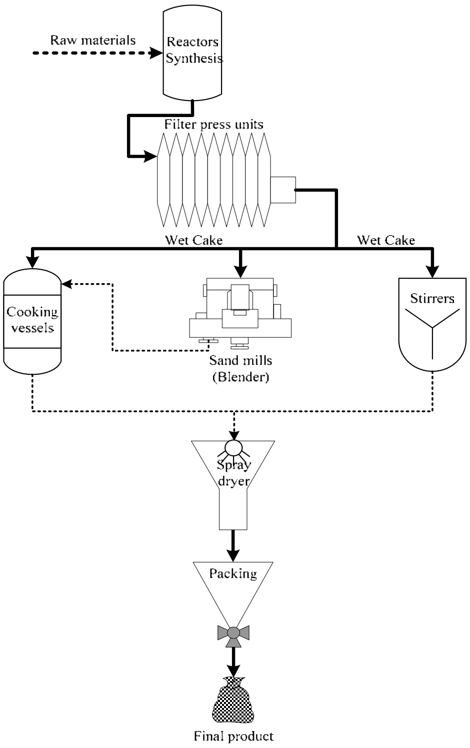


Figure 4.3 General process flow diagram of Plant

4.1.2.2 List of equipment in Plants

1) Vessels

Three types of reaction vessels are used in the production processes which have the capacity of 10 m^3, 15 m^3 and 30 m^3. Specially designed mild steel rubber lined (MSRL) and mild steel rubber lined tile lined vessels (MSRLTL) are used for processing. Different types of Vessels are used for mix cooking of wet cakes as per production specification.

2) Filter Press

Compressed wet cakes are obtained from the filter press after the dye synthesis process. There are twenty–one sets of filter presses in Plant D and five sets in Plant B. Those are continuously producing wet cakes of dyes for vessel cooking. Due to the compressing operation, large amount of wastewater is produced in this operation as Figure in Appendix A.

3) Spray dryer

The main activity of Spray dryer is to convert the feedstock from a slurry form to dry form and produce dry particles at the outlet. It has the special fluid back system associated with cyclone arrangement. Concentrated feedstock is fed as small droplets and forming a spray with the aid of nozzles (atomization). Then, the atomized liquid is brought into contact with hot gas and finally produces relatively uniform dry particles as an output. There are four spray dryers in the processing Plant. Among the four, three of Spray dryers are operated continuously and one is operated sporadically as per production demand. The operating rates of spray dryers are 1200 L/h, 900 L/h, 650 L/h and 200 L/h. The spray dryer is equipped with wet scrubber arrangement which is used to prevent the pollutants and dust particles to mix with air. As a result of scrubber arrangement gas emissions and pollutant compounds are mixed with water and disposed to wastewater drains as Figure in Appendix A.

4) Stirrer

This stirrer is high speed used for dissolving wet cake that is easy soluble with water. After stirrer, dye liquid is subjected to spray dryer directly without going to the vessels. There have two stirrers in Plant B as Figure in Appendix A.

5) Sand mill

Sand mills are used in the production unit prior to the Spray drying. Especially for reducing the size of the particles and make it suitable to feed the fluid in to spray dryer. There are three sand mills in Plant B and the usage of this equipment is based on the consistency of the dye slurry involves in the process as Figure in Appendix A.

6) Nauta mixer

There are nine mixers in the Plant B. This is mainly used for standardization. It has a specially designed double helix type blades that enhance the fineness by upward movement by each pitch incorporating spiral rotation. Moreover, these mixers are installed in both horizontal and vertical arrangement for efficient operational sequences as Figure in Appendix A.

4.1.3 Water consumption

The overall daily consumption of water is about 700 m^3 and the ground water has been the source for supply to Plant operation. The industry pays around 15 Baht per m^3 to the Provincial Waterworks Authority (PWA) for ground water consumption. About 30 m^3 of water is used for each batch where one slot of productions involves 10 batches Approximately 180 m^3 of water is used for washing of equipment, floors and for other washing purposes. The remaining quantity 100 m^3, 40 m^3 and 50 m^3 are consumed for ice production, steam production, and bathroom and toilets respectively. The percentage of water consumption is presented in Figure 4.4.

Eco–mapping of water consumption and wastewater generation is presented in Figure 4.5. Figure 4.5 shows Plant B, C, and D to have high water consumption where it involves production processes and cleaning after each batch of production. At the same time wastewater generation is also high. In the case of Plant A, water consumption is moderate for it is used in boilers for steam production. In this case, a moderate quality wastewater is generated from the packing units, where water is used for cleaning of hopper after each type of dye packing. Also, the amount of water consumption and wastewater generation is moderate in canteen due to their use for cleaning utensils. Similarly, moderate water consumption and wastewater generation is noticed in wastewater treatment plant, where water is used for backwashing and other washing purposes of Plant workers. Compared to all of the units of the Plant, water consumption and wastewater generation is very small at toilets.

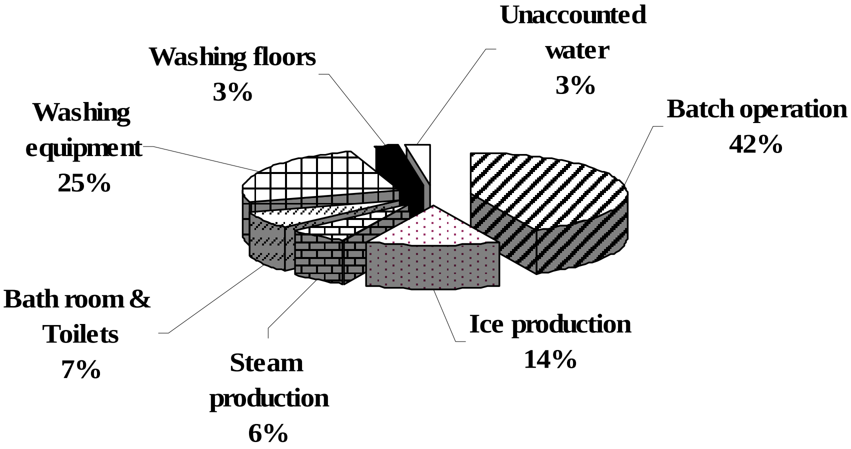


Figure 4.4 Water consumption in Plants

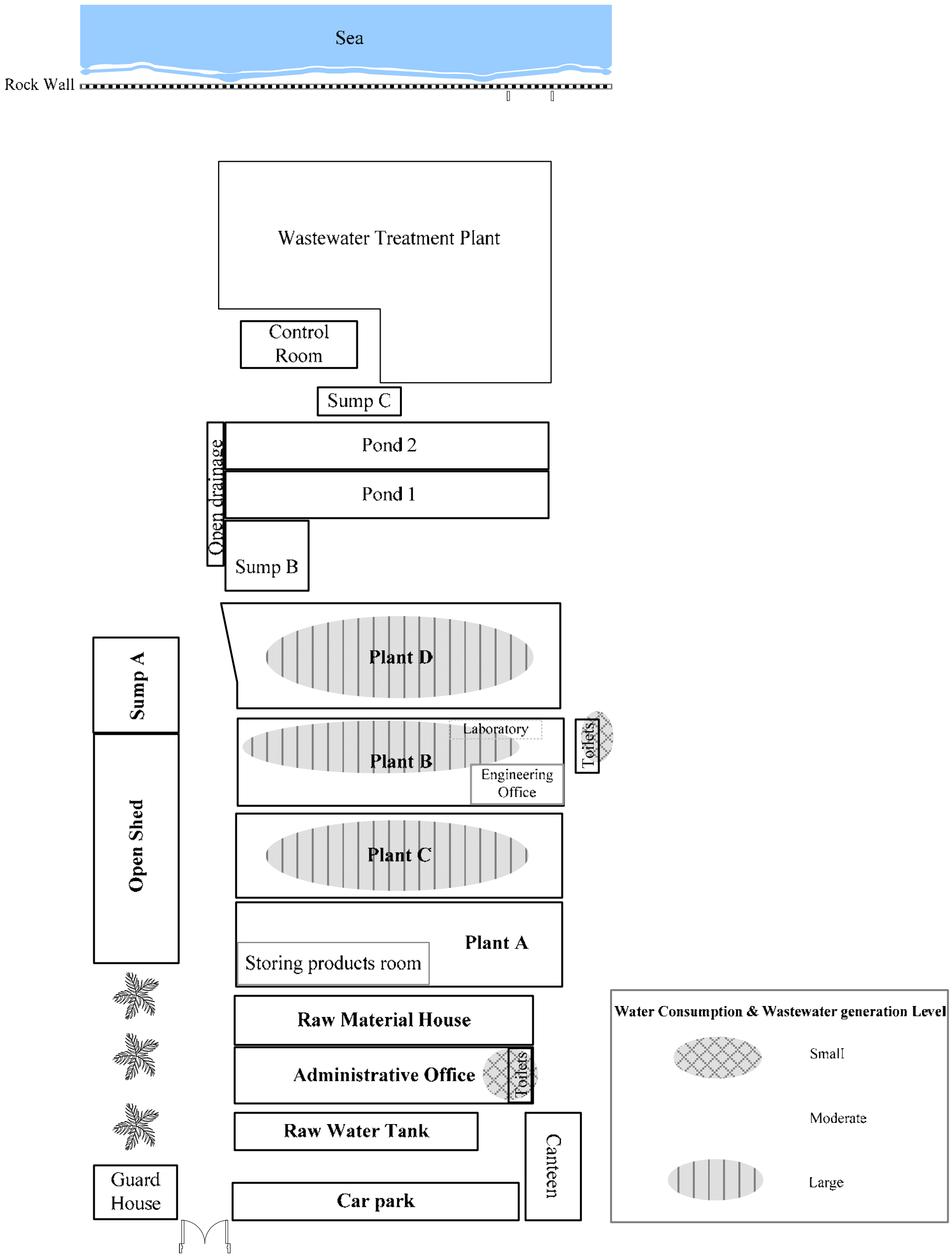


Figure 4.5 Eco-mapping of water consumption and wastewater generation

4.1.4 Washing practices in Plant B and D

1) Vessels

In order to change the color of the dye and change the batch for different color usage, the vessels are completely filled with water and following a complete flushing and finally the washed water is disposed to drains.

2) Filter press Spray Dryer and Nauta Mixer

Manually operated rubber hoses are used for washing operations and it has been observed that individual skill and handling behavior have been the major factors to decide the consumption of water for specific equipment washing. Especially, in the absence of highly pressurized water supply in the hose lines, inefficient usage of water has been monitored.

4.1.5 Drainage pattern in Plants

In Plant B and D, internal drainage paths collect all kind of wastewater from the sources and the collected wastewater is directed to the main drainage. Linked drainage pattern inside the production Plant tend to provide gravitational flow of wastewater from the sources. Based on the present phenomenon, the internal drainage networks obtain both washing water and processed water and divert the combination to the main drainage. Absence of segregation practices and inefficient mixing of wastewater resulted in deteriorating treatment efficiency. Existing drainage systems of a dye manufacturing industry under this study is shown in Figure 4.6.

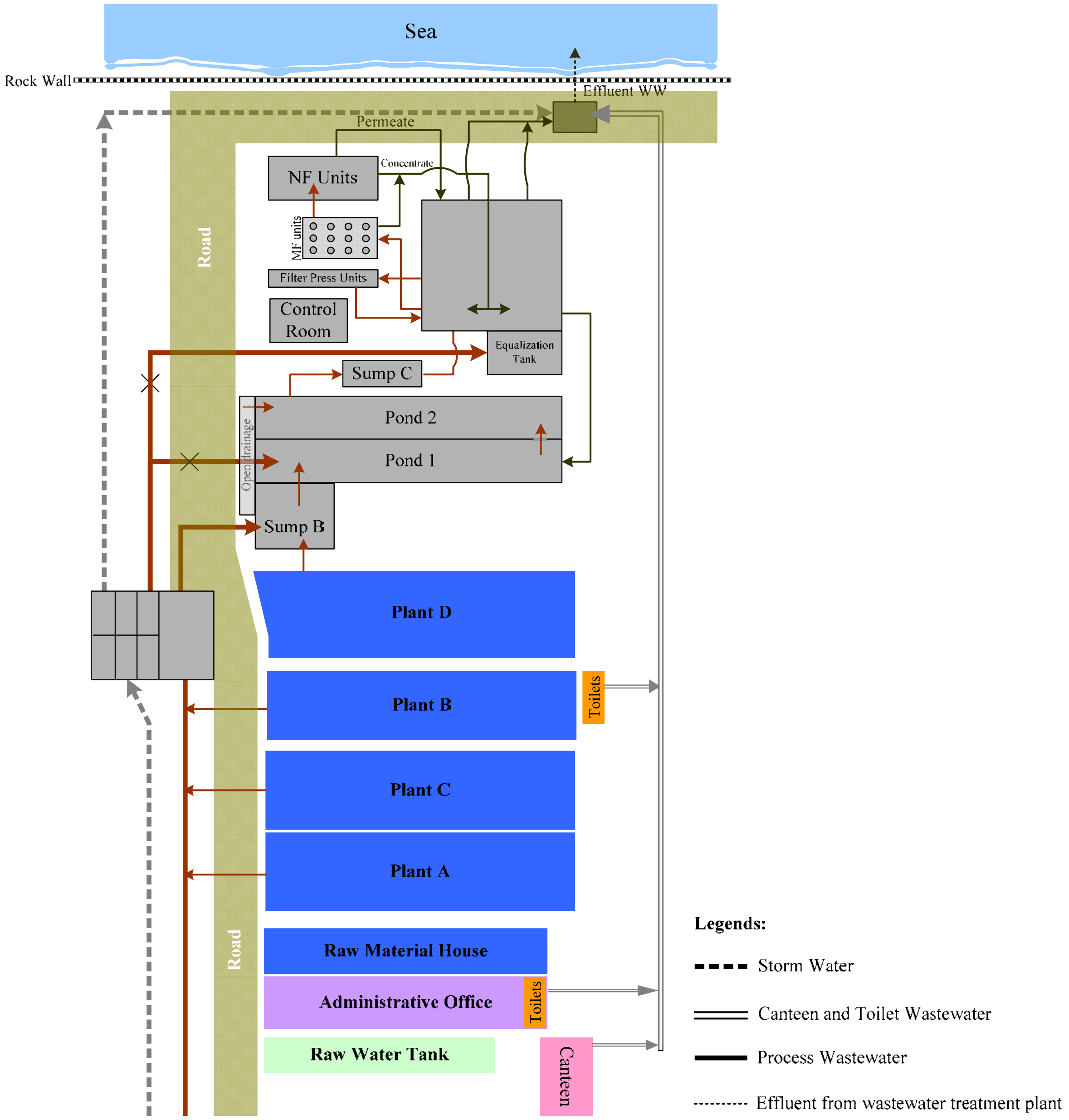


Figure 4.6 Overall drainage layout

4.1.6 House keeping practices

Generally, the appearances of floor surfaces in Plant B and D reveal two significant properties. In Plant B, high roughness and irregularities on the floors tend to provide temporary stagnation of washed water. Due to these reasons, it does not have the gravitational draining characteristics. In order to remove the pollutants from the floors, water is highly consumed than the average requirement. Different size rubber hoses are used for washing floors and some equipment. Apart from the usual requirement, the quantity of water for washing purposes and the adequate pressure level are determined by particular equipment operator/laborer. At the same time, factory's maintenance team has taken necessary measures to avoid the wastage of dye particles that spill from the vessels. Especially, when spill occurs, without disposing them to the drainages, the spilled dye particles are recovered and reused for the process. Whereas, in Plant D, the floor is specially designed with moderate slopes and natural gravity tends to provide easy drainage of water through individual collection traps which collect wastewater from individual equipment outlet and divert it to main drainage. Photographs of house keeping practices are presented in Appendix A.

4.1.7 Current status of wastewater treatment plant

The wastewater treatment plant consists of five main units. They are two collection ponds, filter presses, microfiltration units, nanofiltration units and carbon adsorption unit. Finally, the effluent is discharged to the sea as shown in Figure 4.7. Filter presses and microfiltration units are set up as pretreatment units before wastewater is subjected to nanofiltration unit (NF). The performance of these units are not satisfactory and the NF is also not possible to function effectively because wastewater characteristic before passing through NF was found to be high in TSS value as presented in Figure 4.8. The nanofiltration units begin to foul at this high TSS and TDS. The reason for the high value of TSS, TDS, and COD value in the NF feed was found to be the recirculation of NF concentrate. Therefore, treatability studies for other options of treatment were investigated.

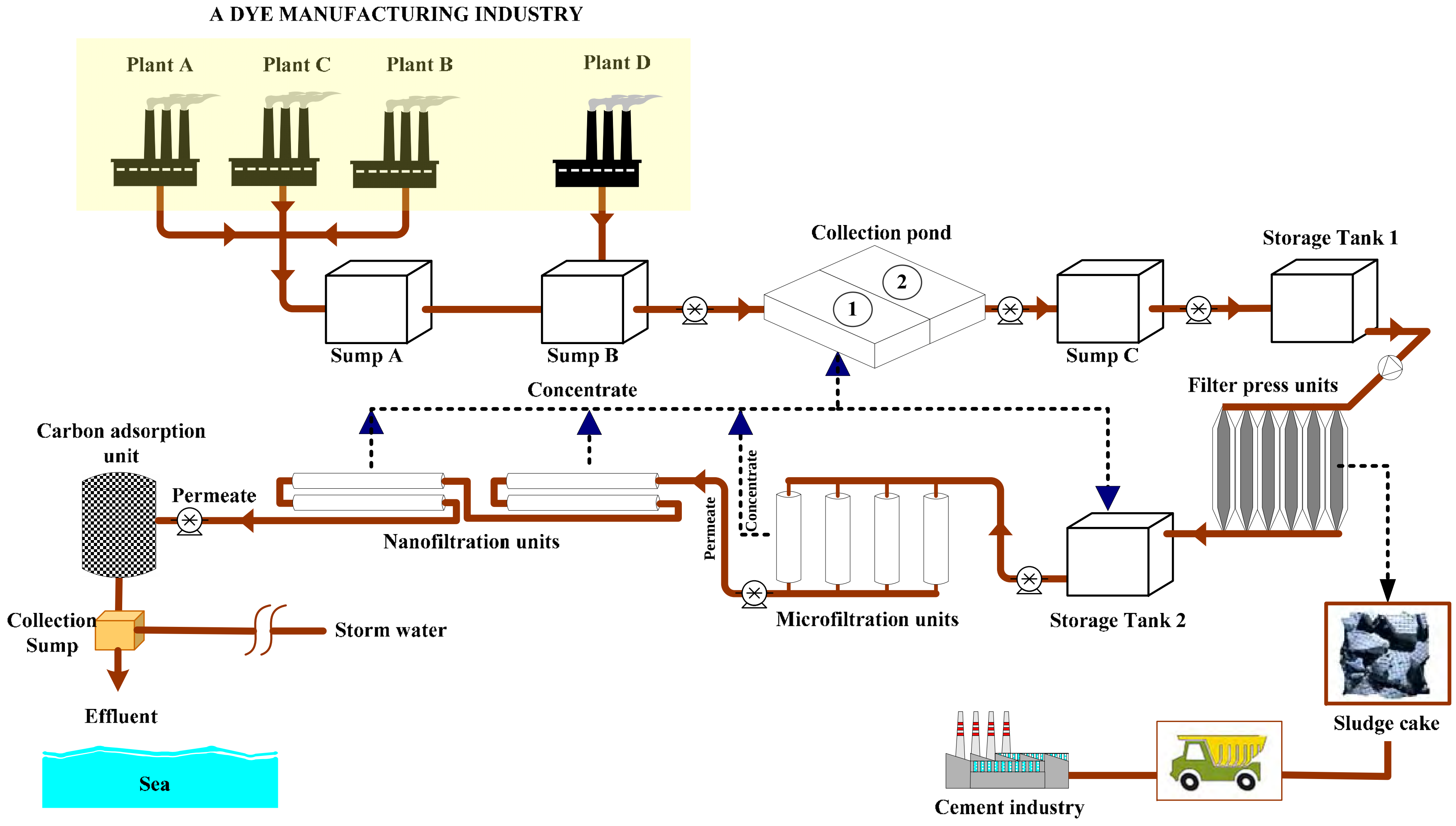


Figure 4.7 Wastewater treatment plant

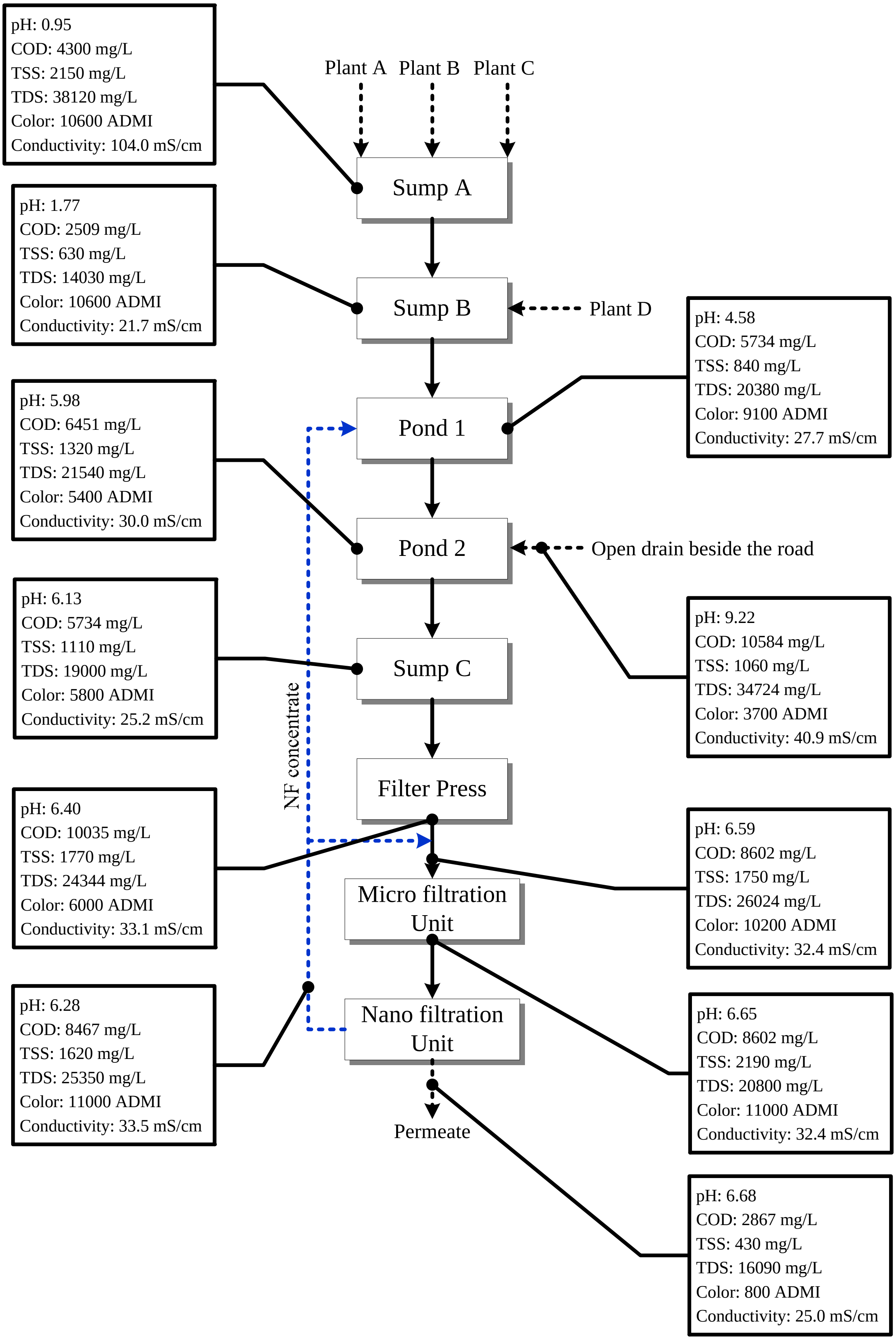


Figure 4.8 Evaluation characteristics of wastewater in different locations sampling point in the wastewater treatment plant

4.1.8 Characteristics of wastewater

The influent wastewater characteristics from the production processes and other sources to the treatment unit showed high color, COD, TSS, TDS value and heavy metals such as Ca, Cr, Cu, Li, Mg and Fe as indicated in Table 4.2. From the analysis of results, the efficiency of the Plant was found to be low. The wastewater characteristics were found below the Thailand Industrial Effluent Standards especially for the parameters TSS, TDS, COD, total nitrogen and Cr. Removal efficiency of wastewater treatment plant is presented in Figure 4.9.

