

CHAPTER II

RESEARCH BACKGROUND

2.1 Textile industry

The textile industry is one of the Thailand's major industries. Textile manufacturing begins with the production of raw fiber. The fiber can either be harvested from natural sources (e.g., wool, cotton) or manufactured from regenerative cellulosic materials, or it can be entirely synthetic. In the textile manufacture, the fiber passes through four main stages of processing (US EPA, 1996):

- Yarn production
- Fabric production
- Finishing
- Fabrication

During the finishing stage, most woven fabrics retain the natural color of the fibers from which they are made. For most cases, hence, these fabrics must undergo further processing, which can include bleaching, printing, dyeing, mechanical finishing, preshrinking, and shaping.

Color in the effluent from dyeing and printing operations has recently gained increasingly concerns as it is widely recognized as a compliance problem that must be addressed. The effluent from most textile dyeing operations generally has a dark reddish-brown hue which is aesthetically unpleasing when discharged to receiving waters. Color can be easy to detect (depending on the flow of the receiving stream), and even trace quantities of commercial textile colorants in wastewater are readily evident to the naked eye.

2.2 Basic dyes

"Cationic dyes" or commonly known as basic dyes are widely used in acrylic, nylon, silk, and wool dyeing. Basic dyes were the first synthetically manufactured dye class. They were initially used to dye silk and wool (along with other additives such as mordant), but they exhibited poor fastness properties. Modified basic dyes have been developed and are now used exclusively to color synthetic fibers such as acrylic, modified nylons and polyesters, in which their fastness is acceptable. Basic dyes are

rarely used on natural fibers, both because of their poor light and washfastness and because of the need for mordants. Basic dyes have limited water solubility and are applied in weakly acidic dyebaths. Ionic bonds are formed between the cation in the dye and the anionic site on the fiber.

In brief, basic dyes are among the brightest dyes available: they have unlimited color range and good fastness properties. Basic dyes are strongly bound and do not migrate easily which promotes the use of basic dye. However, basic dyes exhibit high aquatic toxicity. Table 2.1 shows the toxicity of the 16 selected most hazardous dyes. Cationic dyes are quite toxic compared with other types (US EPA, 1996).

The basic dyes examined in this work include methylene blue (MB), Astrazon[®] Blue FGRL (AB), and Astrazon[®] Red GTLN (AR). Astrazon[®] Blue FGRL (AB), Astrazon[®] Red GTLN (AR) and Astrazon[®] Golden Yellow GL-E (AY) were supplied by Dystar Thai Co., Ltd. Astrazon[®] Blue FGRL consists of two main components, which are C.I. Basic Blue 159 and C.I. Basic Blue 3. The ratio of the two components is approximately 5:1 by weight, respectively. Astrazon[®] Red GTLN also consists of two main components, i.e. C.I. Basic Red 18:1 and C.I. Basic Yellow 28. The ratio of the two components is approximately 40:1 by weight, respectively. Astrazon[®] Golden Yellow GL-E has only one main component, which is C.I. Basic Yellow 28. All chemical structures are shown in Fig. 2.1. The dye information gathered from the Material Safety Data Sheet (MSDS) is tabulated in Table 2.2.

2.3 Treatments of color effluents

This section illustrates the critical study of the most widely used methods of dye removal from dye-containing industrial effluents. Currently the main methods are both by chemical and physical means with active research concentrating on cheaper and more effective alternatives.

2.3.1 Chemical methods

➤ Oxidative processes

The main oxidizing agent is usually hydrogen peroxide (H₂O₂). This agent needs to be activated by some means, for example, ultra violet light. Many methods of chemical decolorization vary depending on the way in which H₂O₂ is activated (Slokar and Le

Marechal, 1997). Chemical oxidation removes the dye from the dye-containing effluent by oxidation resulting in aromatic ring cleavage of the dye molecules (Raghavacharya, 1997).