Table 4.2 Dyes wastewater characteristics

Parameter	Unit	Sump B	Sump C	Effluent	Quality Wastewater Thai Standard
pH	-	1.77	6.13	6.68	5.5-9.0
Conductivity	mS/cm	21.7	25.2	25.0	-
Color	ADMI	10600	5800	800	Not objectionable
TSS	mg/L	630	1110	430	≤ 50 or 150*
TDS	mg/L	14030	19000	16090	≤ 3,000 or 5000*
COD	mg/L	2509	5734	2867	≤120 or 400*
Total Nitrogen (TN)	mg/L	115.3	305.0	115.4	≤ 20 or 60*
Calcium (Ca)	mg/L	28.430	41.730	41.290	-
Cobalt (Co)	mg/L	2.237	2.880	0.033	-
Chromium (Cr)	mg/L	2.312	70.460	3.615	≤ 0.25
Copper (Cu)	mg/L	18.810	21.085	0.041	≤ 2.0
Lithium (Li)	mg/L	0.150	7.890	7.15	-
Manganese (Mn)	mg/L	0.133	0.305	0.153	≤ 5.0
Molybdenum (Mo)	mg/L	0.026	0.010	0.005	-
Nickel (Ni)	mg/L	0.090	0.044	0.000	≤ 1.0
Lead (Pb)	mg/L	0.009	0.018	0.000	≤ 0.2
Strontium (Sr)	mg/L	0.093	0.275	0.145	-
Magnesium (Mg)	mg/L	8.210	12.710	12.000	-
Cadmium (Cd)	mg/L	0.001	0.010	0.000	≤ 0.03
Iron (Fe)	mg/L	11.400	7.570	0.886	-
Zinc (Zn)	mg/L	0.127	0.371	0.005	≤ 5.0

Note: * Depending on receiving water or type of industry under consideration of Thai Pollution Control Committee (PCC)

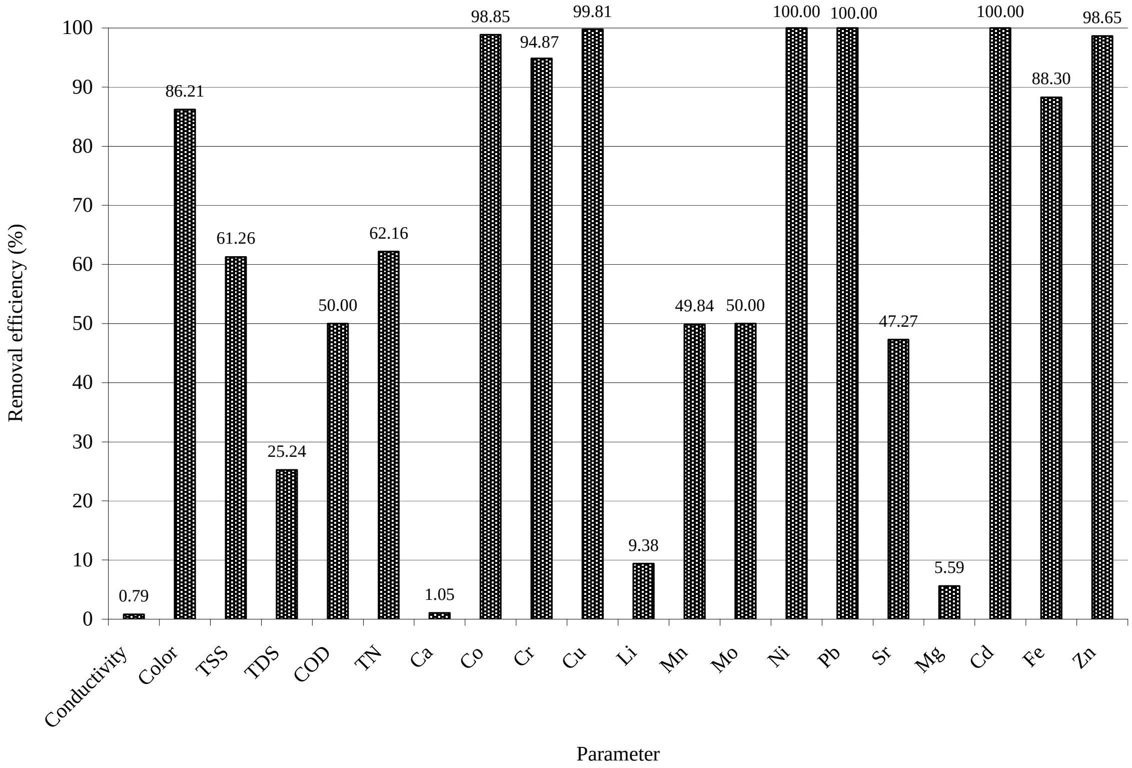


Figure 4.9 Overall efficiency of wastewater treatment plant

4.2 Pollution level in production processes

This study was performed on the wastewater sample from six locations in the production process. The characteristics of the samples were determined in order identify pollution level and to classify into two major groups, high concentration and low volume wastewater, and low concentration and high volume wastewater based on the pollutants levels. From the samples characteristics, the wastewater from washing spray dryer in acid dye producing process, blender in reactive dye and acid dye producing process is showed lower COD, TDS and TSS values compare to the wastewater generated from other equipments. The results are shown in Figure 4.10, 4.11 and 4.12.

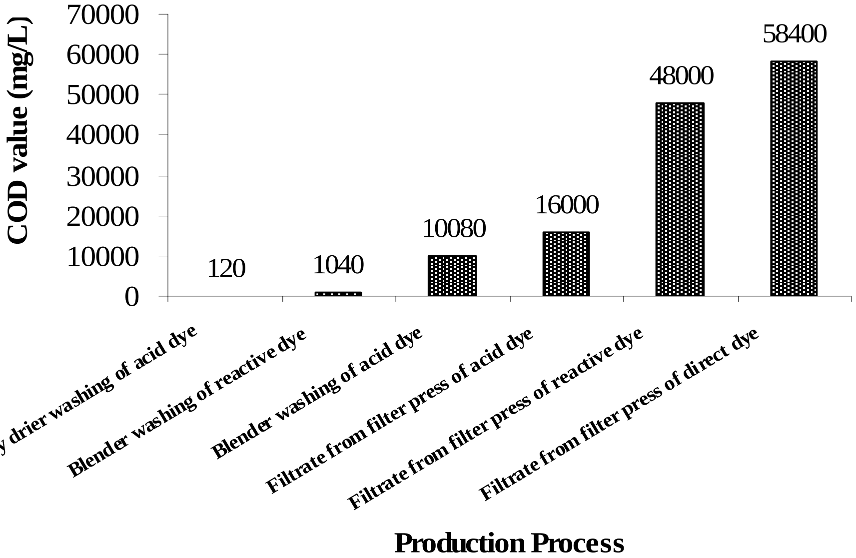


Figure 4.10 COD value of wastewater from production processes

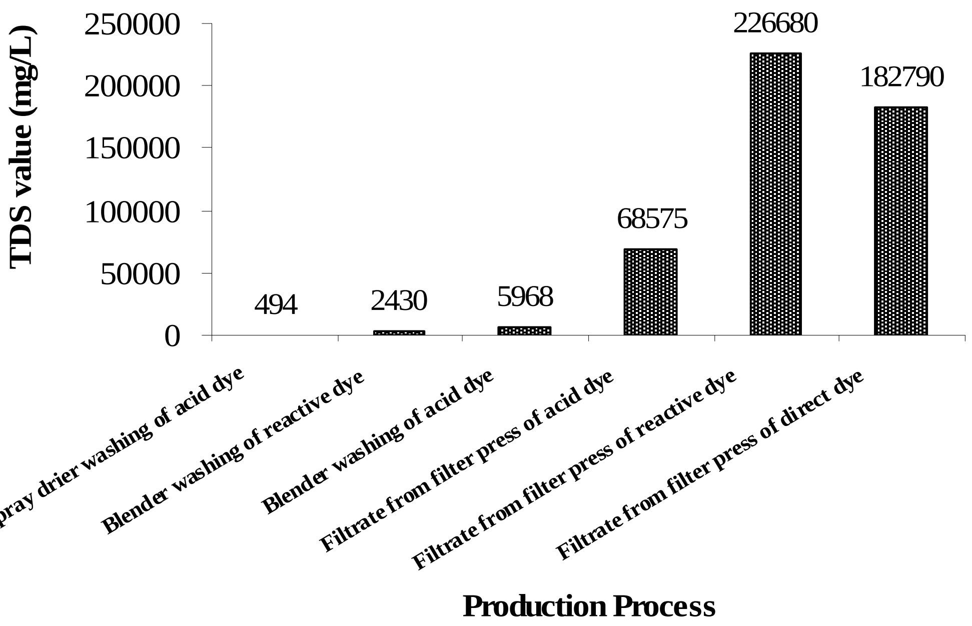


Figure 4.11 TDS value of wastewater from production processes

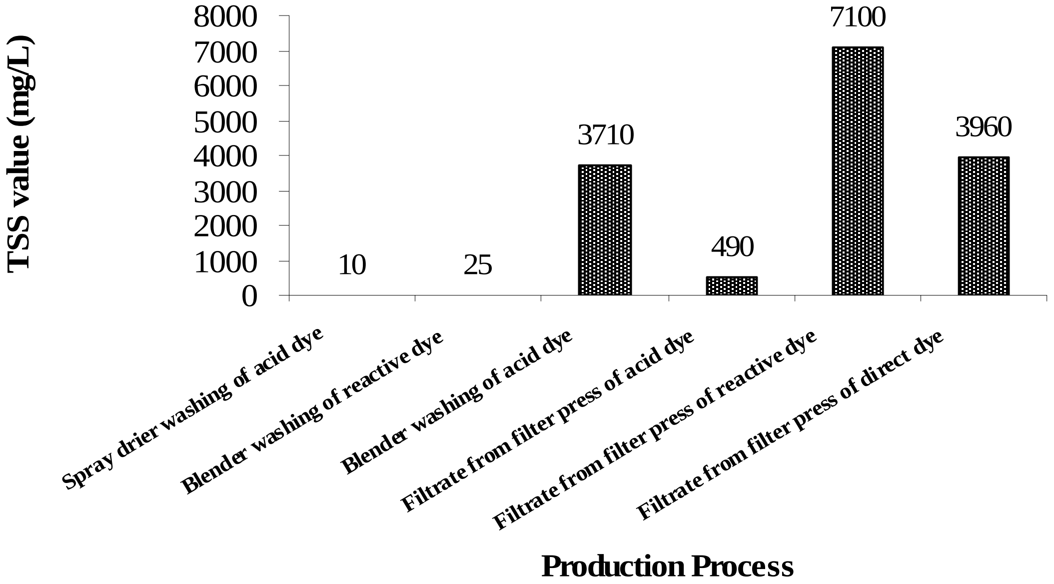


Figure 4.12 TSS value of wastewater from production processes

4.3 Treatability studies on dyes wastewater

For the treatability study, chemical coagulation using PACl, $FeCl_3$ and Ciba X-COL 7105; Fenton's method and Membrane filtration were performed. The removal efficiency of the options mentioned was analyzed to identify an appropriate treatment option to improve the existing wastewater treatment process.

4.3.1 Chemical coagulation

The optimum dosage of the coagulants PACl, $FeCl_3$ and Ciba X-COL 7105 were determined using Jar test apparatus. The results of the experiment are presented in the following paragraphs.

Option A: Polyaluminium Chloride (PACl)

Polyaluminium Chloride is one coagulant widely applying in potable water and industrial wastewater treatment for removing the colloidal particles in water or wastewater. It is a high molecular weight inorganic polymer. The physical and the chemical properties of PACl is presented in Appendix D. The results of Jar test in this experiment are presented in Figure 4.13 and 4.14. The optimum dosage of PACl 10% solution is found to be 500 ppm. Reduction in pH value was observed with increasing PACl dosage. At the optimum dosage, about 65% of COD reduction and 70% of color reduction was achieved. However, color removal was found to be high with increasing dosage of coagulant.

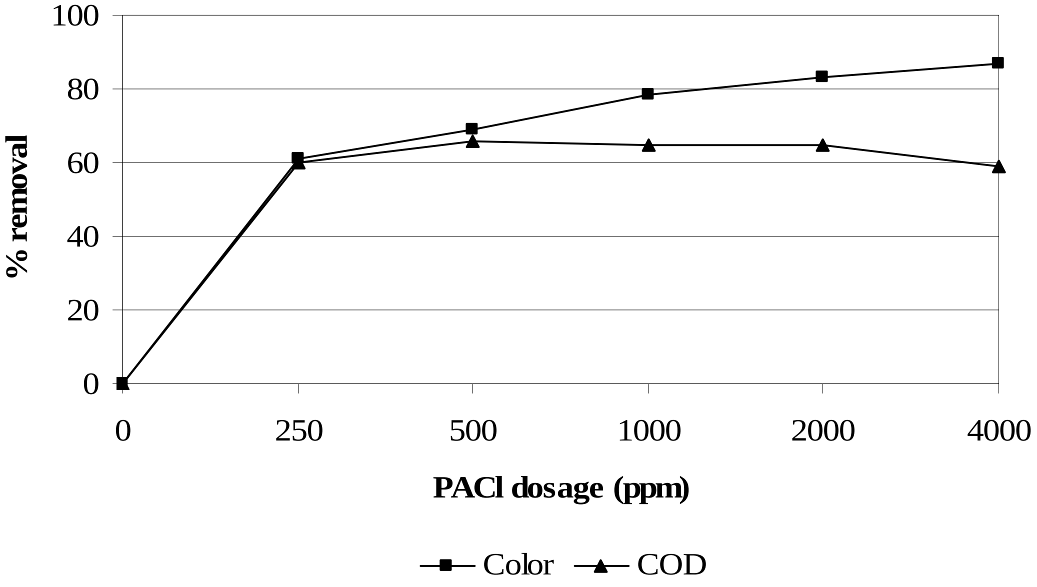


Figure 4.13 Removal efficiency of PACl

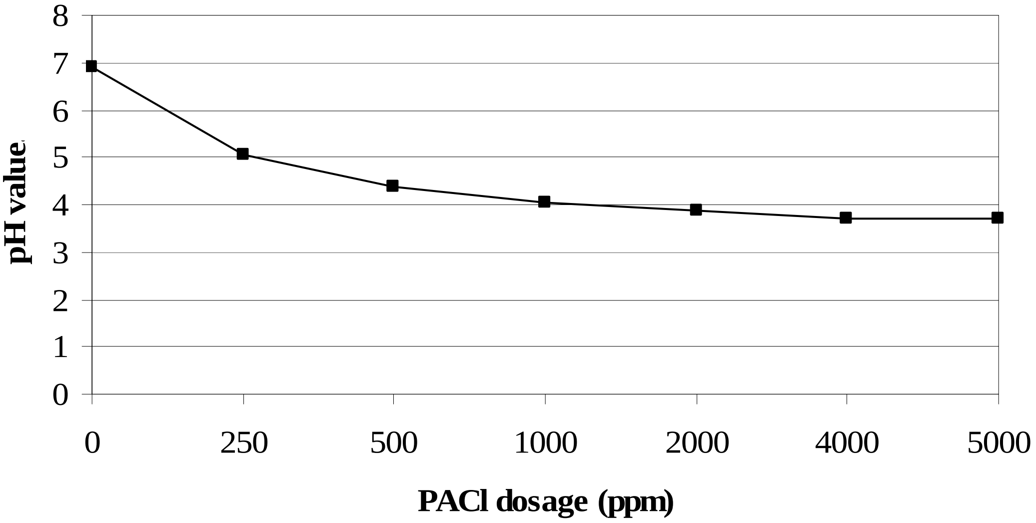


Figure 4.14 pH value of wastewater after adding by PACl

Option B: Ferric Chloride ($FeCl_3$)

The optimum dosage was found to be 6000 ppm. At the optimum dosage, about 80% of color removal and around 58% of COD removal was achieved as showed in Figure 4.15. The pH value of supernatant was found to be acidic throughout the experiment ranging from 2.0 – 2.2 as presented in Figure 4.16.

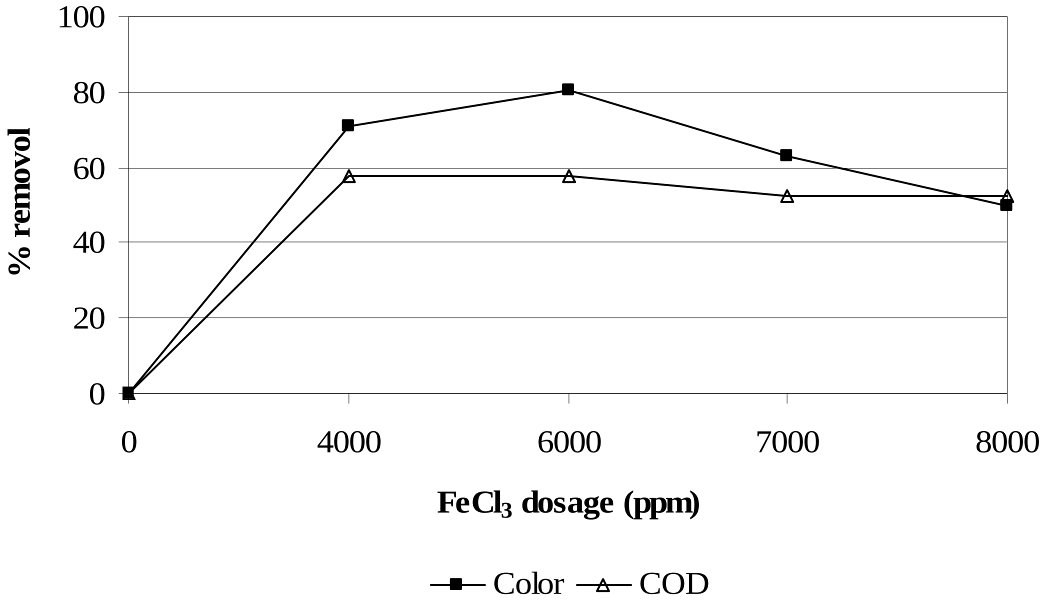


Figure 4.15 Removal efficiency of $FeCl_3$

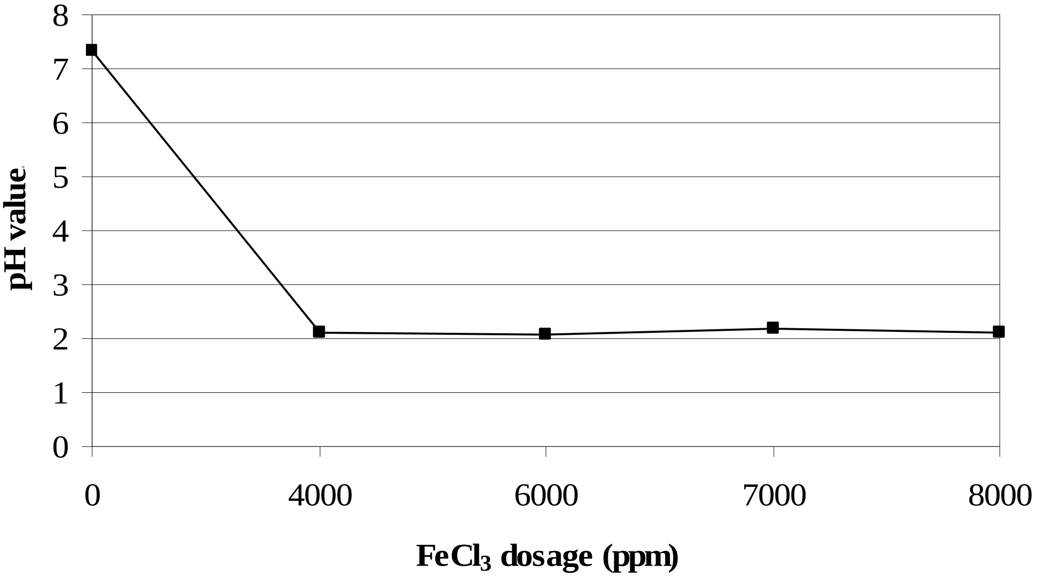


Figure 4.16 pH value of wastewater after adding by $FeCl_3$

Option C: Ciba X-COL 7105

In the range of 6000 – 9000 ppm dosage of Ciba X-COL 7105, there is considerable 60% reduction in COD as showed in Figure 4.17. In term of color removal, higher the dosage higher the color removal and almost 100% of color removal efficiency was found as showed in Figure 4.17. The optimum dosage of 6000 ppm was selected to be enough effective in the removal of COD and color. Compared to other coagulants, a neutral pH value was observed at different dosage levels as showed in Figure 4.18. Figure 4.19 presents the color removal using Ciba X-COL 7105 at different dosages. Therefore, this coagulant is found to be effective and suitable for pretreatment of wastewater before membrane filtration. However, from observation the volume of sludge produced using this coagulant is relatively high necessitating disposal of sludge following the floc settlement.

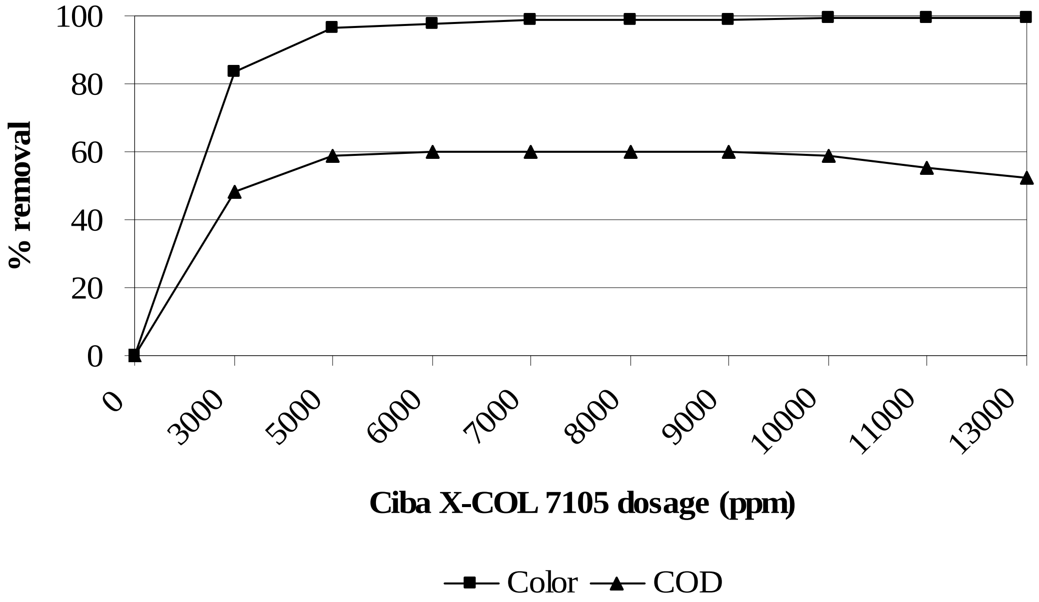


Figure 4.17 Removal efficiency of Ciba X-COL 7105

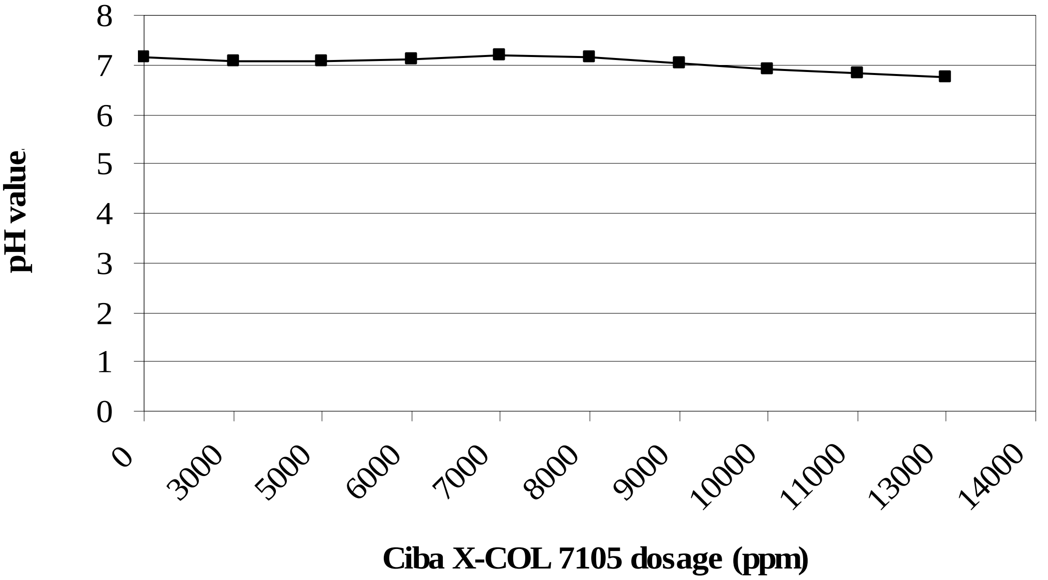


Figure 4.18 pH value of wastewater after adding by Ciba X-COL 7105

Figure 4.19 Color removals at different dosages of Ciba X-COL 7105

Option D: Combination of $FeCl_3$ and Ciba X-COL 7105

From the results obtained for $FeCl_3$ and Ciba X-COL 7105, tests were performed using a combination of these coagulants with the optimum dosage. The test was carried out by initially adding $FeCl_3$ with a dosage of 6000 ppm (optimum dosage) following this pH adjustment was done before adding Ciba X-COL 7105 at varying dosage. The optimum dosage of Ciba X-COL 7105 was found to be 1000 ppm from the results obtained as presented in Figure 4.20. For Ciba X-COL 7105 being costly chemical, this test was conducted with a combination of coagulant in order to improve the efficiency of COD and color removal as well as considering financial input. The Ciba X-COL 7105 was highly effective at naturalized pH condition of wastewater. A higher removal in the case of COD and color was observed with the combination of $FeCl_3$ and Ciba X-COL 7105 compared to that samples using only with one coagulant $FeCl_3$.

In additional, the test on sludge volume index (SVI) was conducted on the samples obtained from the combined coagulation using $FeCl_3$ and Ciba. The results showed SVI of about 460 mL/g indicating poor settling sludge which requires coagulant aid (flocculant) to enhance good settling of sludge. Nevertheless, volume of sludge decreased with increasing time as presented in Figure 4.21.

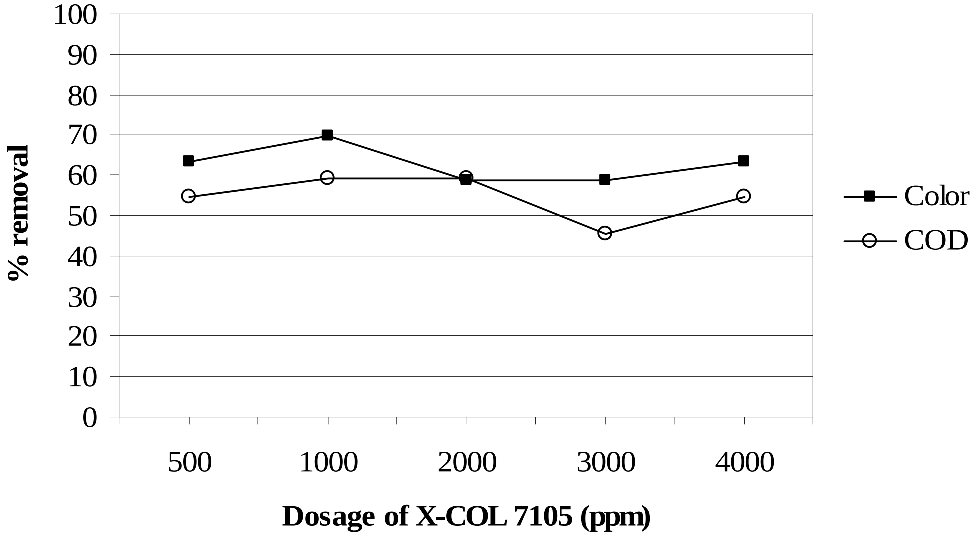


Figure 4.20 Removal efficiency of combination $FeCl_3$ and Ciba X-COL 7105

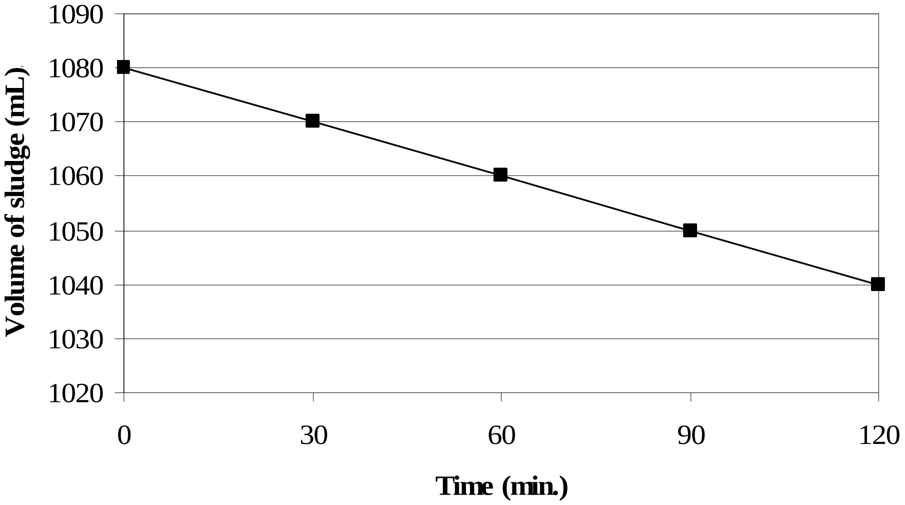


Figure 4.21 Variation volume of sludge with time

4.3.2 Fenton's method

Option E: Fenton's reagent

Based on the observations, Fenton's reagent was found to be an effective treatment for dye wastewater in lab scale. A COD rate of 60 – 90% reduction was achieved at all combinations of $Fe^{2+}$and H_2O_2 as indicated in Figure 4.22 and 4.23. However, in the case of the presence of residual H_2O_2, COD reduction is affected by increases the actual COD. Moreover, improvement in COD reduction was observed after pH adjustment to 12 with NaOH. The COD and color removal rate differs in approximately 10% with residual H_2O_2 and without residual H_2O_2. Around 90% in color reduction was achieved by without preventing H_2O_2 reaction. Almost 100% of color reduction was achieved by preventing H_2O_2 reaction. Thus, approximately 86% of COD reduction and 97 % of color reduction was obtained with an optimum dosage of 0.1 M Fe^{2+} and 1.0 M H_2O_2 within 40 minutes reaction time. On another hand, foam was generated continuously in during added reagent that is one barrier of this method was observed. The step reaction of Fenton's reagent for pretreatment dye wastewater at the optimum dosage as presented in Figure 4.24.

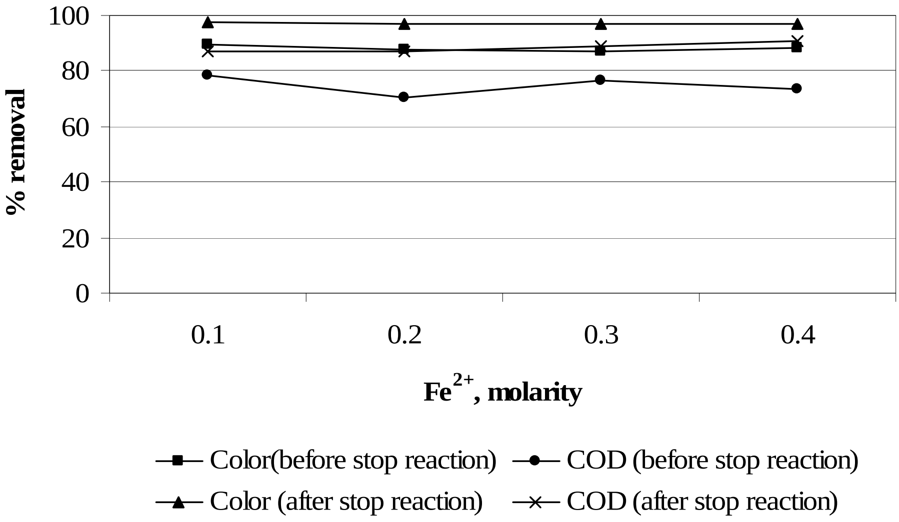


Figure 4.22 Removal efficiency of Fenton's reagent by fixing H_2O_2 dosage at 1.0 M

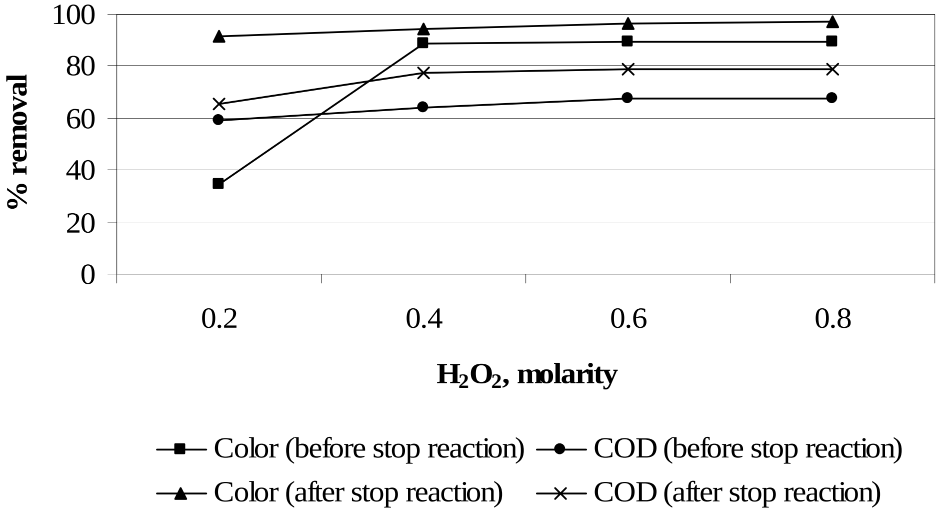


Figure 4.23 Removal efficiency of Fenton's reagent by fixing Fe^{2+} dosage at 0.1 M

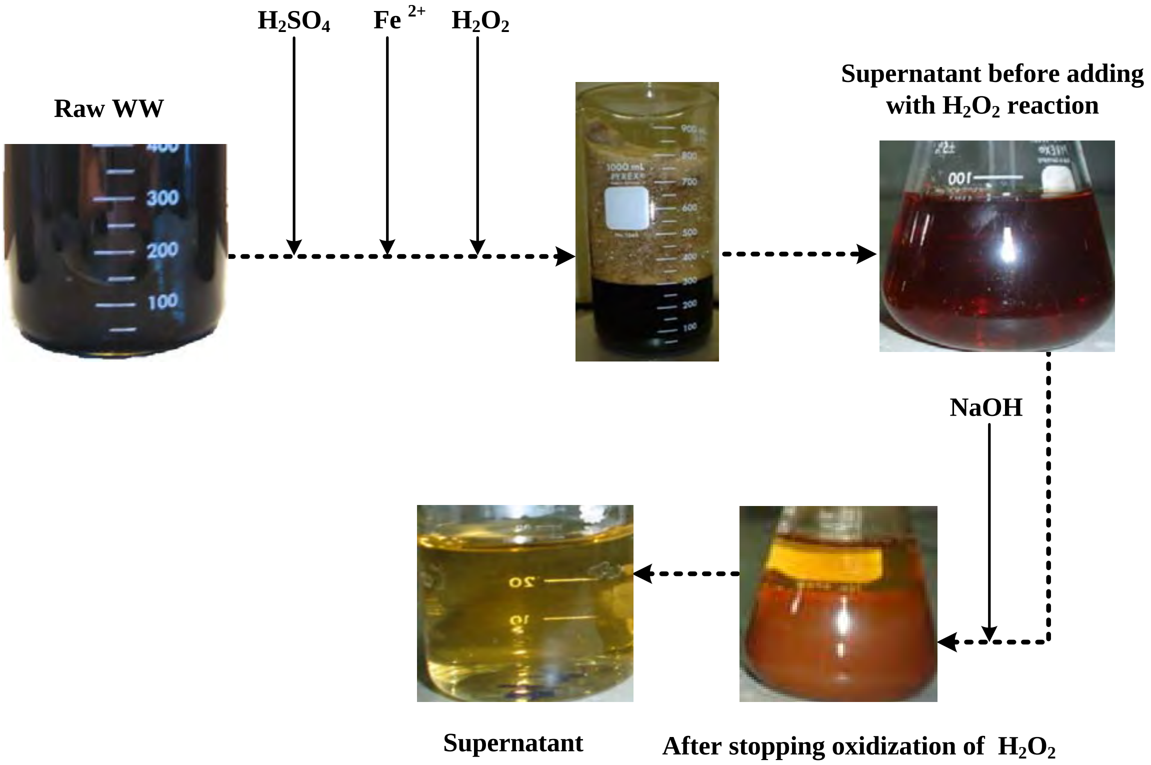


Figure 4.24 Pretreatment of wastewater using Fenton's reagent at the optimum dosage

4.3.3 Summary of the options for pretreatment

The results are summarized in Table 4.3 presenting the optimum dosage, pH value and removal efficiency for different options. From the results, Fenton's reagent and Ciba X-COL 7105 showed highly effective in color and COD removal compared to other options. The results for removal efficiency of combined $FeCl_3$ and Ciba X-COL 7105 were noticed to fall between the results obtained for Fenton's reagent and Ciba X-COL 7105. The removal efficiency of all the analyzed options is shown in Figure 4.25.

Table 4.3 Summary the optimum dosage in the difference options

Coagulant	Optimum dosage (ppm)	Approximate pH of supernatant	Average Color removal (%)	Average COD removal (%)
PACl	500	4.0	69	65
$FeCl_3$	6000	2.0	80	58
Ciba X-COL 7105	6000	7.0	97	60
$FeCl_3$ + Ciba X-COL 7105	6000 + 1000	7.0	87	58
Fenton's reagent (Fe^{2+} + H_2O_2)	0.1 M + 1.0 M	12.0	97	86

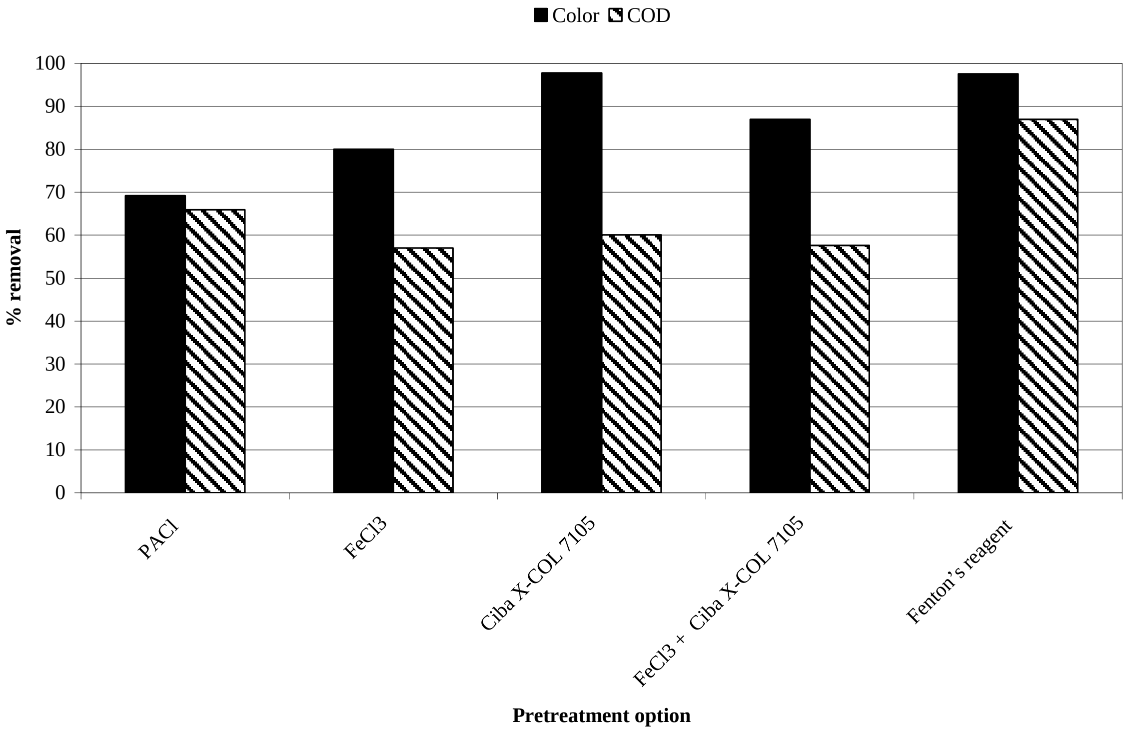


Figure 4.25 Summary color and COD removal efficiency in different options

4.3.4 Membrane testing

Two membranes, ultrafiltration (UF: PES10) and nanofiltration (NF: XN45) were tested in cross flow system module for the study. The results of permeate characteristics are presented in the Appendix C and Figure 4.26. From the results, efficiency of NF was found to be higher than UF. About 99% of Color removal and 74% of COD removal was achieved using cross flow NF. In the case of heavy metals, more than 98% removal of seven metals out Co, Cr, Cu, Mo, Ni, Pb, Fe, 90 – 95% removal of two metals Cd and Zn, 60 – 80% removal of four metals, Ca, Mn, Sr, and Mg was achieved using cross flow NF. However, 95% of the parameters meet the Thai Industrial Effluent Standard. Thus, providing cross flow NF to be highly effective option for wastewater treatment. The permeate obtained from NF, UF and raw wastewater is presented in Figure 4.27. In the case of permeate flux, UF was found to be higher than NF as presented in Figure 4.28 and Table 4.4. Thus, it indicated that UF has pore size bigger than NF and as a result lower removal efficiency of wastewater comparing with NF. In addition, permeate flux of UF was decreased with increase time while permeate flux of NF was found to be stable during 45 min. at pressure 5 bar.

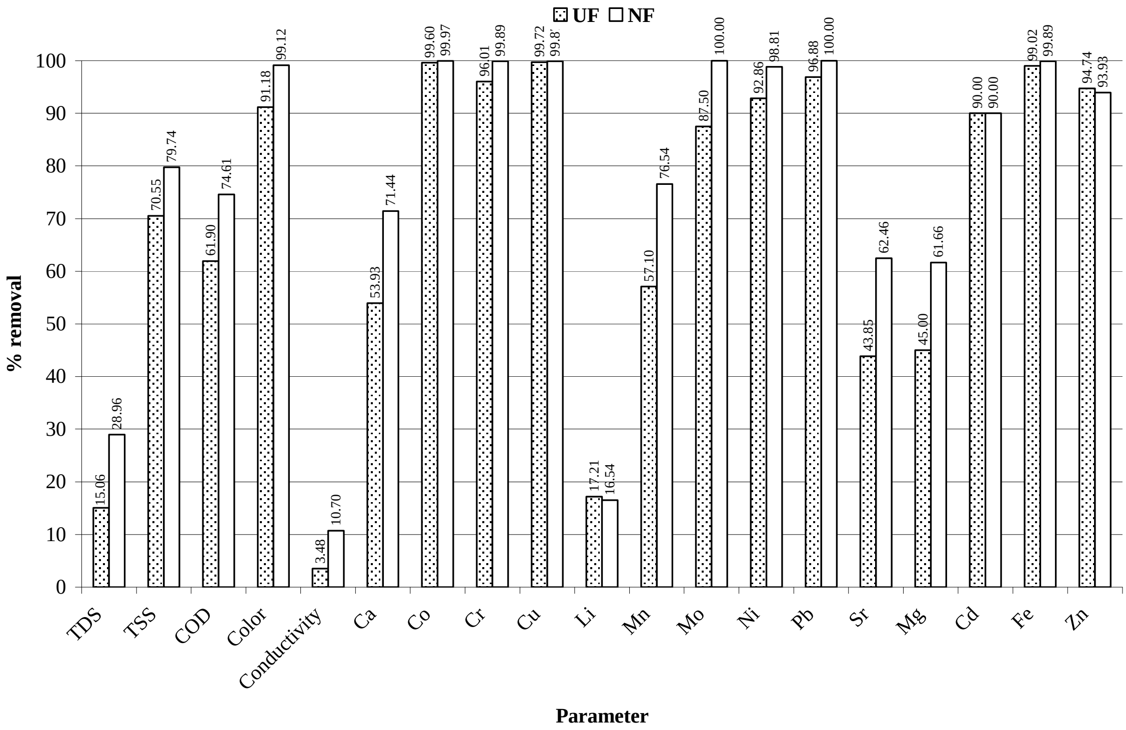


Figure 4.26 Color and COD removal efficiency of the permeate

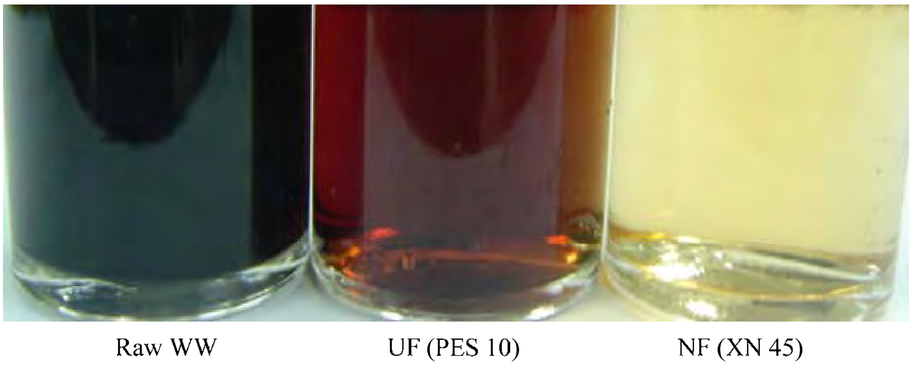


Figure 4.27 Permeate appearances from membrane testing in cross flow system

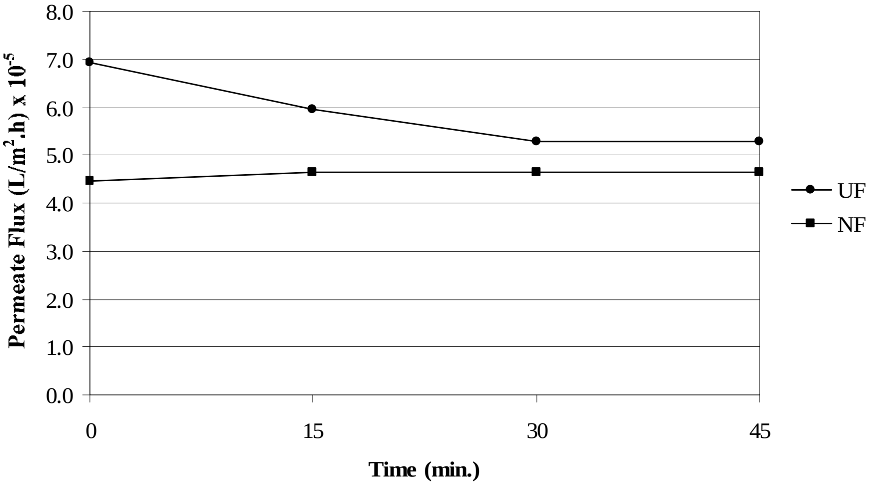


Figure 4.28 Variation of flux with time in different the membranes filtration

Table 4.4 Relative of the permeate flux with time

Time	Ultrafiltration (PES 10)		Nanofiltration (XN 45)	
	Permeate flowrate (mL/min.)	Permeate Flux ($L/m^2.h$)	Permeate flowrate (mL/min.)	Permeate Flux ($L/m^2.h$)
0	1.75	6.94×10^{-5}	1.25	4.46×10^{-5}
15	1.50	5.95×10^{-5}	1.17	4.64×10^{-5}
30	1.33	5.28×10^{-5}	1.17	4.64×10^{-5}
45	1.33	5.28×10^{-5}	1.17	4.64×10^{-5}

4.4 Financial analysis

4.4.1 Pretreatment cost analysis

Table 4.5 presents, the cost of pretreatment options. It was found that the cost in wastewater pretreated using PACl was low comparing to Ciba X-COL 7105 and Fenton's reagent. For Ciba X-COL 7105 and Fenton's reagent were found to be effective, but costly is high and complicate using for Fenton's reagent. Thus, combination between $FeCl_3$ and Ciba X-COL 7105 is found to be economical.

Table 4.5 Summary of the cost analysis

Option	Chemical name	Estimated Cost (Baht / m^3 of WW)	Removal Efficiency (%)	
			Color	COD
A	PACl 10% solution	48	69	65
B	$FeSO_4 \cdot 7H_2O$ (commercial grade)	60	80	58
C	Ciba X-COL 7105	420	97	60
D	Combined $FeSO_4 \cdot 7H_2O$ + Ciba X-COL 7105	163	87	58
E	Fenton's reagent	131,725	97	86

4.5 Proposed option for modification of wastewater treatment system

In order to reduce load of mixed wastewater on treatment units and to improve the treatment efficiency of the Plant, wastewater can be segregated in two parts as low concentration wastewater and high concentration wastewater. The low concentration, wastewater can be passed through the nanofiltration unit directly. Meanwhile, the high concentration wastewater has to be pretreated using coagulants in order to reduce the load on filtration unit. Correlating the results for the wastewater characteristics and water consumption, about 70% of high water consumption and high concentration of pollutants were noticed in the wastewater sourcing from production process and washing and about 30% of lower pollutant concentration was noticed in wastewater from other sources. Therefore, about 80% of high concentration wastewater generated from production process has to be pretreated and then passed to membrane filtration unit. The remaining 20% of low concentrated wastewater can be directly sent to membrane filtration unit without pretreatment.

From the treatability tests and cost analysis, option D pretreatment with combination $FeCl_3$ and Ciba X-COL 7105 is considered suitable high concentration wastewater where, effective color and COD removal can be achieved. Following that cross flow nanofiltration can be carried out. The sludge from sedimentation units after pretreatment and concentrate from the membrane filtration units can be sent to sludge thickener. The proposed option for improving the existing wastewater treatment system is presented in Figure 4.29.