➤ H_2O_2 -Fe(II) salts (Fentons reagent)

Fentons reagent is a suitable chemical means of treating wastewaters which contains compounds that are resistant to biological treatments or are poisonous to living biomass (Slokar and Le Marechal, 1997). This method uses the combined action of adsorbing and bonding to remove dissolved dyes from wastewater and has been shown to be effective in decolorizing both soluble and insoluble dyes (Pak and Chang, 1999). The performance of this technique is dependent on the final floc formation and its settling quality. Although cationic dyes do not coagulate at all, acid, direct, vat, mordant and reactive dyes usually coagulate, the resulting floc can be of poor quality and does not settle well, yielding mediocre results (Raghavacharya, 1997). The sludge generation through the flocculation of the reagent and the dye molecules also requires further management and often is regarded as additional environmental problems.

➤ Ozonation

The use of ozone was first pioneered in the early 1970's. Ozone is an excellent oxidizing agent due to its instability. Oxidizing by ozone is capable of degrading chlorinated hydrocarbons, phenols, pesticides, and aromatic hydrocarbons (Lin and Lin, 1993). Chromophore groups in the dyes are generally organic compounds with conjugated double bond that can be broken down forming smaller molecules, resulting in reduced coloration (Peralto-Zamora et al., 1999). These small molecules may have increased carcinogenic or toxic properties, and so ozonation should be applied with care. One disadvantage of ozonation is its short half-life, typically in the range of 20 min. This can be further shortened with the presence of salts, pH, and temperature. Therefore ozone cannot be stored but has to be generated on-site. This often requires a costly installation of additional equipment (Xu and Lubren, 1999).

➤ Photochemical oxidation

This method degrades dye molecules to CO_2 and H_2O (Yang et al., 1998) by UV treatment in the presence of H_2O_2 . Degradation is caused by the production of high concentration of hydroxyl radicals. UV light may be used to activate chemicals such

as H_2O_2 , and the rate of dye removal is influenced by the intensity of UV radiation, pH, dye structure, and the dye bath composition (Slokar and Le Marechal, 1997). This may be set-up in batch or in continuous modes (Namboodri and Walsh, 1996). Depending on initial materials and the extent of the decolorization treatment, additional by-products, such as, halides, metals inorganic acids, may be produced (Yang et al., 1998).

➤ Sodium hypochlorite (NaOCl)

This method attacks at the amino group of the dye molecule by OCl^- which initiates and accelerates azo-bond cleavage. An increase in decolorization is seen with an increase in OCl^- concentration. The use of OCl^- for dye removal is becoming less frequent due to its high negative potential particularly if this water is released into the waterway (Slokar and Le Marechal, 1997) as this can increase the contamination level of the by-products such as aromatic amines which are carcinogenic, or otherwise toxic molecules.

2.3.2 Physical methods

➤ Membrane filtration

This method has ability to clarify, concentrate, and separate dye continuously from effluent (Mishra and Tripathy, 1993; Xu and Lebrun, 1999). Despite its several advantages such as resistance to temperature and microbial attack, its disadvantages make it unsuitable for real applications. The major drawbacks are membrane replacement, disposal problems, and possibility of clogging.

➤ Ion exchange

Ion-exchange has not been widely used for the treatment of dye-containing effluents, mainly due to the opinion that ion-exchanger cannot accommodate a wide range of dyes and the resin could be costly. Moreover, this method is not effective for non-ionic chemicals such as disperse dyes.

➤ Adsorption

Most of the used dyes are resistant to bio-degradation or photo-oxidation. Adsorption techniques have gained its popularity recently due to their efficiency in the removal of such dye pollutants. Adsorption has been found to be highly efficient in terms of

initial cost, ease of operation, and insensitivity to toxic substances. Adsorption produces a high quality product, and is a process which is economically feasible (Choy et al., 1999). The adsorption capacity is influenced by many physio-chemical factors, such as dye/sorbent interaction, sorbent particle size, temperature, pH, and contact time (Kumar et al., 1998).