The process modification involves pretreatment with coagulation where, coagulants have to undergo rapid mixing for uniform dispersion of chemical in the wastewater and then allowed to slow mixing for floc formation. The chemicals chosen from the treatability test has to undergo both rapid and slow mixing and pH adjustment has to be carried out to maintain suitable pH level to ensure effective treatment. The effluent from the slow mixing units for both the chemicals should be allowed to settle down in the sedimentation tank and then the supernatant from the sedimentation tanks has to be passed to membrane filtration unit. To ensure uniform loading on the membrane filtration units, a mixing tank can be provided for uniform mixing of supernatant from the sedimentation tank and the low concentration wastewater before filtration. The sludge obtained from the sedimentation tanks and the concentrate from the filtration unit can be passed to sludge thickener.

4.6 Recommendation possible in-plant modifications

In this industry high amount of water is consumed for washing purposes especially washing machines, equipments and floor which due to spill of chemicals or raw material from less performance of skill was observed. As a result large amount of wastewater is generated. Hence, by applying simple in–plant modification, this amount of water required and pollutants released can be reducing drastically as mentioned below:

- Replacing manually operated tap values by using high pressure hoses (spray nozzles) for cleaning equipments and others washing purposes in order to reduce the amount of wastewater generation and water consumption as well.

- Good housekeeping practices for example handling raw material, charging raw material, washing practices during production process has to be implemented and trained staffs to avoid spillage and wastage. Also checking leakage and repairing pipe, valve, connections, closing valve of tap water after using should be done regularly.

- Routine maintenance and repair of equipment is a valuable means for prevention releases to the environment.

- Collection dust in scrubbers to avoid emission losses and air pollution problem in order to recycle into the production process or other saleable product, such as a black dye. However, careful control of the dust collected from the various dye classes that must be maintained to prevent contamination.

- Material losses from transfer to operations using conveyer equipment for solids and pipelines or pumps for liquids are better.

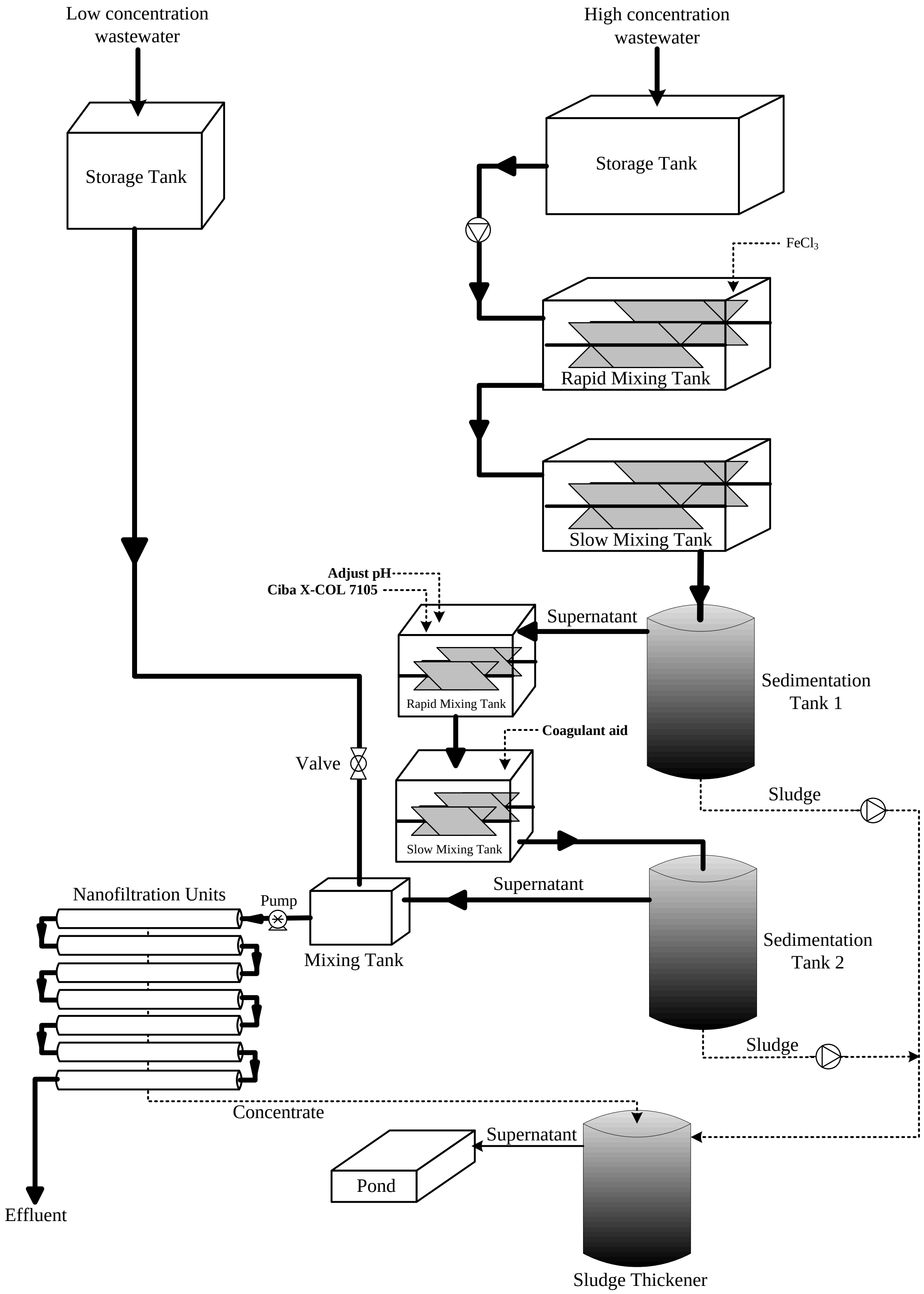


Figure 4.29 Proposed modification of the existing wastewater treatment system

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

- This industry produced four major types of dyes are produced where, three are water soluble dyes; acidic dye, reactive dye, and direct dye and one water insoluble disperse dye. About 200 types of dyes are produced in this industry. Apart from the raw materials, about 700 m^3 of water has been consumed in the production process. About 600 – 650 m^3 of wastewater is generated.

- Water consumption and wastewater generation shows, higher water consumption and wastewater generation is noticed in the Plant B, C and D after each batch of production process and very low at toilets and moderate generation from Plant A after dye packing and from wastewater treatment plant from backwashing and from canteens. The overall washing practices and housekeeping was noticed to be poor in the Plant. Thus, the simple guidelines for conserving water and minimizing waste generation are provided especially using high pressure spray nozzles for washing equipments such as filter press, vessel, Nauta mixer and for others purposes. Moreover, the drainage pattern of the Plant showed ineffective drainage system where, wastewater from different sources are mixed up and diverted to the main drain towards the treatment plant.

- In this context, to identify the appropriate treatment option for treating wastewater to reduce the pollution level from the industry, treatability study was performed. To perform this study initially wastewater characteristics was determined. From the results, the wastewater was found to contain high color, COD, TSS, TDS and some heavy metals such as Co, Cr, Cu, Mg, Fe and Li. Comparing to the Thailand Effluent Standards, the parameters TSS, TDS, COD, Total nitrogen and Cr was found to exceed the limit. The efficiency of the treatment plant was found to be very low because the pretreatment system has failed due to this the NF units are also not possible to work effectively.

- The treatability study on pretreatment options using coagulation, Fenton's reagent and membrane filtration was performed. From the analysis for coagulation, combination of $FeCl_3$ and Ciba X-COL 7105 was found to be effective in the removal of color and COD from wastewater compared to other options, such as Ciba X-COL 7105, $FeCl_3$ and Fenton's reagent alone. Though Ciba X-COL 7105 and Fenton's method were found to very effective in removal of color and COD, the financial analysis revealed the options to be not economical especially Fenton's method. In the case of combination of $FeCl_3$ and Ciba X-COL 7105, it is economical and effective in removal of color and COD. Only draw back with this option is, the poor sludge settling that requires coagulant aid (flocculant) to enhance settling. An optimum dosage of about 6000 ppm of $FeCl_3$ and 1000 ppm of Ciba X-COL 7105 was found to be effective. Thus for pretreatment of wastewater, option with combination of $FeCl_3$ and Ciba X-COL 7105 and a coagulant aid was found to be more effective.

- The tests on membranes, ultrafiltration (UF) and nanofiltration (NF) membrane in a cross flow module, showed NF highly effective in the removal of COD and obviously color compared to UF. The quality of permeate from NF were about 95% of all parameter within the limits of Thailand Industrial effluent Standards.

- An overall process modifications is required for the existing treatment plant system where, the wastewater segregation can be the first step. The wastewater segregation can be done by separating high concentration wastewater and low concentration wastewater in order to reduce load on treatment units and have an effective treatment. The low concentration wastewater generated can be directly passed through NF unit without pretreatment and high concentration wastewater can be pretreated using option with combination of $FeCl_3$ and Ciba X-COL 7105 and coagulant aid before subjecting to NF. Thereafter, concentrate that is generated from nanofiltration and sludge from the pretreatment can be sent to sludge thickener.

5.2 Recommendations for further study

- Pretreatment of both of segregated wastewater i.e. low concentration wastewater and high concentration should be investigate with using the proposed option and subject the supernatant to the membrane filtration and determine the removal efficiency and permeate flux.

- Appropriate treatment option for the concentrate and the sludge generated after filtration and pretreatment should be evaluated.

- The physical and chemical characteristics of sludge cake and its potential to be recycled as a by product has to be investigated.

- Options for cleaner production and potential of permeate for reuse or recycle and recovery should be investigated.

- Since most of the raw materials used for production of dyes are toxic, and chemicals involved are benzene, naphthalene, quinoline and others, the state of occupational health of workers should also be focused.

- As the effluent is discharged into the sea (the gulf of Thailand), the effect on ecosystem should be investigated.

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APPENDIX A

Dyes Production Unit and List of equipments

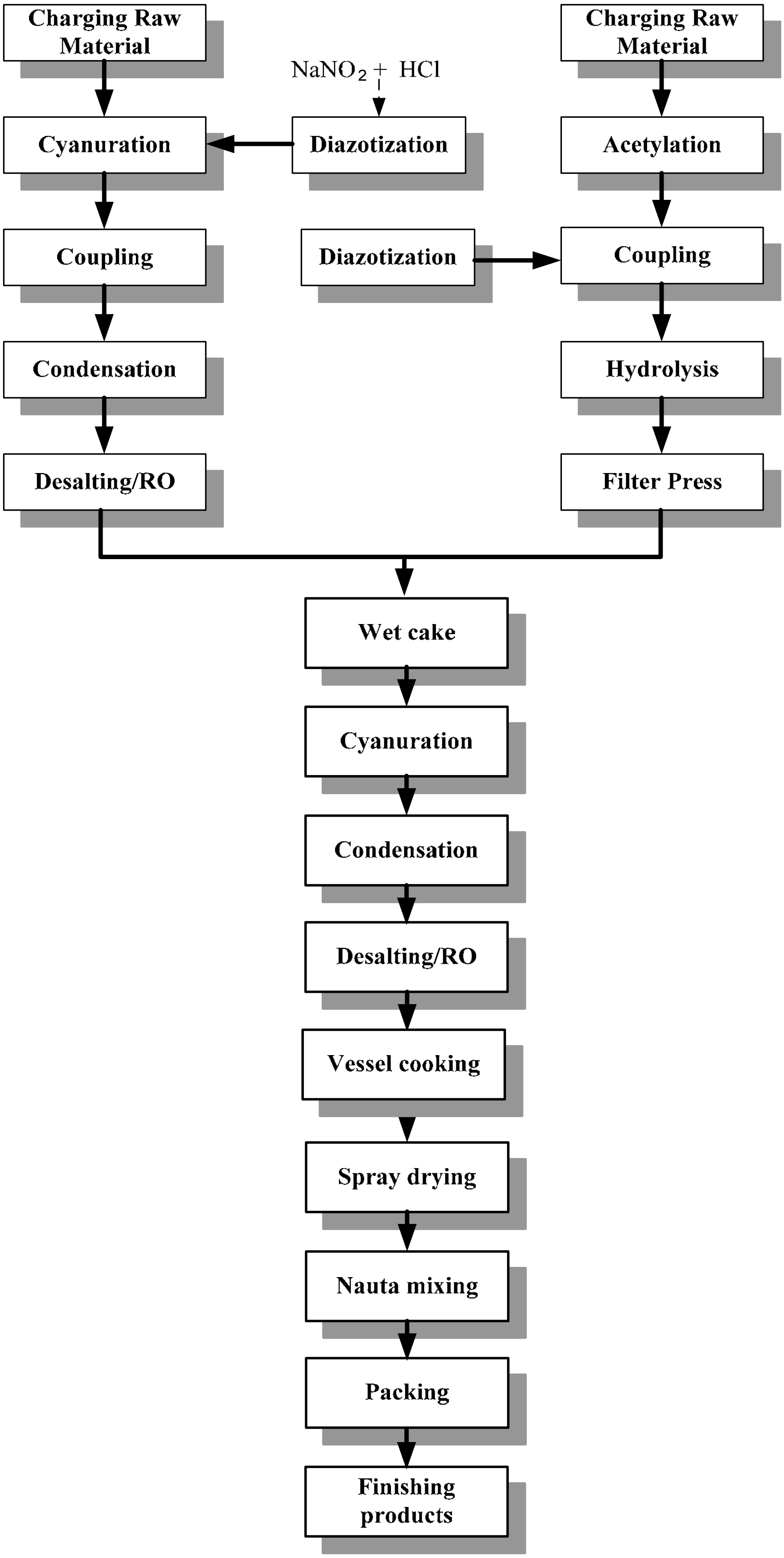

Figure A-1: Reactive dyes production process

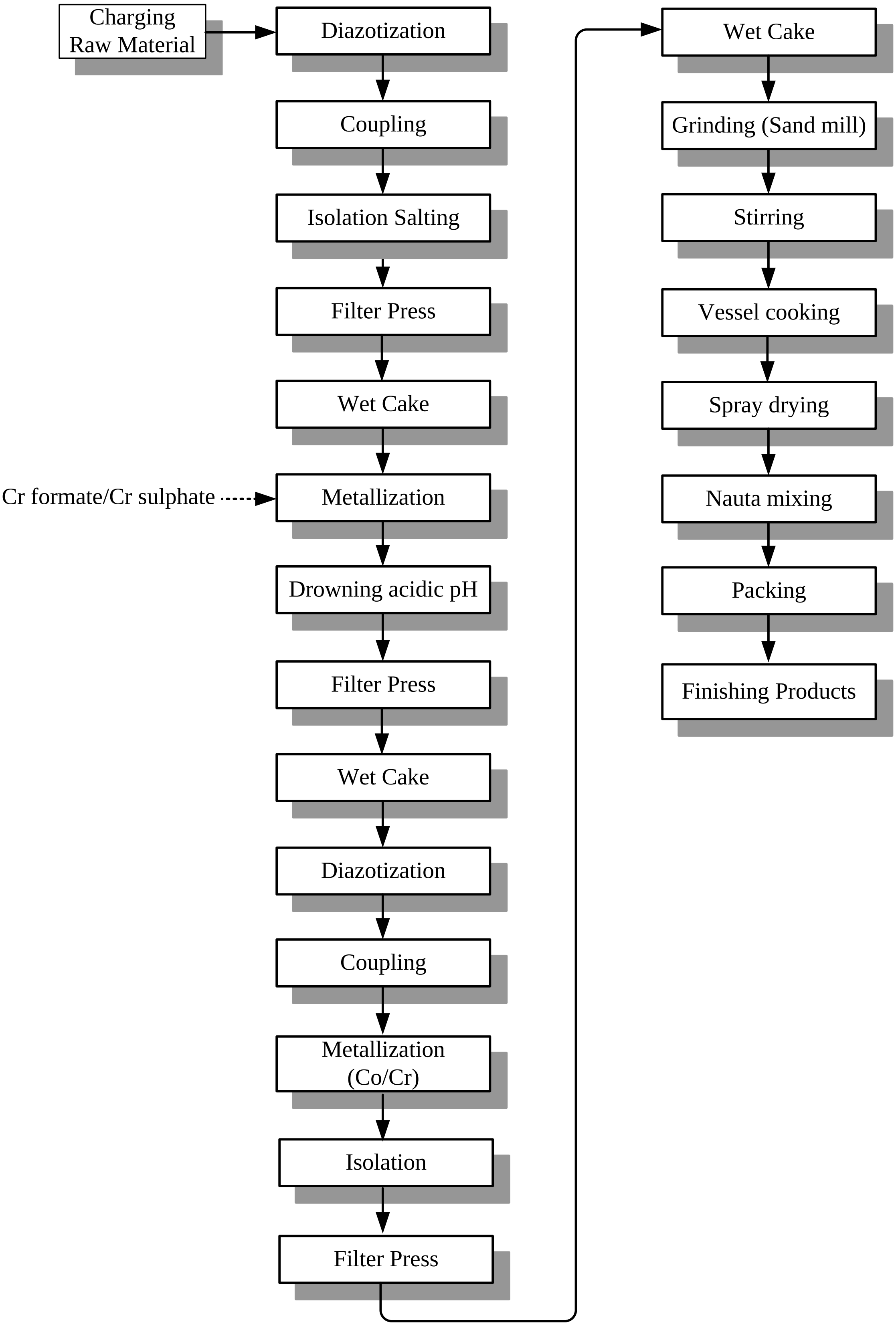

Figure A-2: Acid dyes production process

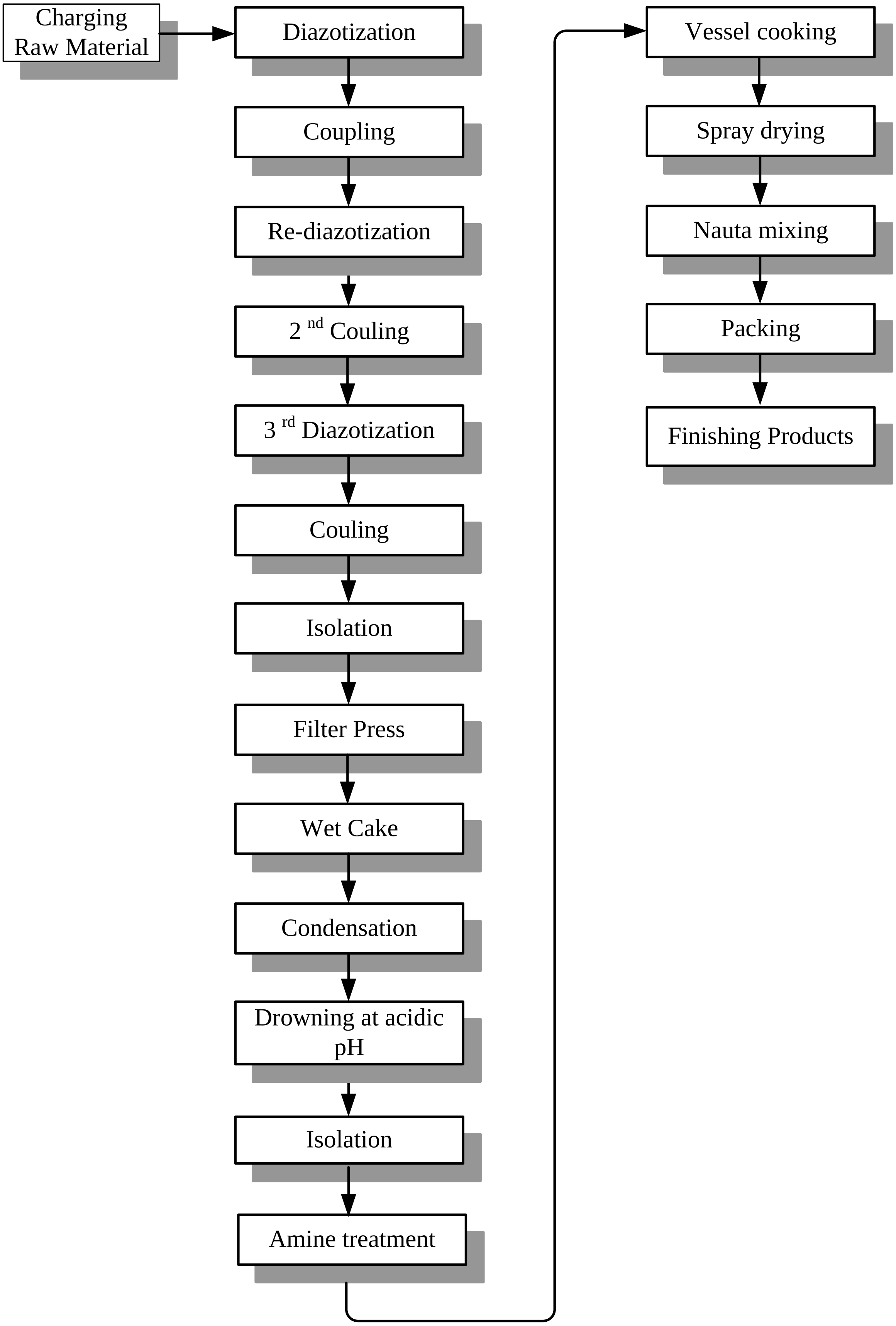

Figure A-3: Direct dyes production process

Table A-1: Definition of specific technical terms used in different stages of dyes synthesis

Specific technical term	Definition
Diazotization	In this stage is combination of amine-Naphthalene diazo component is prepared. Then, it reacts with HCl and $NaNO_2$ in the temperature range 0 – 5˚C/ 0 – 10˚C.
Couping	Coupling components, water, ice and caustic soda (Sodium bicarbonate) are mixed together with raw material in the temperature range of 5 – 10˚C.
Cyanuration	After the coupling, Cyanuric chloride ($C_3Cl_3N_3$) is added into the mixer vessel in order to get the required type of product.
Metallization	Chromium and Cobalt are metal which are added in the metallization stage in the temperature range of 0 – 95˚C.

1) List of equipment in Plant

Figure A-4: Filter Press

Figure A-5: Spray Dryer

Figure A-6: Stirrer

Figure A-7: Sand Mills

Figure A-8: Nauta mixer (Top view)

Figure A-9: Nauta mixer (Side view)

2) House keeping practices in Plant

Figure A-10: Wastewater from wet scrubber

Figure A-11: Chemical Spilled

Figure A-12: Ice spilled

Figure A-13: Spilling of dye during production

Table A-2 Water consumption

Type of Use	Quantity (m^3)
Batch operation	300
Ice production	100
Stream production	40
Bath room & Toilets	50
Washing equipment	150
Washing floors	30
Unaccounted water	30

APPENDIX B

Eco–mapping: Urban

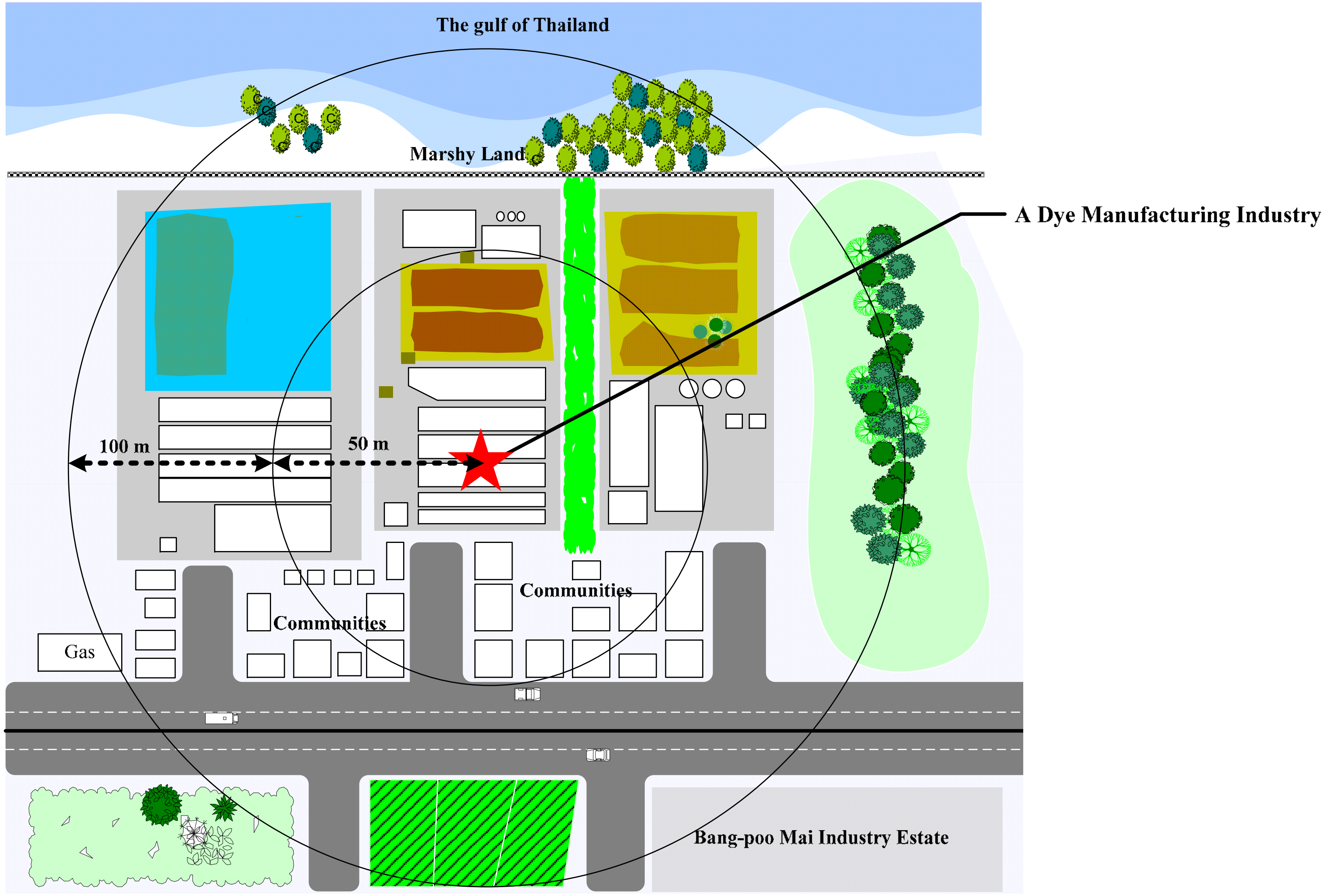

Figure B-1: Eco-mapping of urban

APPENDIX C

Experiment results

Table C-1: Wastewater characteristic in production processes

Process	pH value	TSS (mg/L)	TDS (mg/L)	COD (mg/L)
Blender washing of reactive dye	7.56	25	2430	1040
Blender washing of acid dye	9.67	3710	5968	10080
Filtrate from filter press of acid dye	8.20	490	68575	16000
Filtrate from filter press of reactive dye	6.82	7100	226680	48000
Filtrate from filter press of direct dye	7.95	3960	182790	58400
Spray drier washing of acid dye	8.41	10	494	120

Table C-2: Jar test by using Polyaluminium Chloride (PACl) as coagulation

Dosage (ppm)	pH value	Color (ADMI)	% Color removal	COD (mg/L)	% COD removal
0	6.92	6000	0.00	8602	0.00
250	5.05	2350	60.83	3427	60.16
500	4.38	1850	69.17	2932	65.91
1000	4.04	1300	78.33	3046	64.59
2000	3.86	1000	83.33	3046	64.59
4000	3.72	800	86.67	3541	58.84
5000	3.69	800	86.67	N/A	N/A

Table C-3: Jar test by using $FeCl_3$ as coagulation

Dosage (ppm)	pH value	Color (ADMI)	% Color removal	COD (mg/L)	% COD removal
Raw wastewater	7.35	6200	-	8231	-
4000	2.11	1800	70.97	3466	57.89
6000	2.09	1200	80.65	3466	57.89
7000	2.19	2300	62.90	3899	52.63
8000	2.12	3100	50.00	3899	52.63

Table C-4: Jar test by using Ciba X-COL 7105 as coagulation

Dosage (ppm)	pH value	Color (ADMI)	% Color removal	COD (mg/L)	% COD removal
0	7.14	6000	0.00	6160	0.00
3000	7.08	1000	83.33	3174	48.47
5000	7.09	227	96.22	2540	58.77
6000	7.11	132	97.80	2460	60.06
7000	7.21	87	98.55	2460	60.06
8000	7.15	67	98.88	2460	60.06
9000	7.03	60	99.00	2460	60.06
10000	6.90	50	99.17	2540	58.77
11000	6.84	48	99.20	2746	55.42
13000	6.75	45	99.25	2936	52.34

Table C-5: Jar test by combination between $FeCl_3$ and Ciba X-COL 7105 as coagulation (Run 1)

Dosage of Ciba X-COL 7105 (ppm)	Dosage of $FeCl_3$ at 6000 ppm				
	pH value	**Color (ADMI)**	**% Color removal**	**COD (mg/L)**	**% COD removal**
500	2.30	2300	63.49	4400	54.55
1000	2.29	1900	69.84	3960	59.09
2000	2.24	2600	58.73	3960	59.09
3000	2.23	2600	58.73	5280	45.45
4000	2.22	2300	63.49	4400	54.55
Raw wastewater	7.31	6300	-	9680	-
Dosage of $FeCl_3$ (ppm)	**Dosage of Ciba X-COL 7105 at 1000 ppm**				
	pH value	**Color (ADMI)**	**% Color removal**	**COD (mg/L)**	**% COD removal**
2000	4.55	7800	32.17	11000	28.57
4000	2.84	3000	73.91	7040	54.29
6000	2.29	2000	82.61	6600	57.14
8000	2.24	2400	79.13	6160	60.00
10000	2.15	2100	81.74	62.86	62.86
Raw wastewater	7.31	11500	-	15400	-

Table C-6: Jar test by combination between $FeCl_3$ and Ciba X-COL 7105 as coagulation (Run 2)

Coagulants	Color (ADMI)	% Color removal	COD (mg/L)	% COD removal
$FeCl_3$ at 6000 ppm + Ciba X-COL 7105 at 1000 ppm	1550	86.97	6345	57.58
Raw wastewater	11900	-	14956	-

Table C-7: Sludge Volume Index (SVI) analysis

Volume of wastewater	Sample	Time measuring the settled volume of sludge (mL)				
		0 min.	**30 min.**	**1 hr**	**1.30 hrs**	**2 hrs**
1 L	1	1080	1070	1060	1050	1040
	2	1080	1070	1060	1050	1040
	Average	1080	1070	1060	1050	1040

****** Suspended solid of this wastewater = 2326.7 mg/L

Calculation of SVI as below:

$$\text{SVI} = \frac{\text{Settled sludge volume (mL/L) X 1000 mg/g}}{\text{Suspended solids (mg/L)}} = \text{mL/g}$$

$$\text{Thus,} \quad \text{SVI} = \frac{1070 mL/L \quad x \quad 1000 mg/g}{2326.7 mg/L}$$

$$= 459.88 \text{ mL/g} \sim 460 \text{ mL/g}$$

Table C-8: Fenton’s reagent analysis

Fe^{2+} (M)	H_2O_2 1 .0 M									
	Supernatant before stop reaction					Supernatant after stop reaction				
	pH value	Color (ADMI)	% Color removal	COD (mg/L)	% COD removal	pH value	Color (ADMI)	% Color removal	COD (mg/L)	% COD removal
0.1	2.14	612	89.80	1440	78.67	12	149	97.52	880	86.96
0.2	2.13	726	87.90	2000	70.37	12	174	97.10	880	86.96
0.3	2.11	766	87.23	1600	76.30	12	182	96.97	760	88.74
0.4	1.97	719	88.02	1800	73.34	12	173	97.12	640	90.52
Raw wastewater	7.14	6000	-	6751	-	7.14	6000	-	6751	-

H_2O_2 (M)	Fe^{2+} 0.1 M									
	Supernatant before stop reaction					Supernatant after stop reaction				
	pH value	Color (ADMI)	% Color removal	COD (mg/L)	% COD removal	pH value	Color (ADMI)	% Color removal	COD (mg/L)	% COD removal
0.2	2.15	3950	34.17	2762	59.09	12	500	91.67	2324	65.58
0.4	2.14	661	88.98	2411	64.29	12	326	94.57	1534	77.28
0.6	2.11	643	89.28	2192	67.53	12	226	96.23	1447	78.57
0.8	2.09	616	89.73	2191	67.53	12	183	96.95	1403	79.22
Raw wastewater	7.14	6000	-	6751	-	7.14	6000	-	6751	-

Table C-9: Permeate characteristic after passing though the membrane

Parameter	Unit	Raw wastewater	Membrane Cross Flow System			
			UF	% removal	NF	% removal
TDS	mg/L	32770	27835	15.06	23280	28.96
TSS	mg/L	1545	455	70.55	313	79.74
COD	mg/L	16909	6442	61.90	4,294	74.61
Color	ADMI	10200	900	91.18	90	99.12
Conductivity	mS/cm	40.2	38.8	3.48	35.9	10.70
Ca	(mg/L)	59.095	27.228	53.93	16.878	71.44
Co	(mg/L)	10.305	0.041	99.60	0.003	99.97
Cr	(mg/L)	117.180	4.671	96.01	0.133	99.89
Cu	(mg/L)	9.155	0.026	99.72	0.012	99.87
Li	(mg/L)	6.880	5.696	17.21	5.742	16.54
Mn	(mg/L)	0.324	0.139	57.10	0.076	76.54
Mo	(mg/L)	0.016	0.002	87.50	0.000	100.00
Ni	(mg/L)	0.084	0.006	92.86	0.001	98.81
Pb	(mg/L)	0.064	0.002	96.88	0.000	100.00
Sr	(mg/L)	0.301	0.169	43.85	0.113	62.46
Mg	(mg/L)	19.815	10.899	45.00	7.598	61.66
Cd	(mg/L)	0.010	0.001	90.00	0.001	90.00
Fe	(mg/L)	16.045	0.158	99.02	0.017	99.89
Zn	(mg/L)	0.247	0.013	94.74	0.015	93.93

1) Calculation of permeate flux

Permeate flux (L/m^3.h) = $\frac{Q_p}{A}$

Membrane Area (A) = πr^2 **,** r = 3.56 cm^2

$$= 3.14 \text{ x } 3.65^2$$

$$= 41.83 \text{ cm}^2 = 0.42 \text{ m}^2$$

Thus, $\text{Permeate flux} = \frac{Q_p(mL/\min.)}{0.42m^2} x \frac{1L}{1000mL} x \frac{1hr}{60\min.}$

$= \frac{Q_p(mL/\min.)}{25200}$ **;** Qp = Permeate flow rate, mL/min.

APPENDIX D

Coagulant Information

1) Polyaluminium Chloride (PACl)

Description: It is a type of water-soluble inorganic polymers and molecular weight.

Physical and Chemical properties:

Form	Liquid
Appearance and Odor	Colorless liquid with little or no odor
Molecular formula	$Al_n(OH)_mCl_{3n-m}$.
pH	2.0-2.5
Concentration	10% as Al_2O_3
Specific gravity	1.20 at 20 °C

Storage: Bulk quantities should be stored in Ebonite coated steel, rubber-linedmild-steel Glass fiber or plastic tanks. For small packages polyethylene or double skinned polyethylene containers are acceptable.

2) Ciba X-COL 7105 coagulant

Other name: Aqueous solution of a low molecular weight cationic resin.

Description:

- Ciba X-COL 7105 is cationic organic color removal coagulant and highly cationic liquid grade coagulant. It is supplied in a solution form.
- Ciba X-COL 7105 is low molecular weight.
- The main use of Ciba X-COL 7105 is in the treatment of color effluents from the textile industry. Ciba X-COL 7105 is mostly effective in the treatment of dyestuff where reactive dyes are present.
- Ciba X-COL 7105 will proceed as a single stage treatment. However, in many case its performance will be enhanced when used in combination with the appropriate ZETAG or MAGNAFLOC flocculant, which will aid separation of the coagulated material from the supernatant liquors.

Physical and chemical properties:

Form	Liquid
Color	Clear colorless
Relative density	1.3 g/cm^3
Viscosity	Approximately 500 cPs
Flash point (Closed cup)	300˚ C
pH of 1% solution	Approximately 4.5
Storage	At temperature of 10˚ C – 25˚ C a shelf life in excess of 12 months is expected. Prolonged storage at temperatures outside of this range should be avoided where possible. Solution of Ciba X-COL 7105 of 0.5 - 1% which have been prepared should not be kept in excess of

5 days, as after this, loss of product efficiency may occur.

Corrosive Properties:

Ciba X-COL 7105 is moderately corrosive towards mid steel, cast iron, aluminium and zinc surfaces and use of these should be avoided. Recommended materials of construction are stainless steel, fibre glass, polyethylene and polypropylene.

APPENDIX E

Pretreatment Cost Analysis

1) Pretreatment cost analysis

Table E-1: Optimum dosage of coagulants

Treatment Options	Coagulant	Optimum dosage (ppm)	Mass of chemical (kg/L)
A	PACl 10%	500	0.006
B	$FeCl_3$	6000	0.006
C	Ciba X-COL 7105	6000	0.006
D	$FeCl_3$ + Ciba X-COL 7105	6000 + 1000	0.006 + 0.001
E	Fenton's reagent ($Fe^{2+} + H_2O_2$)	0.1 M + 1.0 M	28g + 0.114 L

Table E-2: Cost of Chemicals

Chemical name	Approximate Cost	Source
PACl	8 Baht/kg	Thaiengineering. (2007)
$FeCl_3 \cdot 6H_2O$ (commercial grade)	10 Baht/kg	TACL. (2008).
Ciba X-COL 7105	70 Baht/ kg	TACL. (2008).
H_2SO_4 98% solution	280 Baht/L	EEM Laboratory. (2008)
$FeSO_4 \cdot 7H_2O$ (commercial grade)	10 Baht/kg	PPM chemical. (2008)
H_2O_2	1,150 Baht/ L	EEM Laboratory. (2008)
NaOH (commercial grade)	27 Baht/kg	PPM chemical. (2008)

Option A: Polyaluminium Chloride (PACl)

Calculation cost of chemical

Mass of PACl 10% solution = Density of PACl x volume of chemical used

Where, Density of PACl = 1.20

PACl 10% = 100,000 ppm

Thus, volume of PACl used is 5 mL/L of WW at optimum dosage 500ppm ·········► $C_1V_1 = C_2V_2$

So, Mass of PACl 10% solution = 1.20 x 5 ml
= 6 g/ L of WW
= 0.006 kg/L of WW

Cost of PACl 10% solution (Baht) = Mass of chemical (kg/L of WW) x Chemical price (Baht/kg) x 1000 L/m^3ofWW
= 0.006 mL/L x 8 Baht/L x 1000 L/m^3
= 48 Baht/m^3 of WW

Option B: Ferric Chloride ($FeCl_3$)

Cost of chemical = Mass of chemical (kg/L of WW) x Chemical price (Baht/kg) x 1000 L/$m^3$of WW
= 0.006 kg/L x 10 Baht/kg x 1000 L/m^3
= 60 Baht/m^3 of WW

Option C: Ciba X-COL 7105

Cost of chemical = Mass of chemical (kg/L of WW) x Chemical price (Baht/kg) x 1000 L/$m^3$of WW
= 0.006 kg/L x 70 Baht/kg x 1000 L/m^3
= 420 Baht/m^3 of WW

Option D: Combination of $FeCl_3$ and Ciba X-COL 7105

1) Mass of NaOH

Volume of 1 M NaOH used for pH adjustment was about 30 mL/L of WW that was about 1.2 g/L

Thus, Cost of chemical = Mass of chemical (kg/L of WW) x Chemical price (Baht/kg) x 1000 L/$m^3$of WW
= 0.0012 kg/L x 27 Baht/kg x 1000L/m^3
= 32.4 ~ 33 Baht/m^3 of WW

2) Total cost of chemical = Cost of Option B + [Mass of Ciba X-COL 7105l (kg/L of WW) x Chemical price (Baht/kg) x 1000 L/$m^3$of WW] + Cost of NaOH
= 60 Baht/m^3 of WW +[0.001 kg/L x70Baht/kg x 1000 L/m^3] + 33 Baht/m^3 of WW
= 163 Baht/m^3

Therefore, treatment cost of combination between $FeCl_3$ and Ciba X-COL 7105 is 70 Baht/ m^3 of wastewater.

Option E: Fenton's reagent

1) Mass of 0.1 M Fe^{2+}

1 M Fe^{2+} = 278.01 g (MW of $FeSO_4 \bullet 7H_2O$)
For 0.1 M Fe^{2+} = 27.801 ~ 28 g
= 0.028 kg

Cost of chemical = Mass of chemical (kg/L of WW) x Chemical price (Baht/kg) x 1000 L/$m^3$of WW
= 0.028 kg/L x 10 Baht/kg x 1000 L/m^3
= 280 Baht/m^3 of WW

2) Volume of 1M H_2O_2

Stock solution of 30% H_2O_2 was prepared using 300 g H_2O_2 in 1 L of solution

Where, 1 M = 34 g

For 30% H_2O_2 = 113.3 ~ 114 mL $\cdots\cdots\cdots\blacktriangleright \frac{34g \times 1000mL}{30g}$

= 0.114 L

Thus, cost of chemical = Volume of chemical (L/L of WW) x Chemical price (Baht/kg) x 1000 L/$m^3$of WW
= 0.114 L/L of WW x 1150 Baht/L x 1000 L/m^3
= 131,100 Baht/m^3 of WW

3) Volume of H_2SO_4 98% solution

Volume of H_2SO_4 98% solution used for pH adjustment was about 1 mL/L of WW.

Thus, Cost of chemical = Volume of chemical (L/L of WW) x Chemical price (Baht/L) x 1000 L/$m^3$of WW
= 0.001 L/L of WW x 280 Baht/kg x 1000 L/m^3
= 280 Baht/m^3 of WW

4) Mass of NaOH

Volume of 3 M NaOH used for pH adjustment was about 20 mL/L of WW that was about 20000 mL/m^3 of WW. So, mass of NaOH was used for preparing 3 N NaOH stock solution about 2400 g/m^3 of WW.

Thus, Cost of chemical = Mass of chemical (kg/L of WW) x Chemical price (Baht/kg) x 1000 L/$m^3$of WW
= 2.4 kg/m^3 x 27 Baht/kg
= 64.8 ~ 65 Baht/m^3 of WW

Therefore, treatment cost of Fenton’s reagent is 280+131,100+280+65 = 131,725 Baht/ m^3 of wastewater.

TREATABILITY STUDIES ON THE WASTEWATER FROM A DYE MANUFACTURING INDUSTRY

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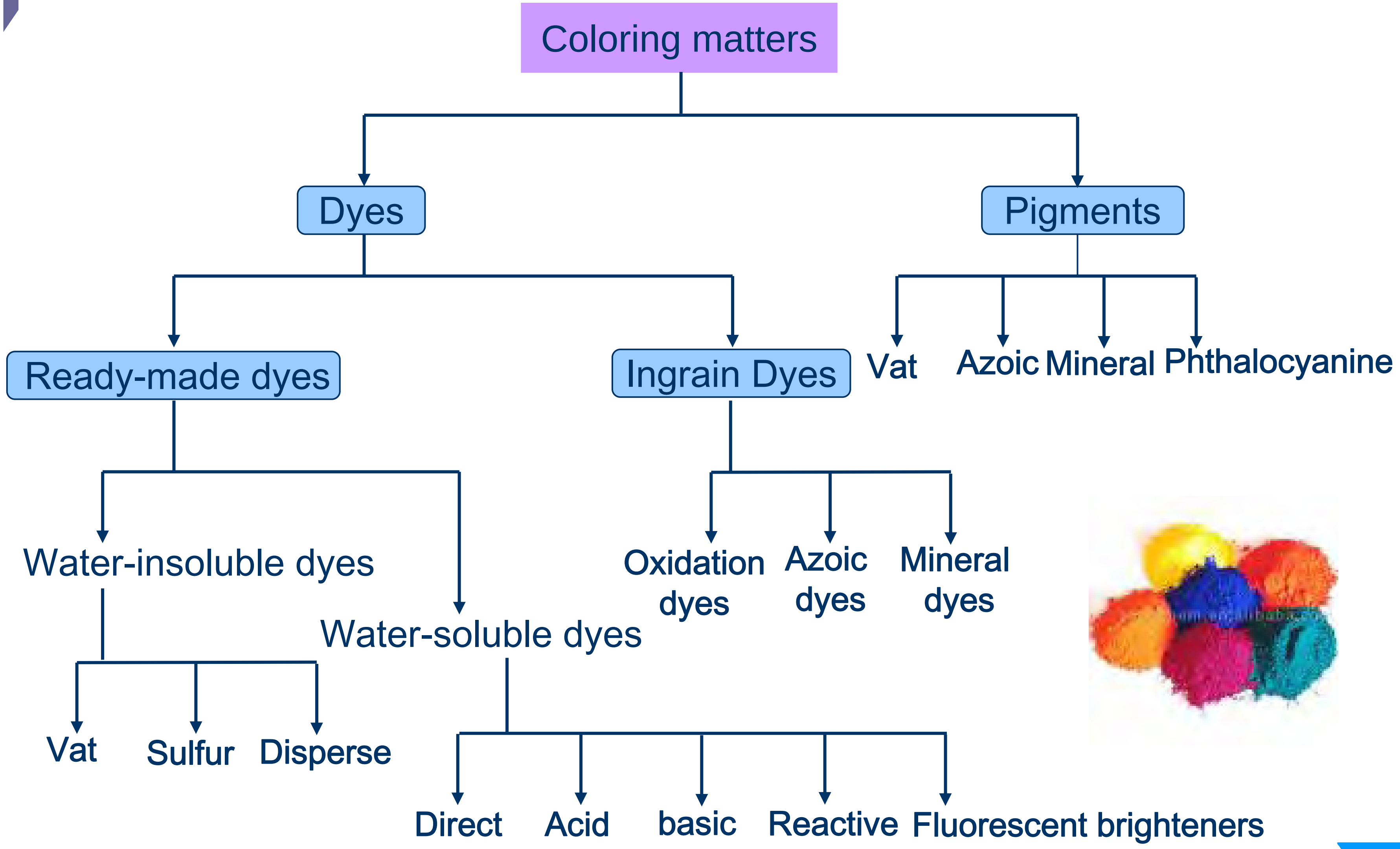
Environmental Engineering and Management
School of Environment, Resources and Development
Asian Institute of Technology

23 April 2008

CONTENTS OF PRESENTATION

- ✍ Literature Review
- ✍ Objectives & Scope of the study
- ✍ Methodology
- ✍ Results & Discussions
- ✍ Conclusions & Recommendations