There are quite a number of research papers regarding the removal of basic dyes by the adsorption process. These treatment methods can conveniently be categorized into two classes as follows:

I. Adsorption using inorganic materials

Examples of inorganic adsorbents used for the removal of dyes are given in Table 2.3. Activated carbon is the most widely used adsorbent since it has excellent adsorption efficacy, but high cost is the major constraint for the use of this technique. Silica is also one of the most effective materials for removing basic dyes, but side reactions, such as air binding and air fouling with particulate matter, prevents it from being used commercially (Robinson et al., 2001).

II. Adsorption using natural materials

The search for new technologies involving the removal of toxic substances from wastewaters has directed attention to biosorption. The major advantages of biosorption over conventional treatment methods include (Kratochvil and Volesky, 1998):

- Low cost;
- High efficiency;
- Regenerative; and
- Minimization of chemical and/or biological sludge

Many investigators have studied the feasibility of using low cost materials for the biosorption of a broad range of dyes. A brief summary of these works are given in Table 2.4.

2.4 Concluding remarks: Advantages and disadvantages of current treatment technologies.

In conclusion, the advantages and disadvantages of current treatment technologies for the removal of dye from industrial effluents are summarized in Table 2.5. Moreover, Thailand is agriculture country and there are varieties of both agricultural and natural excess materials that are readily available. This makes biosorption attractively viable among other techniques. In the next chapter, biosorption was described in detail.

Table 2.1 Effect of 16 dyes on fish, Fathead Minnow (*Pimephales promelas*), in static bioassay (Little and Lamp, 1972)

C.I.number	Dye	LC ₅₀ (mg/l)	Temperature (°C)
42535	Basic Violet 1	0.047	15
42000	Basic Green 4	0.12	18
51005	Basic Blue 3	4	15
21010	Basic Brown 4	5.6	20
25135	Acid Yellow 38	23	15
20170	Acid Orange 24	130	17
15510	Acid Orange 7	165	17
18965	Acid Yellow 17	>180	17
10338	Disperse Yellow 42	>180	15
11855	Disperse Yellow 3	>180	15
30235	Direct Black 38	>180	17
31600	Direct Black 80	>180	17
40000	Direct Yellow 11	>180	17
69015	Vat Brown 3	>180	15
69500	Vat Green 3	>180	15
69825	Vat Blue 6	>180	15

Table 2.2 Physical/ chemical properties, stability, toxicological, and ecological information of the three modeled basic dyes

Parameters	Astrazon® Blue FGRL	Astrazon® Red GTLN	Astrazon® Golden Yellow GL-E	Methylene Blue
Form	Powder	Powder	Powder	Powder
Color	Blue	Red	Yellow	Dark blue
Odor	Odorless	Odorless	Weak odour	Almost odorless
Melting temperature	N/A	Approx. 180°C	N/A	Approx. 180°C
Solubility in water	10 g l ⁻¹	60 g l ⁻¹	60 g l ⁻¹	50 g l ⁻¹
pH value	6.0-7.0	5.5-7.0	3.5-6.0	N/A
Thermal decomposition	>170°C	N/A	N/A	Approx. 180°C
Acute oral toxicity	LD ₅₀ 206 mg kg ⁻¹ (rat)	LD ₅₀ >100 mg kg ⁻¹ (rat)	LD ₅₀ 560 mg kg ⁻¹ (rat)	LD ₅₀ 1,180 mg kg ⁻¹ (rat)
Irritant effect on eyes	Irritant (rabbit eye)	Serious irritant (rabbit eye)	Irritant (rabbit eye)	N/A
Fish toxicity	LC ₅₀ 10-100 mg l ⁻¹	LC ₅₀ 10-100 mg l ⁻¹	Yellow	N/A

N/A = Not Available

Table 2.3 Examples of inorganic adsorbents and its adsorption capacity.