Dyes Classification



Coloring matters

Dyes

Pigments

Ready-made dyes

Ingrain Dyes

Vat

Azoic

Mineral

Phthalocyanine

Water-insoluble dyes

Water-soluble dyes

Oxidation dyes

Azoic dyes

Mineral dyes

Vat

Sulfur

Disperse

Direct

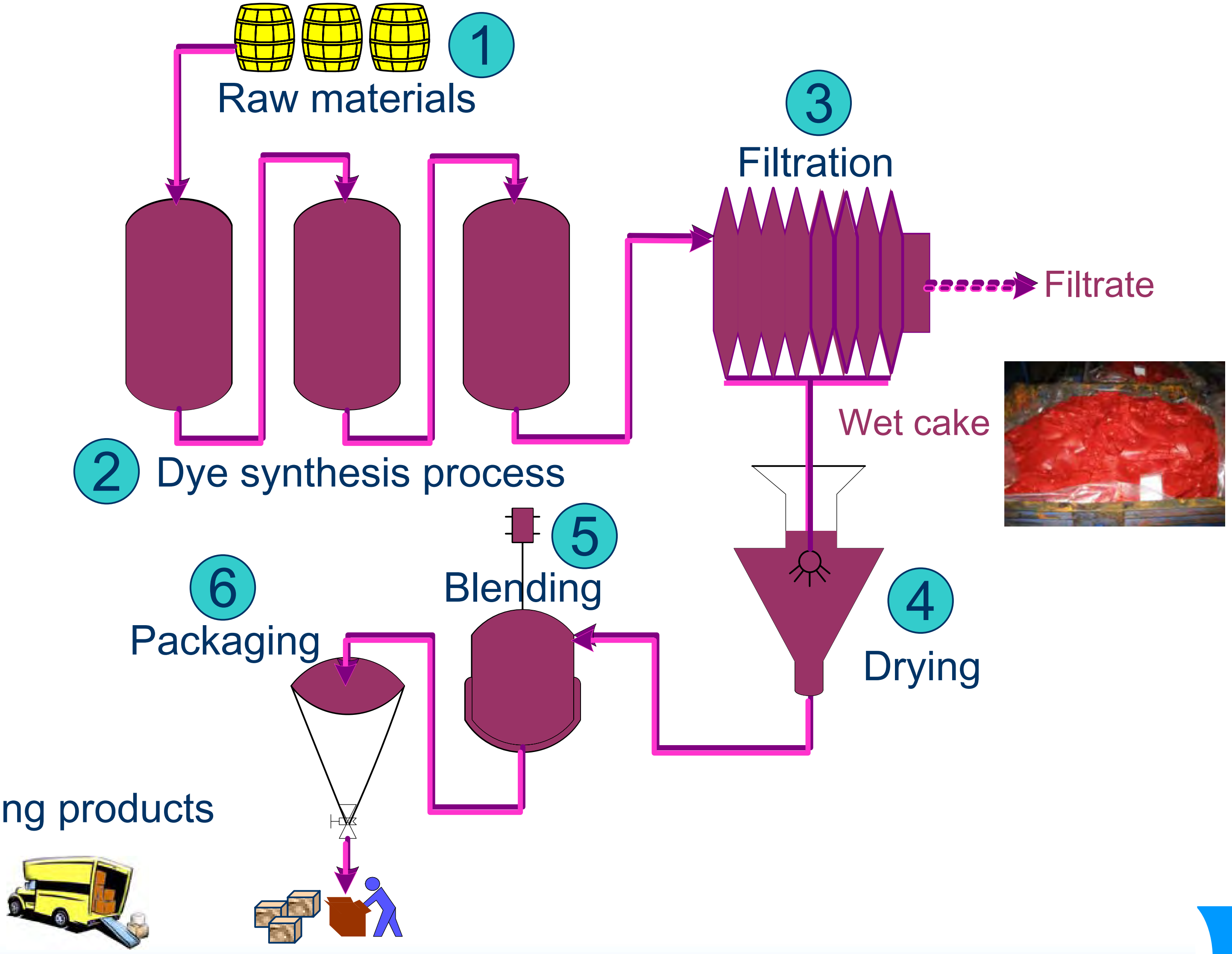
Acid

basic

Reactive

Fluorescent brighteners

Dye Production Process



① Raw materials

② Dye synthesis process

③ Filtration

Filtrate

Wet cake

④ Drying

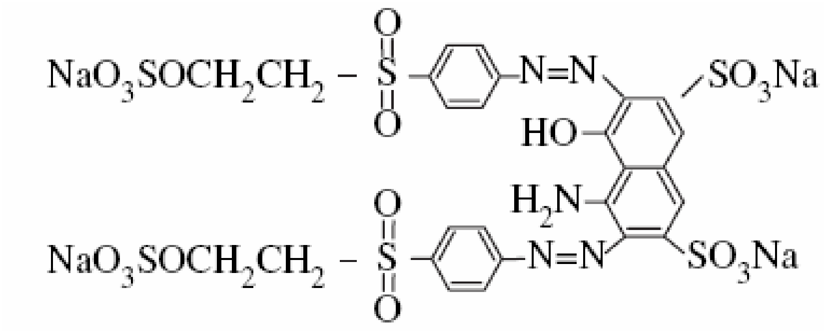
⑤ Blending

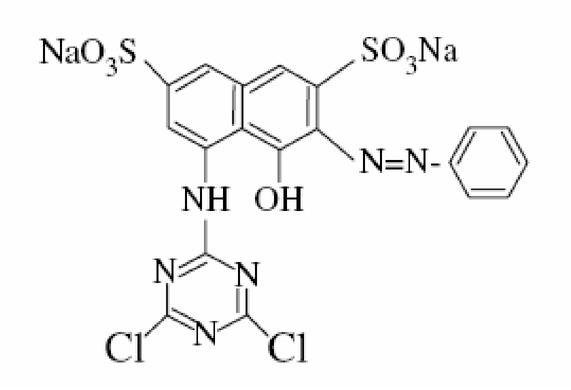
⑥ Packaging

Transporting products

Overview of Dye Manufacturers

- Large amounts of dyes are produced and applied in various industries
- High amount of wastewater is generated and highly variable characteristics
- Dyes are complex compounds with a big complicated molecular structure and toxicity





- Dye wastewater is difficult to treat

Polluting Substances in Dye Wastewater

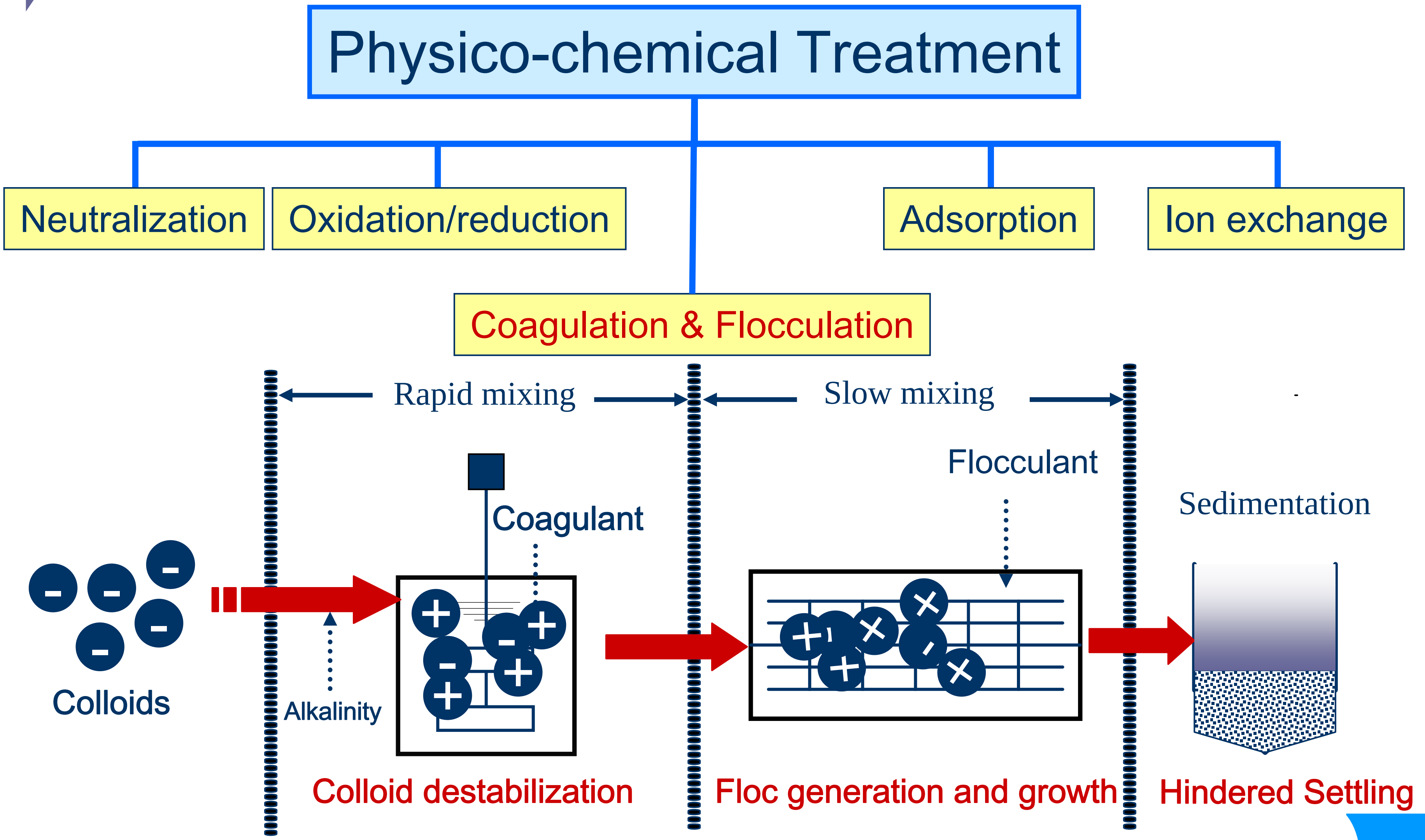
- Physical
  - Gases
  - Liquids
  - Solids
    - Floating
    - Settleable
    - Colloidal
    - Dissolved
- Chemical
  - Organic
  - Inorganic
- Biological
  - Pathogenic
  - Non-pathogenic

Easy

removal

Difficult

Wastewater treatment methods



Physico-chemical Treatment

- Neutralization
- Oxidation/reduction
- Coagulation & Flocculation
- Adsorption
- Ion exchange

Rapid mixing

Slow mixing

Colloids

Alkalinity

Coagulant

Flocculant

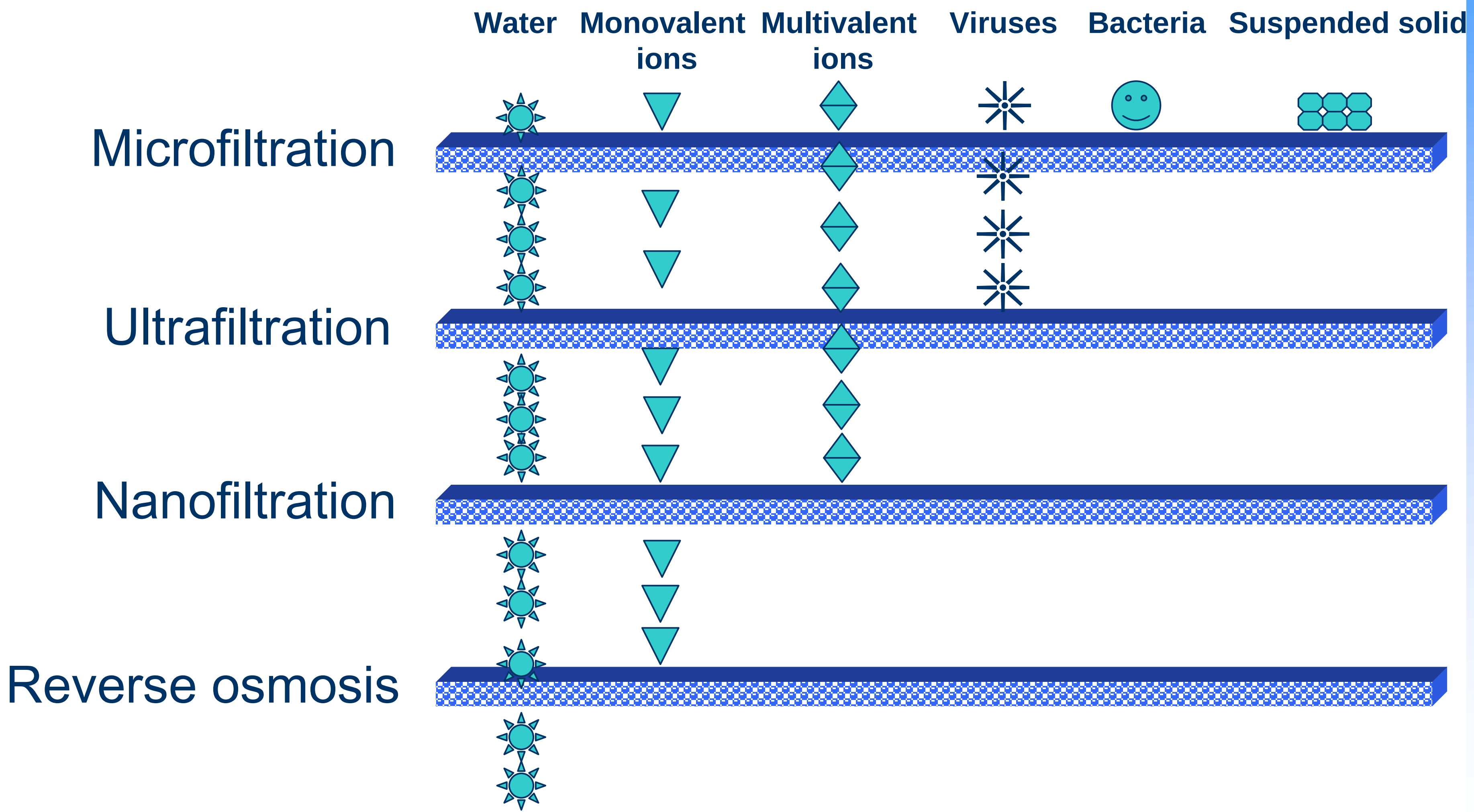
Sedimentation

Colloid destabilization

Floc generation and growth

Hindered Settling

Membrane Technology



Objectives

- To evaluate wastewater quality by conducting physical and chemical analysis, and assess the efficiency of existing treatment plant
- To identify possible in–plant modifications to conserve water and minimize the release of polluting substances in the wastewater
- To identify and recommend appropriate treatment based on the effluent quality standards of Ministry of Industry Thailand

Scope of the Study

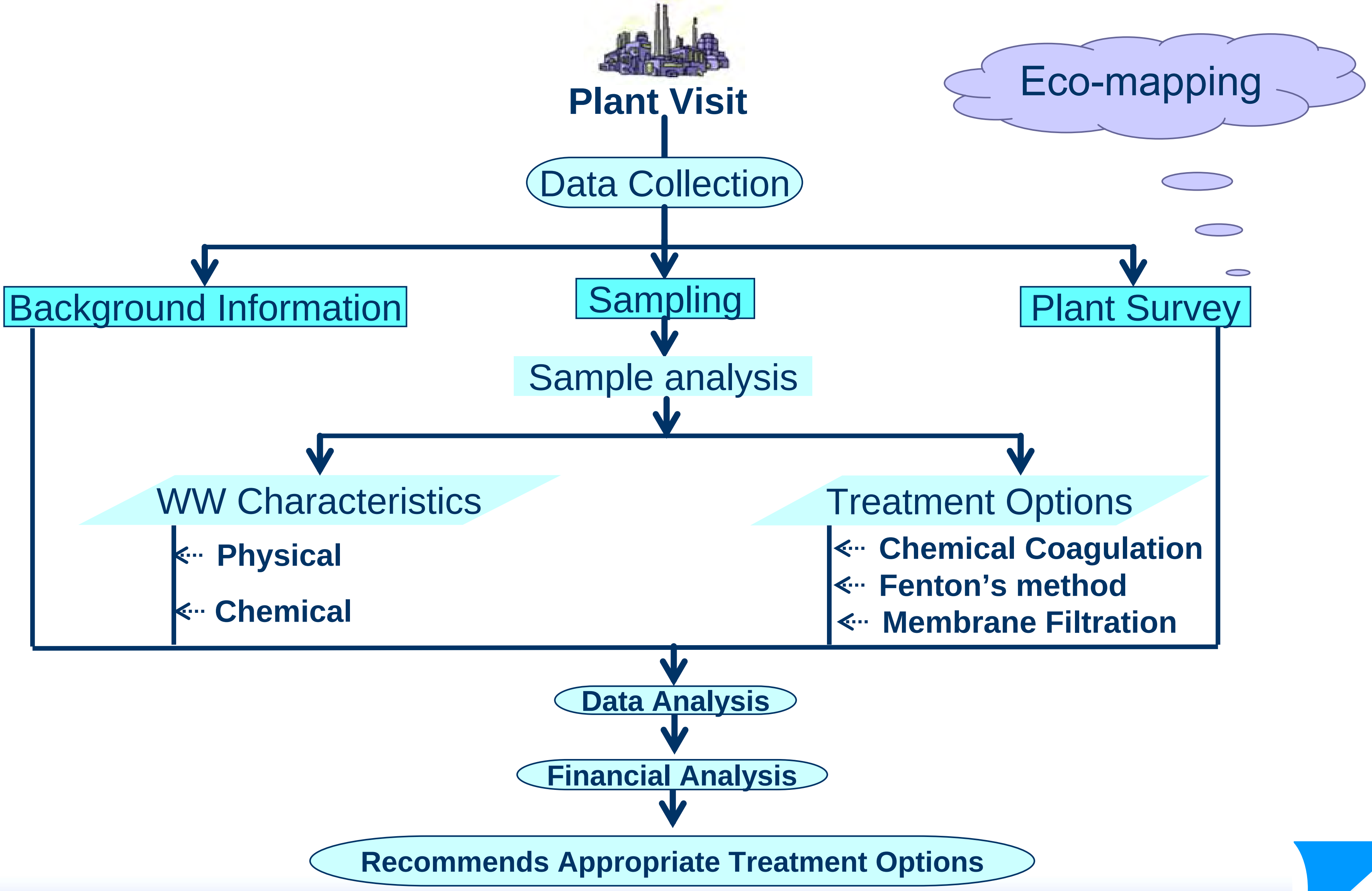
Evaluate an existing situation of dyestuff Plant at Samut Prakan, Thailand

Analyze the production process, Water consumption and characteristics of wastewater generation

Suggest options for reducing water consumption and improving WWTP by treatability studies

Investigate financial analysis for proposing suitable method

Overall Work Approach



Plant Visit

Eco-mapping

Data Collection

Background Information

Sampling

Plant Survey

Sample analysis

WW Characteristics

- **Physical**
- **Chemical**

Treatment Options

- **Chemical Coagulation**
- **Fenton's method**
- **Membrane Filtration**

Data Analysis

Financial Analysis

Recommends Appropriate Treatment Options

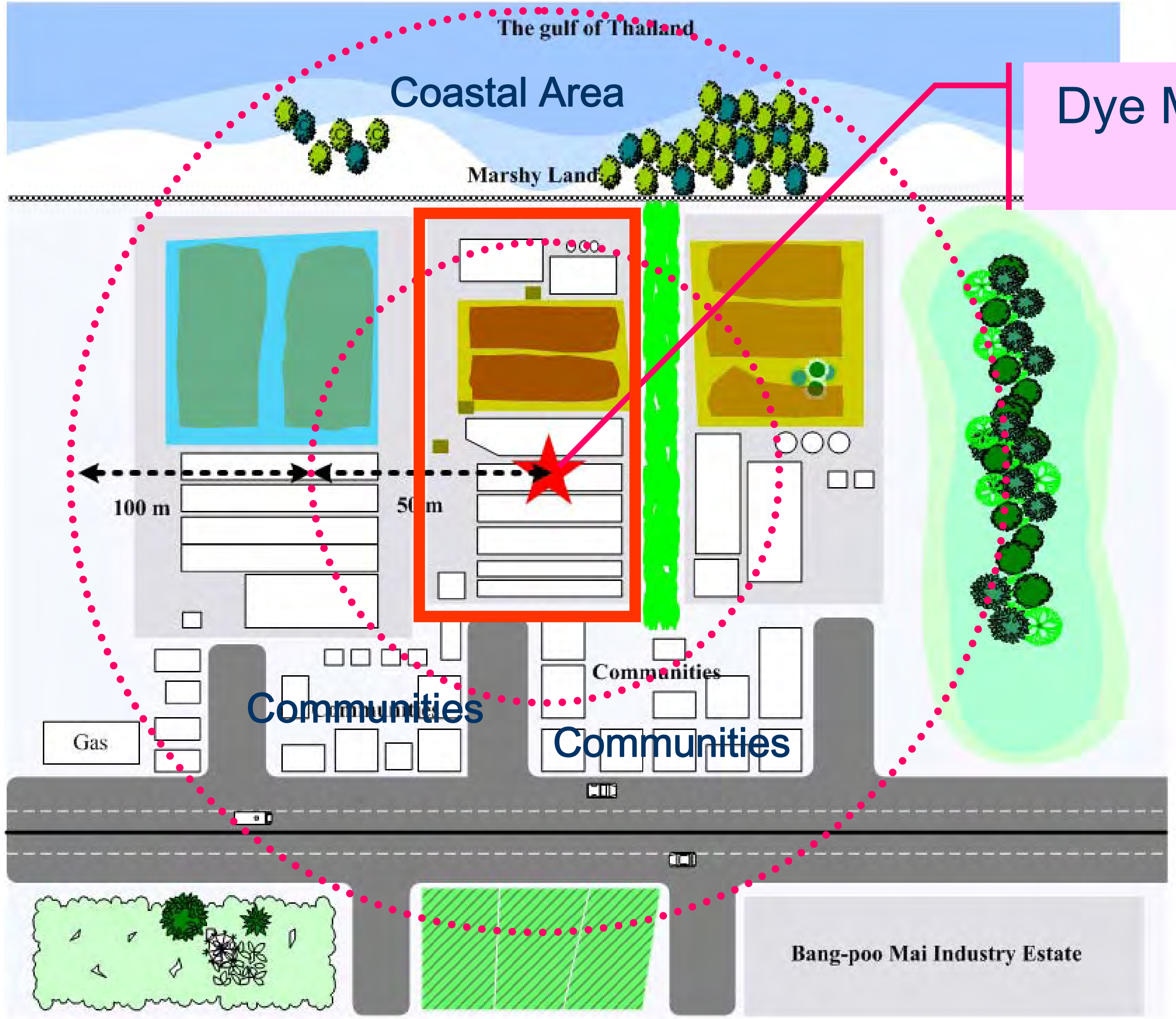
Background Information

Background Data

- Plant Information
  - Plant location
  - Plant layout
  - Time operation
  - Products
  - Raw material used
  - Process flow diagram
- Water Information
  - Plant location
  - Plant layout
- WW Information
  - WW generation
  - Layout of WWTP
  - Layout of drainage system
  - Sludge disposal

Results and Discussions

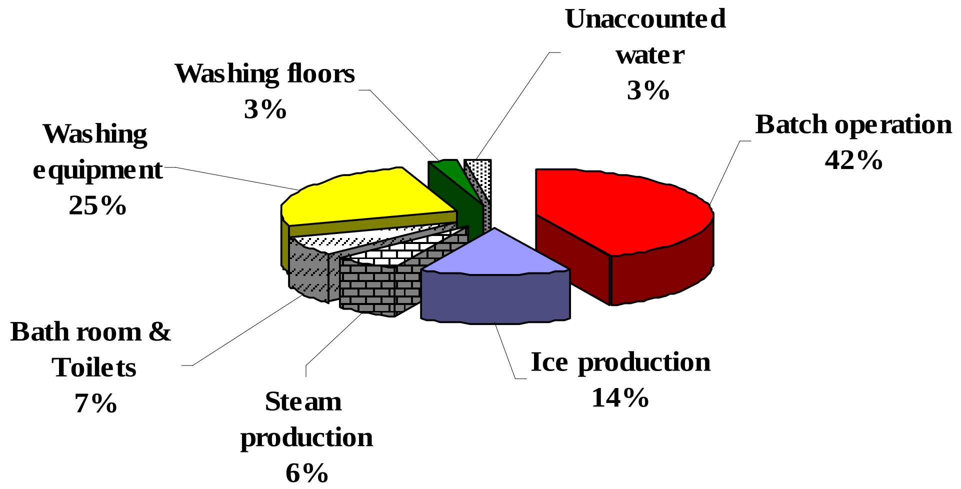
Plant Location



Dye Manufacturing Industry

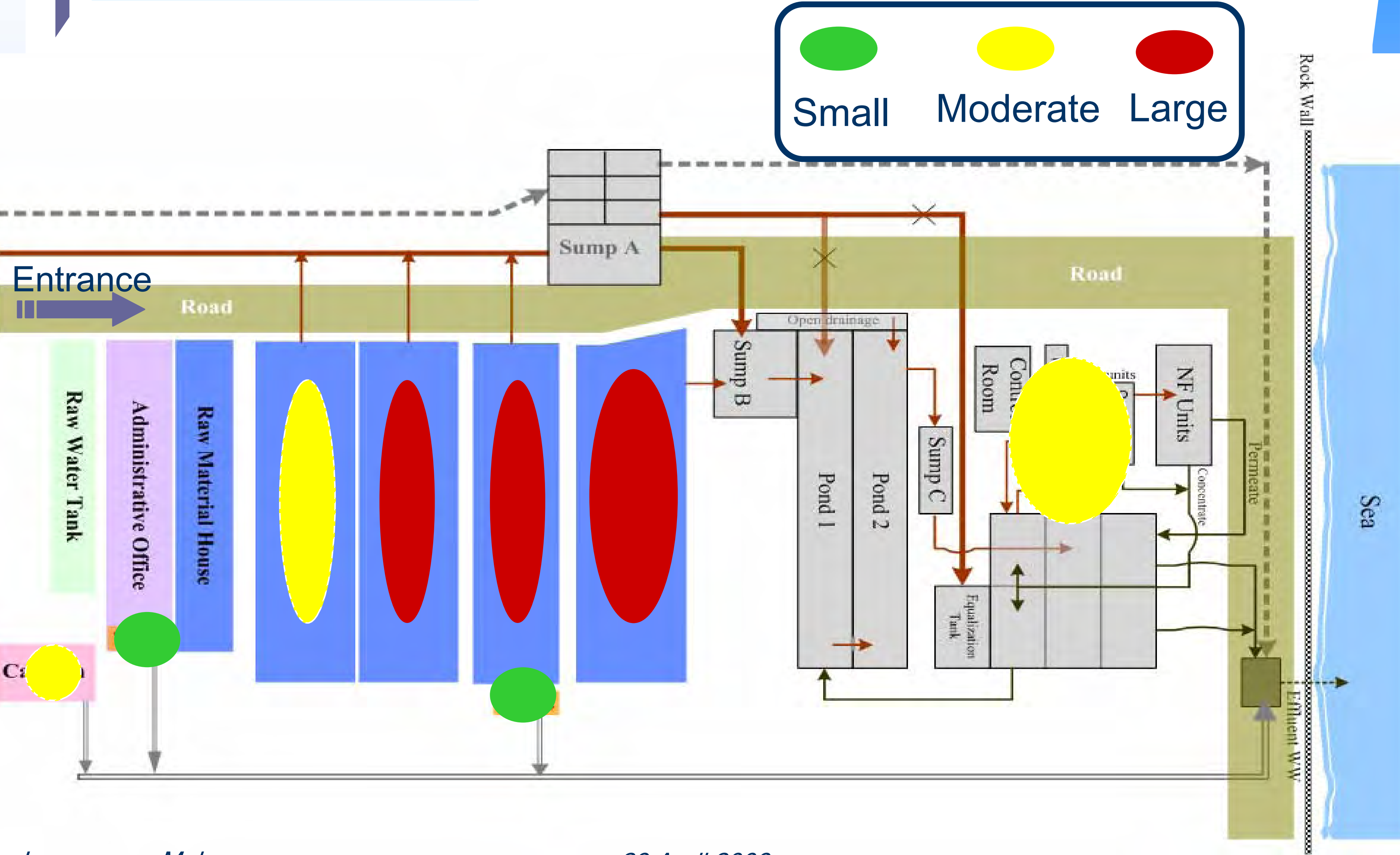
Company Profile

- Produces acid dyes, reactive dyes, direct dyes and disperse dyes
- Duration of a typical batch → ~ 3 days
- Final products → ~ 10 tons/day
- Raw water consumption → ~ 700 m^3/day



- Wastewater generated → ~600 – 650 m^3/day

Eco-mapping: Water consumption and WW generation



🟢 Small 🟡 Moderate 🔴 Large

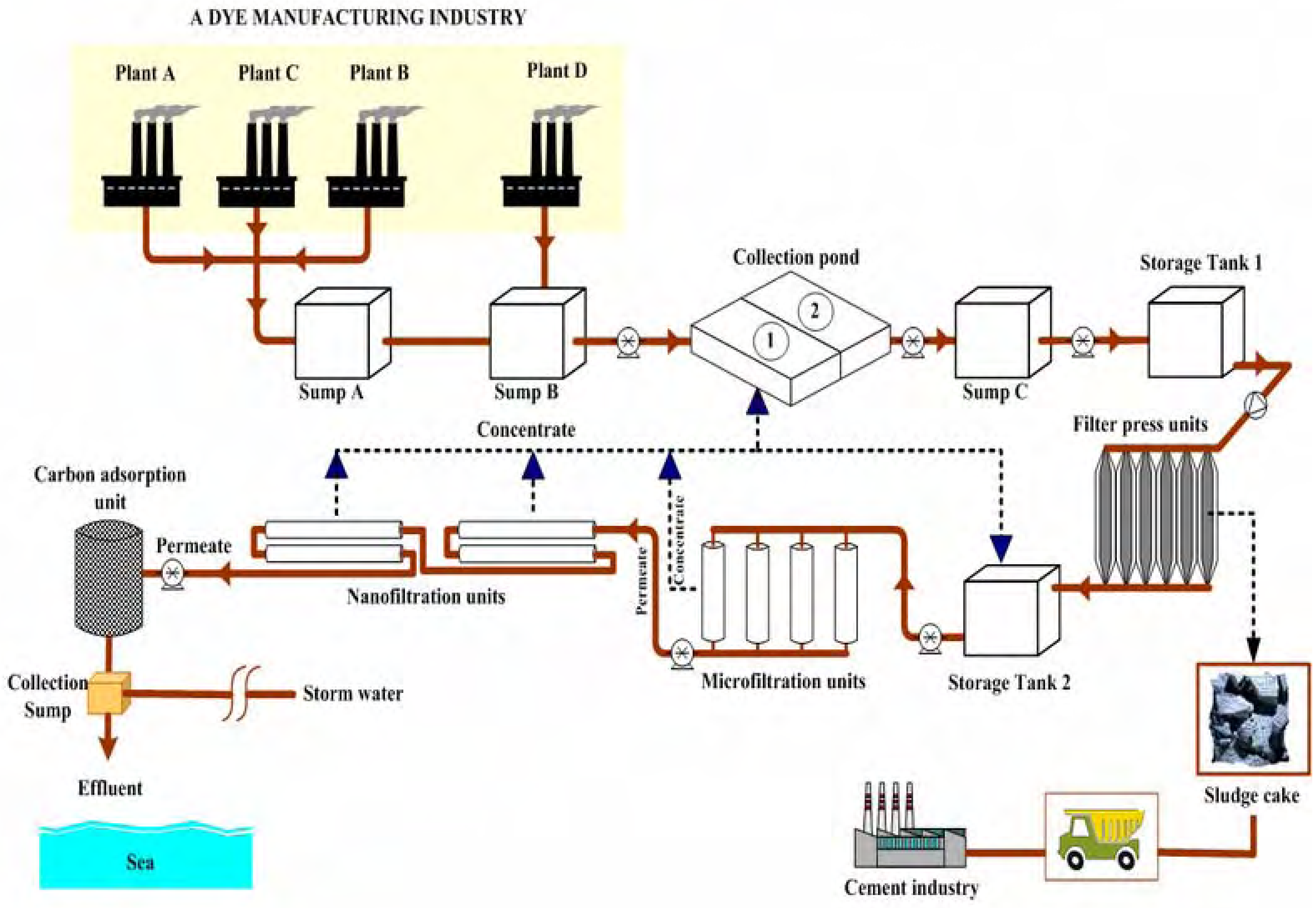
Poor Housekeeping Practices

- Spilling

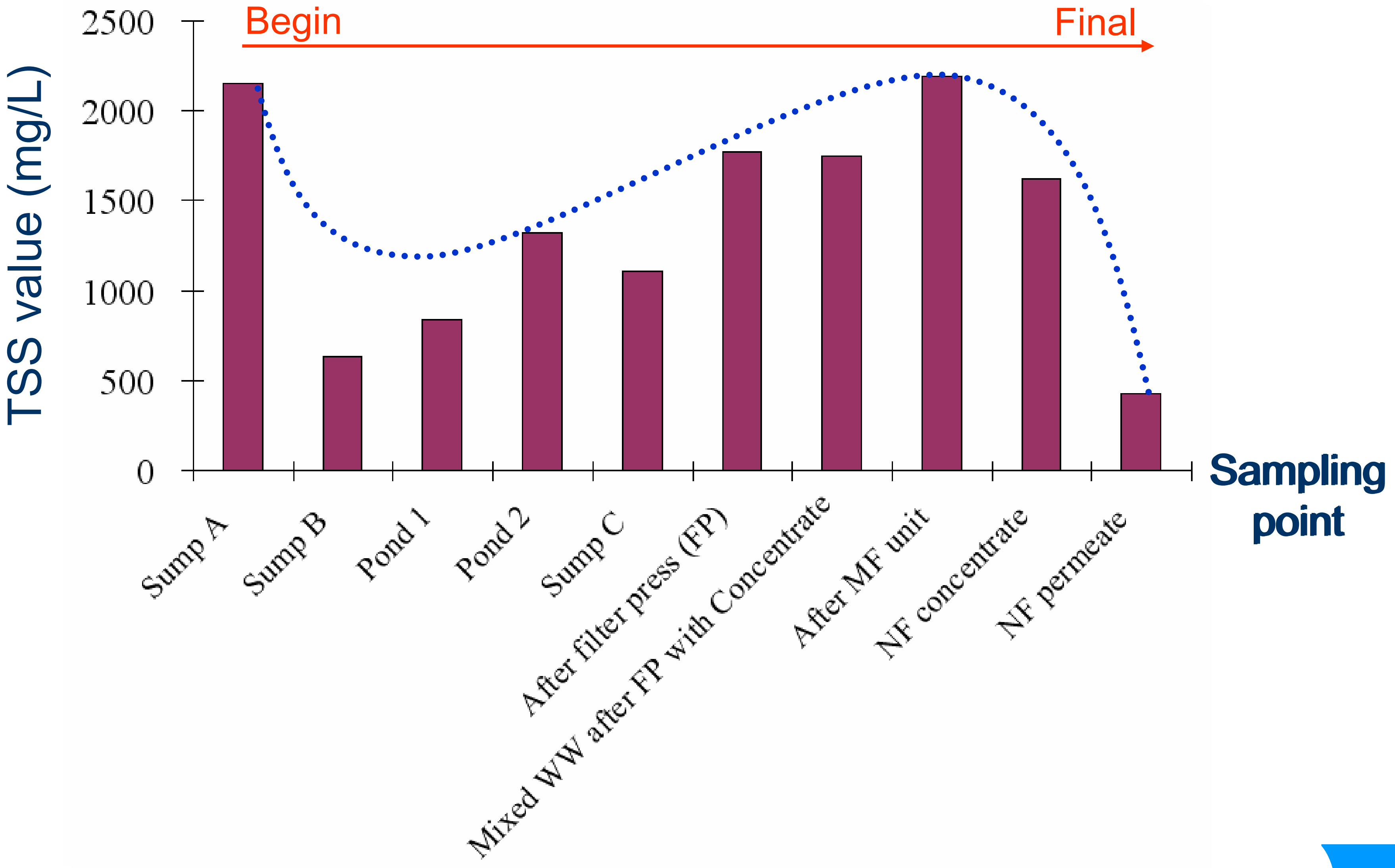
- Washing

- Safety first

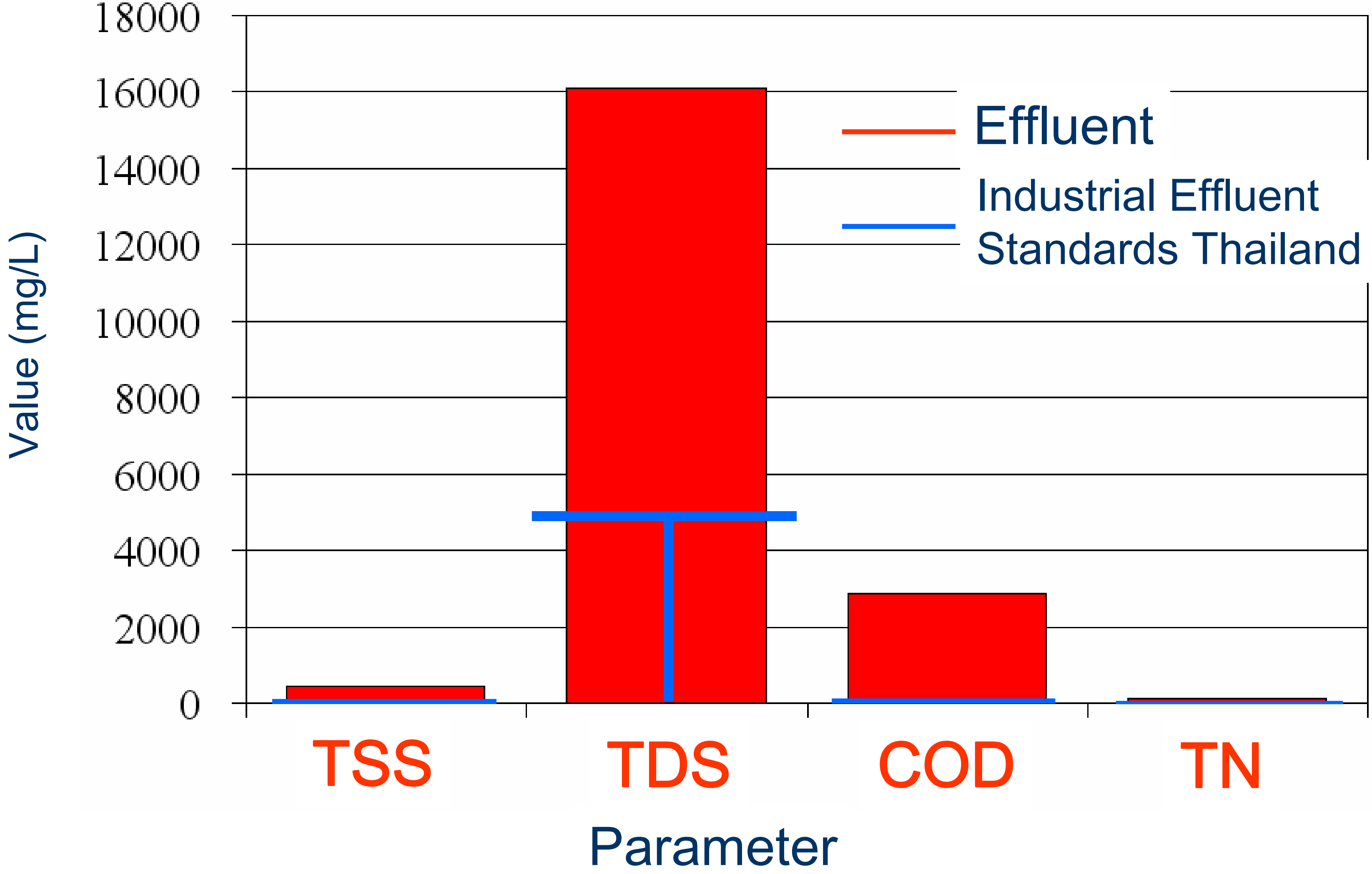
Existing Wastewater Treatment Plant



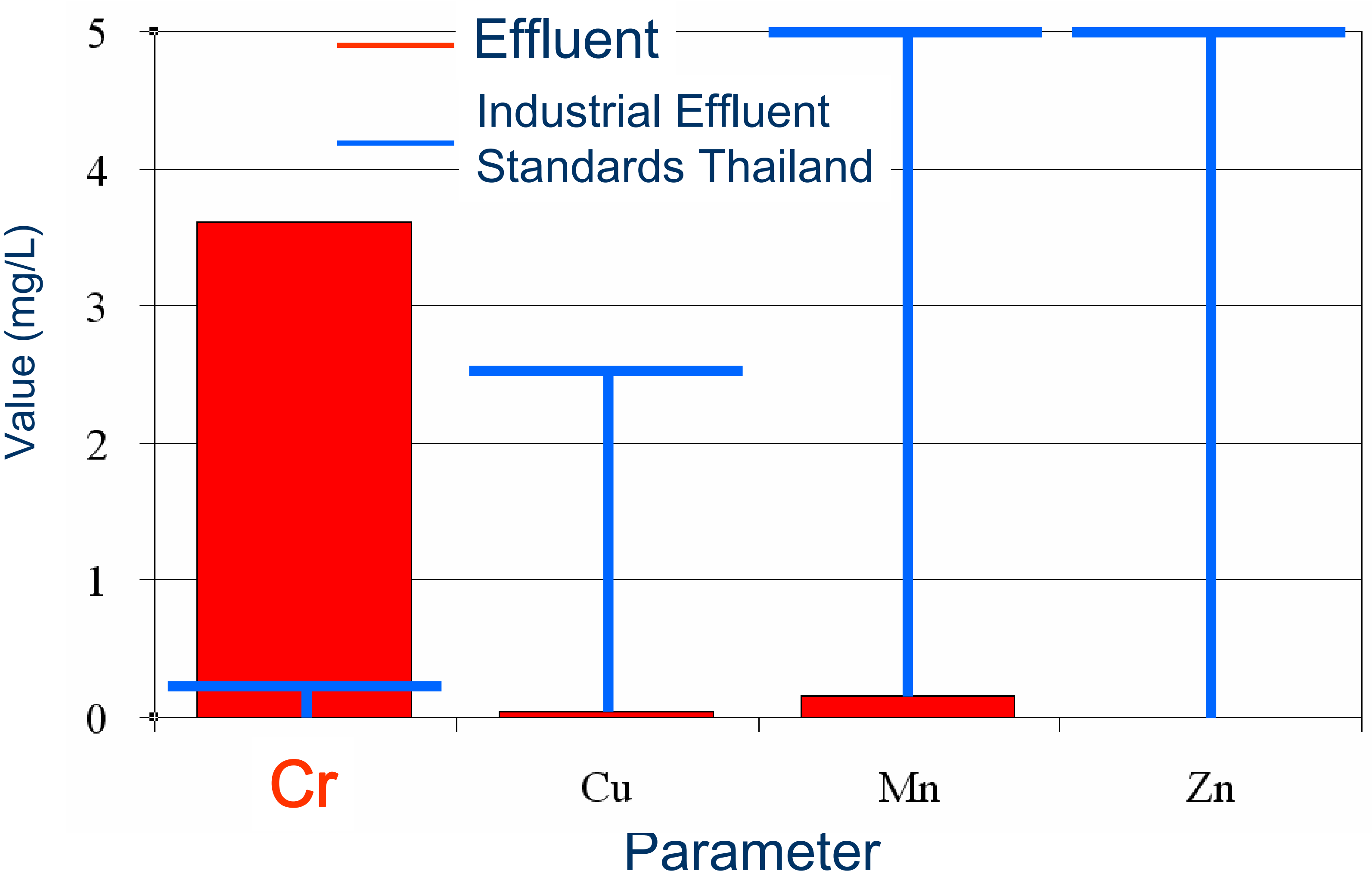
Current Status of Existing WWTP



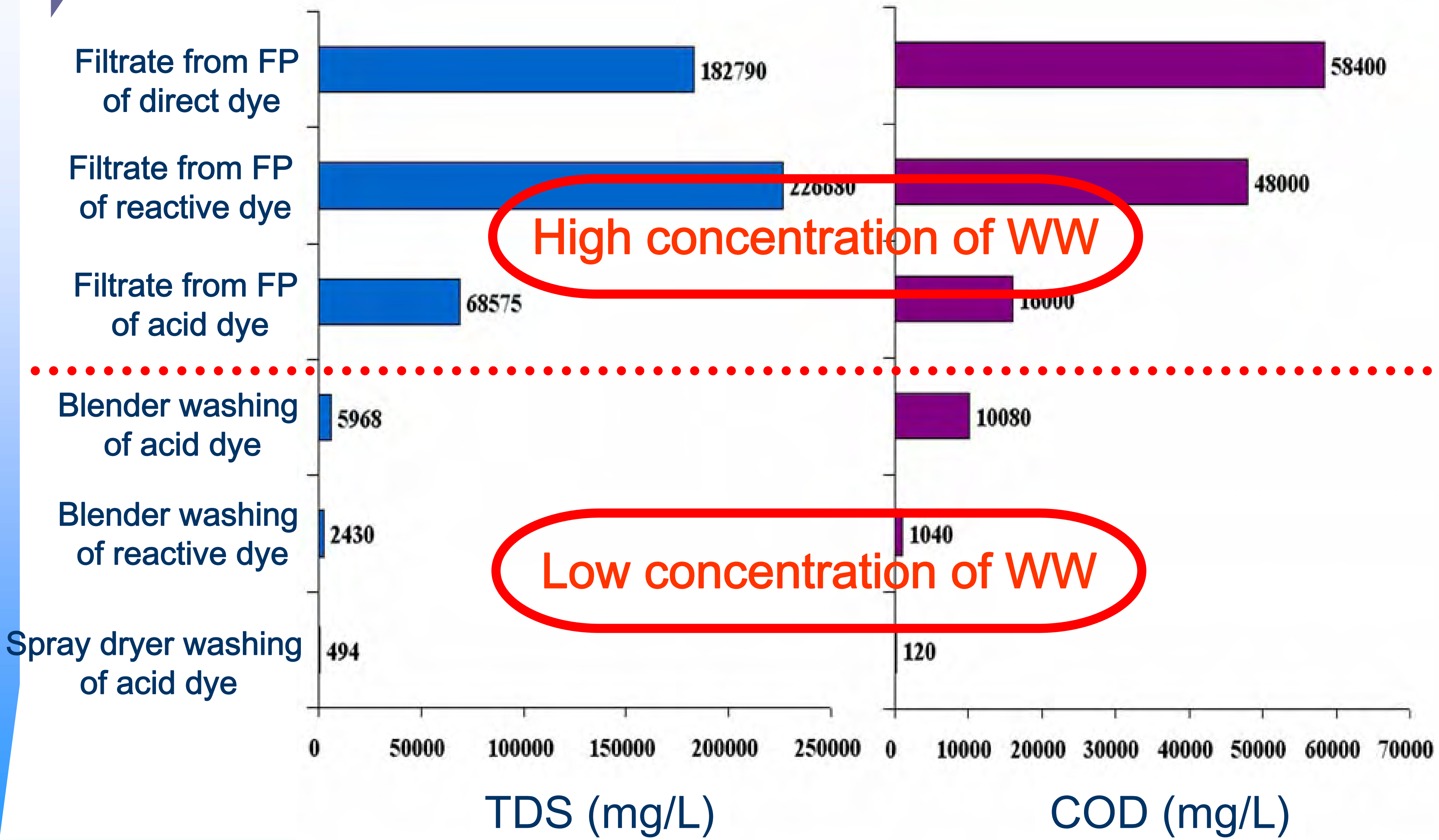
Wastewater Characteristics Compared with Thailand Industrial Effluent Standards



Wastewater Characteristics Compared with Thailand Industrial Effluent Standards



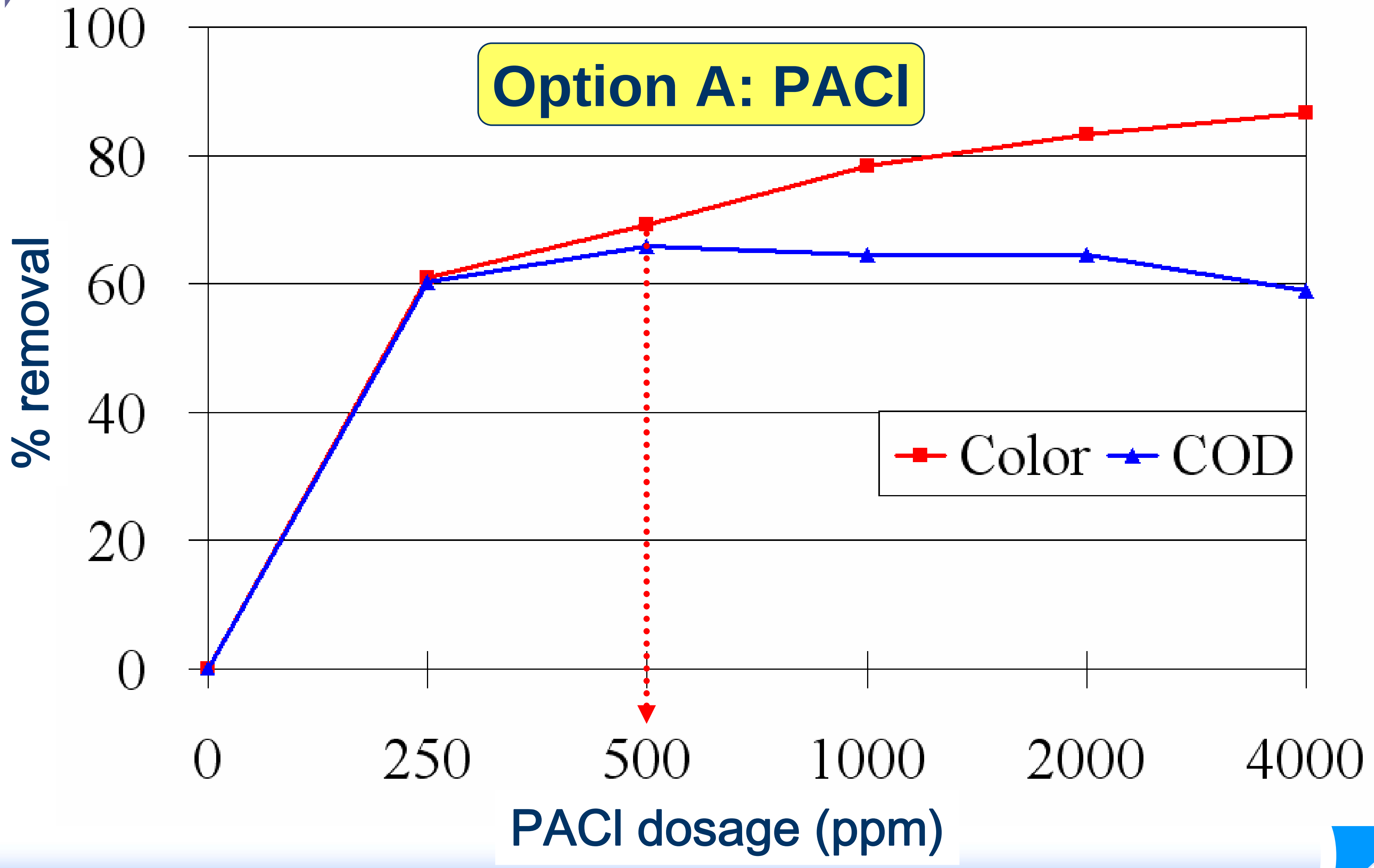
Pollution Level in Production Processes



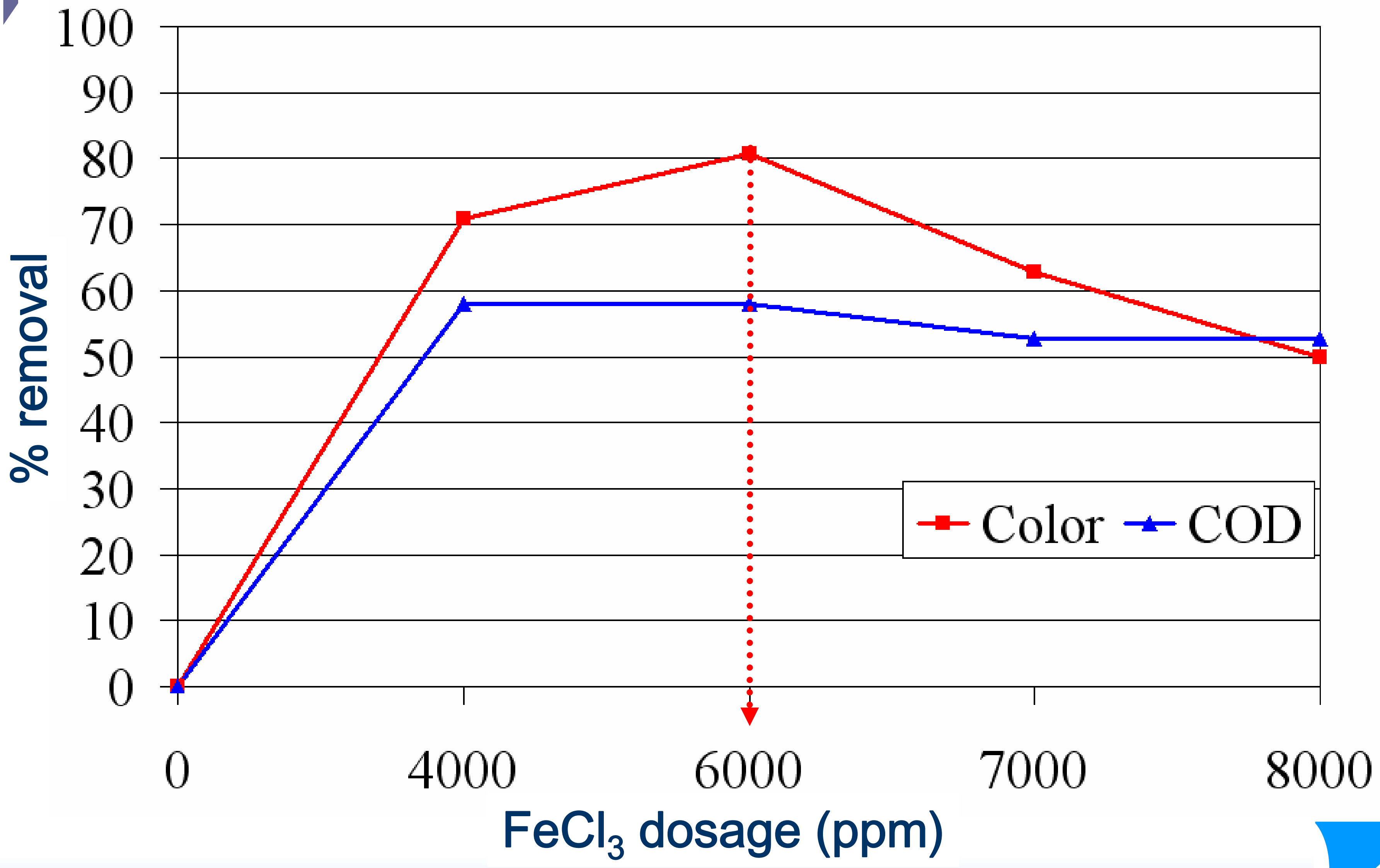
High concentration of WW

Low concentration of WW

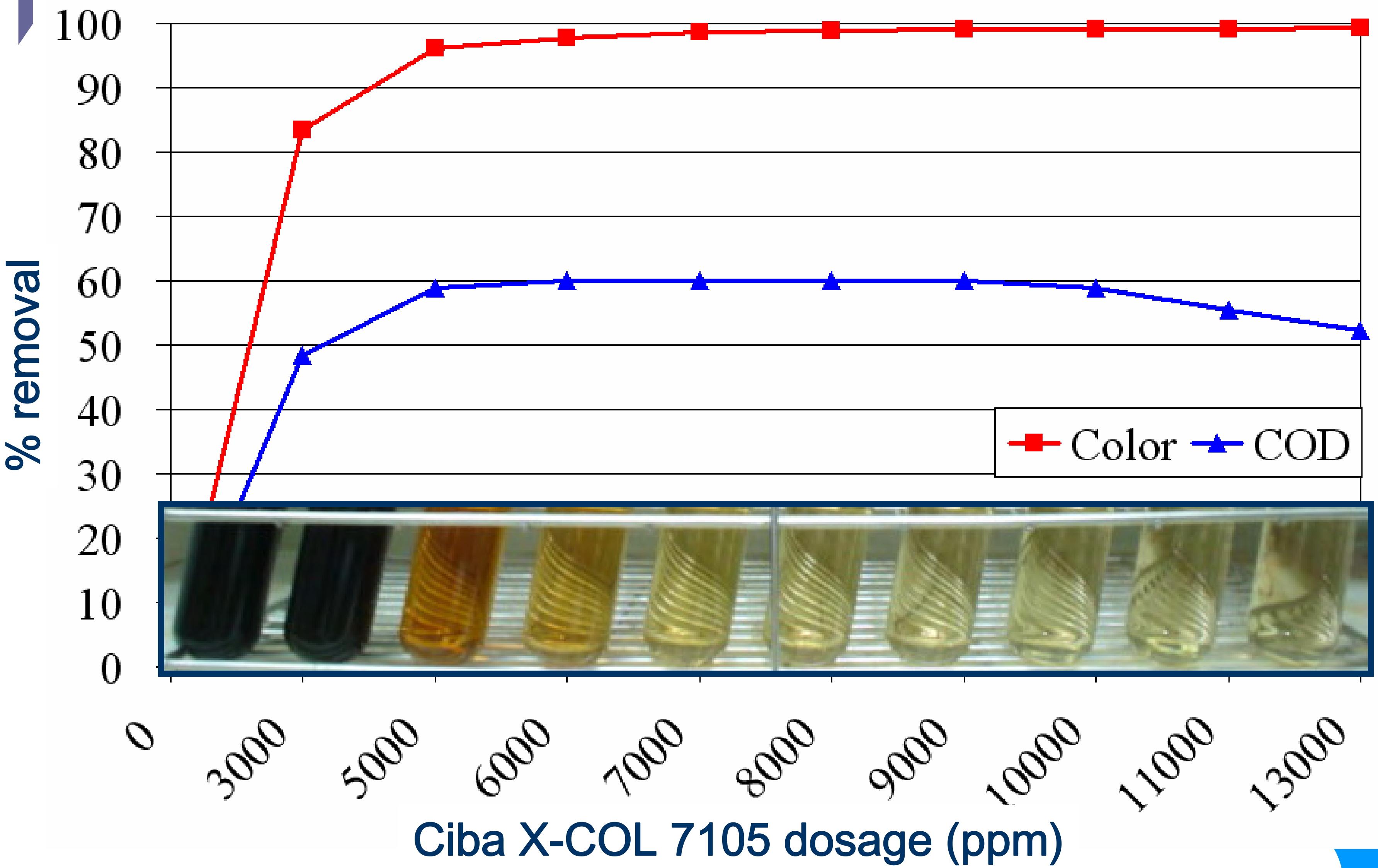
Treatment options



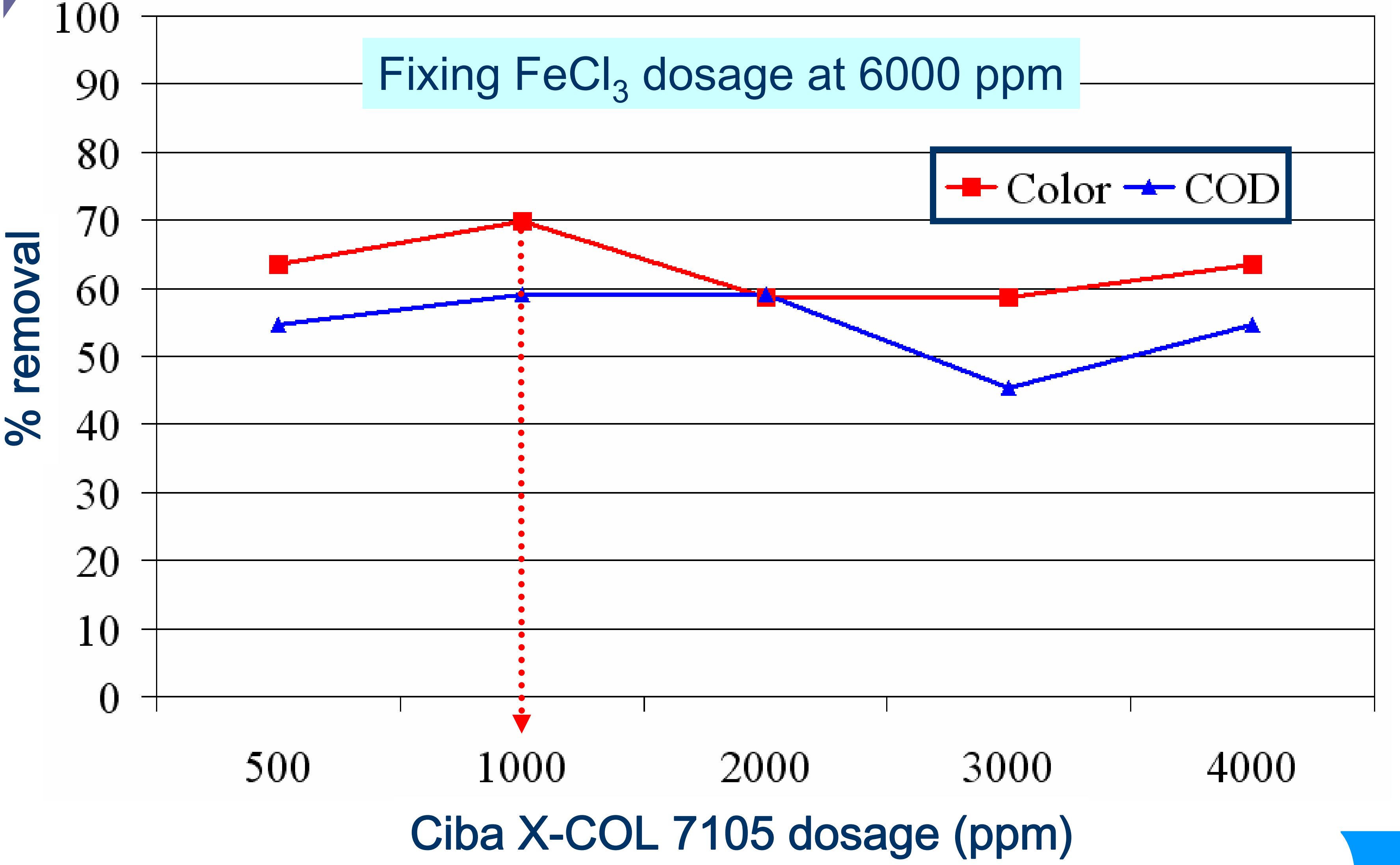
Option B: $FeCl_3$



Option C: Ciba X-COL 7105

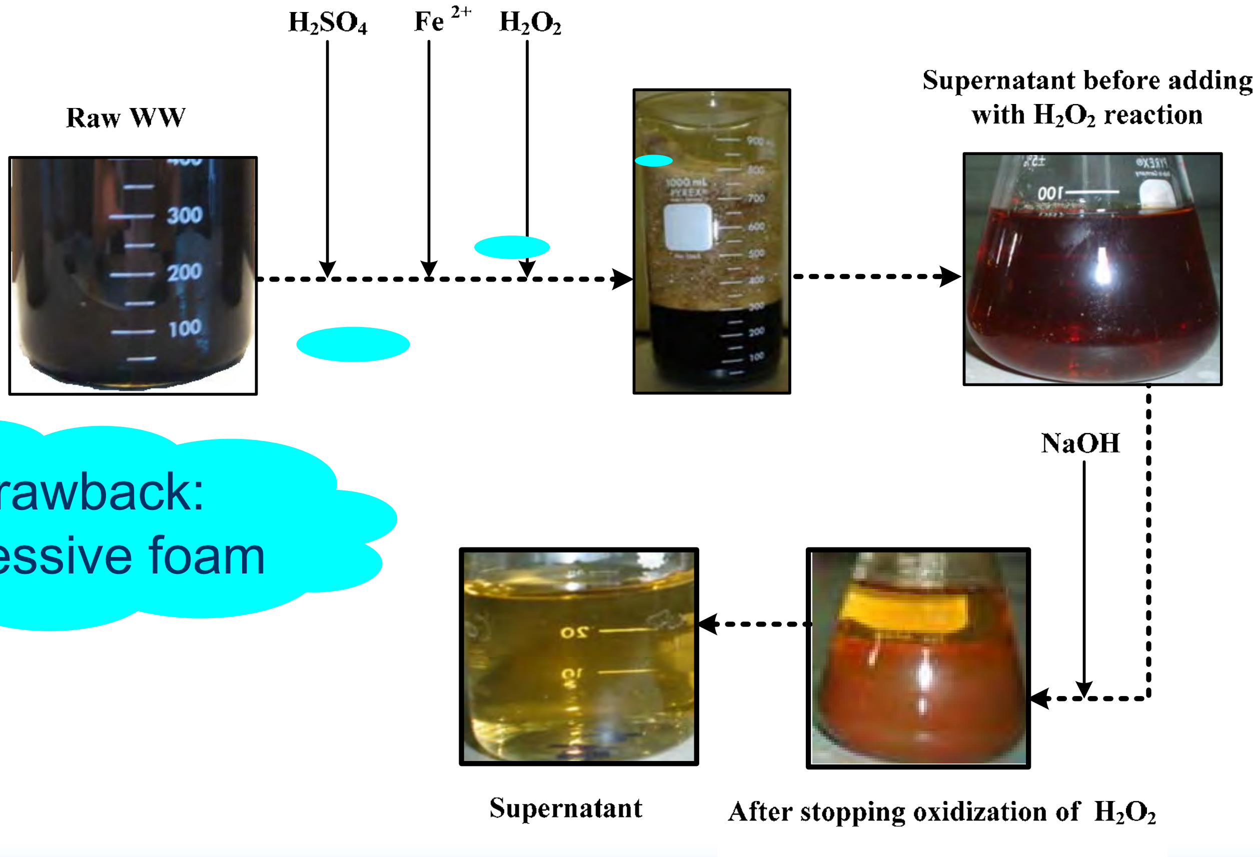


Option D: $FeCl_3$ + Ciba X-COL 7105



Option E: Fenton’s reagent

- Combination Fe^{2+} and H_2O_2 under acidic condition
- COD & Color removal rate differs in approximately 10% with residual H_2O_2 and without residual H_2O_2



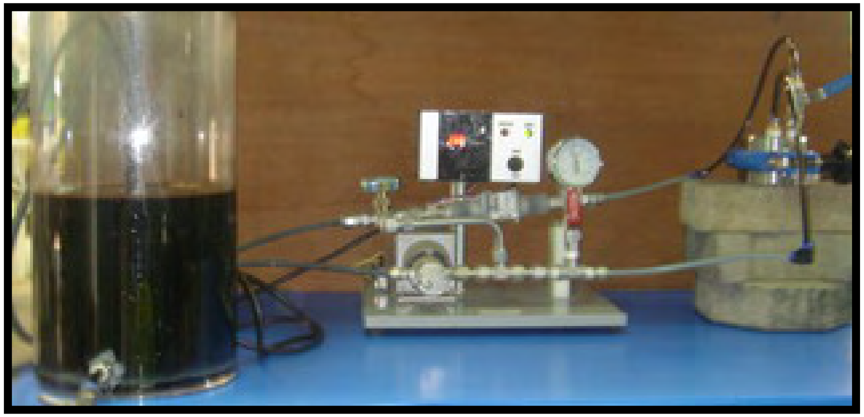
Drawback:
Excessive foam

Summary of Optimum Dosage & Cost Analysis in Different Options

Option	Estimated cost (Baht/m^3 of WW)	Removal Efficiency (%)	
		Color	COD
A	48	69	65
B	60	80	58
C	420	97	60
D	130	87	58
E	132,740	98	87

Membrane Testing

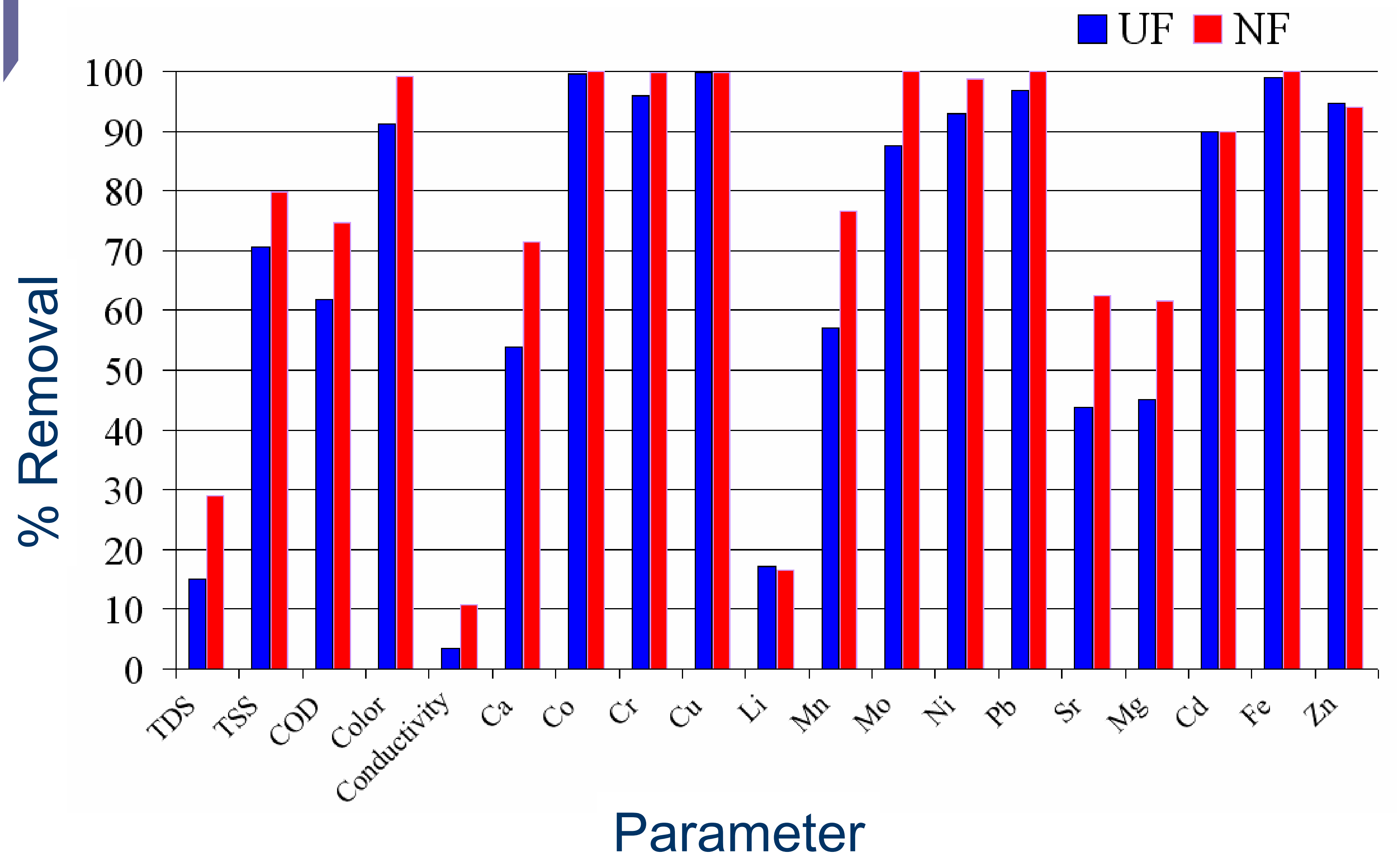
- Permeate flux of UF is higher than NF
- Color removal efficiency of NF was found to be higher than UF
- About 99% of color removal and 74% of COD removal were achieved by using cross flow NF



Raw WW

UF

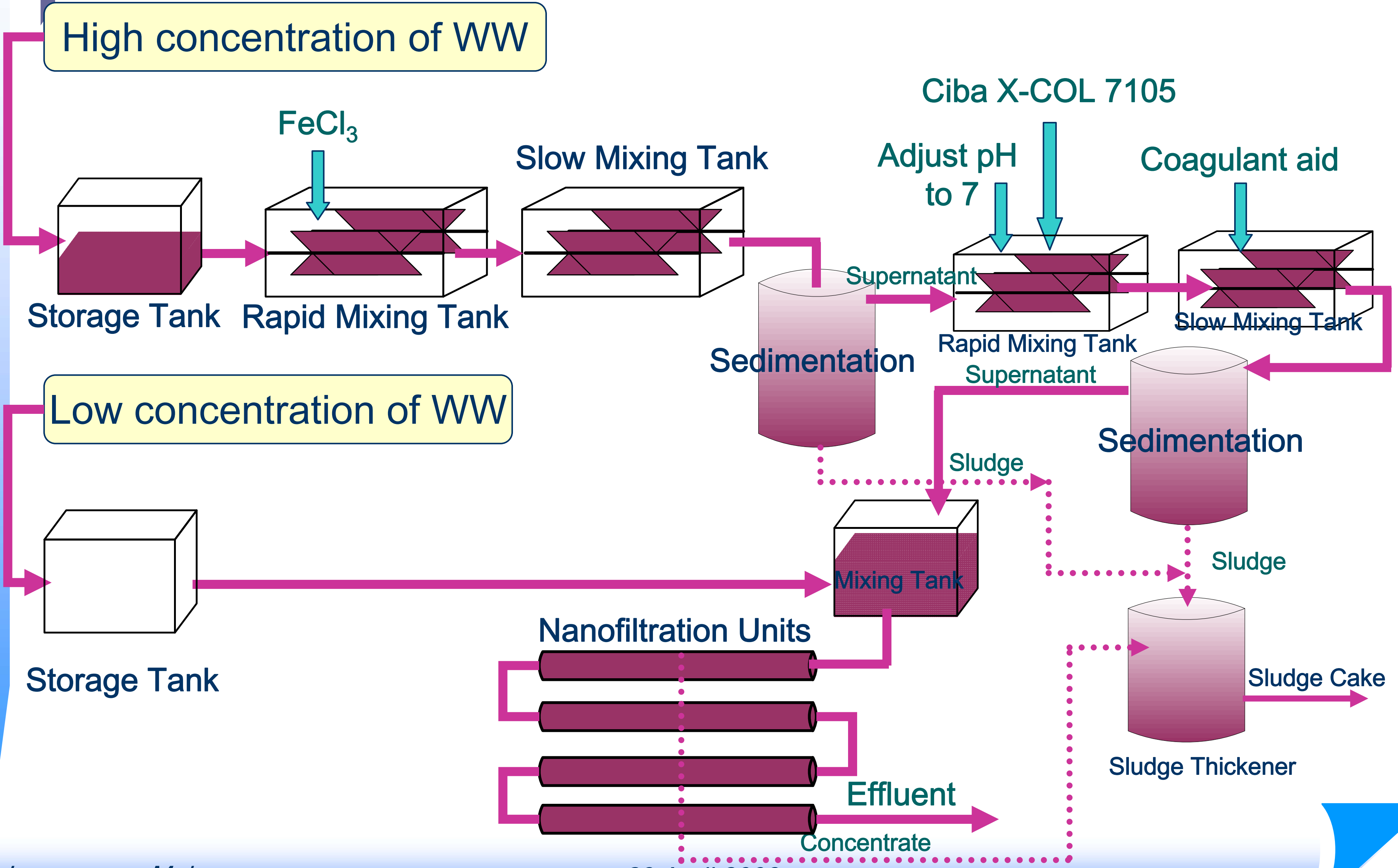
NF


UF
NF
% Removal
100
90
80
70
60
50
40
30
20
10
0
TDS
TSS
COD
Color
Conductivity
Ca
Co
Cr
Cu
Li
Mn
Mo
Ni
Pb
Sr
Mg
Cd
Fe
Zn
Parameter

Conclusions

- Plant A,B & C water consumption & WW generation are high
- Overall washing practices and housekeeping arrangement was noticed to be poor
- Thus, the simple guidelines are recommended such as using high pressure spray nozzles, checking leakage & repairing the pipe line
- WW was found to contain high color, TSS, TDS, and some heavy metal especially Cr
- TSS, TDS, COD, TN and Cr concentration were found to be exceed the limit comparing Thai Effluent Standard
- The efficiency of WWTP was found to be very low

Proposed for WWTP upgrade:



Recommendations

- ✉ Pretreatment of both segregated WW (high conc. & Low conc.) should be investigate with using proposed option
- ✉ Evaluate appropriate treatment options for membrane concentrate disposal & sludge generation
- ✉ Investigate physical & chemical characteristics of sludge cake and its reuse options
- ✉ Investigate options for Cleaner Production and potential of permeate for reuse
- ✉ Examine about state of occupational health of workers in Plant
- ✉ Investigate the effect on coastal ecosystem due to the effluent discharge

Thanks you for your attention