Inorganic adsorbent	Dye	Operation conditions		Adsorption capacity, q_m (mg g ⁻¹)	Ref
		T (°C)	pH		
Carbon	Basic Red 22	25	-	790	Nassar and Magdy, 1997
Carbon	Basic Blue 3	25	-	649	Nassar and Magdy, 1997
Carbon	Basic Yellow 21	25	-	600	Nassar and Magdy, 1997
Activated tyres	Methylene blue	-	-	130	Saniz-Diaz and Griffith, 2000
Activated sewage char	Methylene blue	-	-	120	Saniz-Diaz and Griffith, 2000
Amorphous silica	Methylene blue	-	5.0	26.5	Woolard et al., 2002
Zeolite	Methylene blue	-	5.0	12.7	Woolard et al., 2002

Table 2.4 Examples of biosorbents used for adsorption used for adsorption of basic dyes

Biosorbent	Dye	Operation conditions		Biosorption capacity, q_m (mg g ⁻¹)	Ref
		T (°C)	pH		
<u>Algal and fungal sorbent</u>					
<i>Pithophora sp.</i> (raw)	Malachite green	30	5.0	64.4	Kumar et al, 2005
<i>Caulerpa scalpelliformis</i>	Basic yellow	30±1	6.0±0.1	27.0	Aravindhan et al., 2007
<i>Aspergillus niger</i>	Basic blue 9	-	-	18.5	Fu and Virarahavan, 2000
<u>Part of plants and its product</u>					
Bark	Methylene blue	-	-	915	McKay et al., 1999
Cotton waste	Safranine	-	-	875	McKay et al., 1999
Rice husk	Safranine	-	-	838	McKay et al., 1999
Linseed cake	Basic Blue 41	30	-	573	Liversidge et al., 1997
Sugar-industry mud	Basic Red 22	-	-	519	Magdy and Daiullah, 1998
Tree fern	Basic Red 13	40	5.0	408	Ho et al., 2005
Palm-fruit bunch	Basic Yellow 21	25	-	327	Nassar and Magdy, 1997
Rice husk	Methylene blue	-	-	312	McKay et al., 1999
Cotton waste	Methylene blue	-	-	278	McKay et al., 1999
Palm-fruit bunch	Basic Red 18	-	-	242	Nassar et al., 1995
Peat	Basic Blue 69	80	-	226	Ho and McKay, 1998b
Palm-fruit	Basic Red 22	25	-	180	Nassar and

bunch					Magdy, 1997
Jack fruit peel	Malachite Green	32	6.0	166	Inbaraj and Sulochana, 2002
Bagasse pith	Basic Blue 69	-	-	158	McKay et al., 2003
Giant duckweed	Methylene blue	25	9.0	145	Waranusantigul et al., 2003
Mango seed kernel powder	Methylene blue	30	8.0	143	Kumar and Kumaran, 2005
Granular kohlrabi peel	Neutral red	20±2	5.0	112	Gong et al., 2007
Palm-fruit bunch	Basic Blue 3	25	-	92.3	Nassar and Magdy, 1997
Raw date pits	Methylene blue	20	-	80.3	Robinson et al., 2001
Bagasse pith	Basic Red 22	-	-	77.0	McKay et al., 2003
Wood	Basic Blue 69	-	-	71.9	Ho and McKay, 1998
Yellow passion fruit waste	Methylene blue	25	8.0	44.7	Pavan et al., 2007
Garden grass	Methylene blue	30	8.0	31.0	Kumar and Porkodi, 2007
Orange peel	Congo Red	29	7.7	22.4	Namasivayam et al., 1996
Chaff	Methylene blue	25	-	20.3	Han et al., 2006
Orange peel	Rhodamine B	29	7.7	3.23	Namasivayam et al., 1996

Table 2.5 Advantages and disadvantages of various treatment methods for the removal of dyes

Physical/chemical methods	Advantages	Disadvantages
Fenton reagent	Effective decolorization of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical oxidation	No sludge production	Formation of by-product
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Biosorption	Uses biomass raw materials which are either abundant or wastes from other industrial operations	Biosorbent is less stable, pretreatment might be necessary in some cases.
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved oxygen

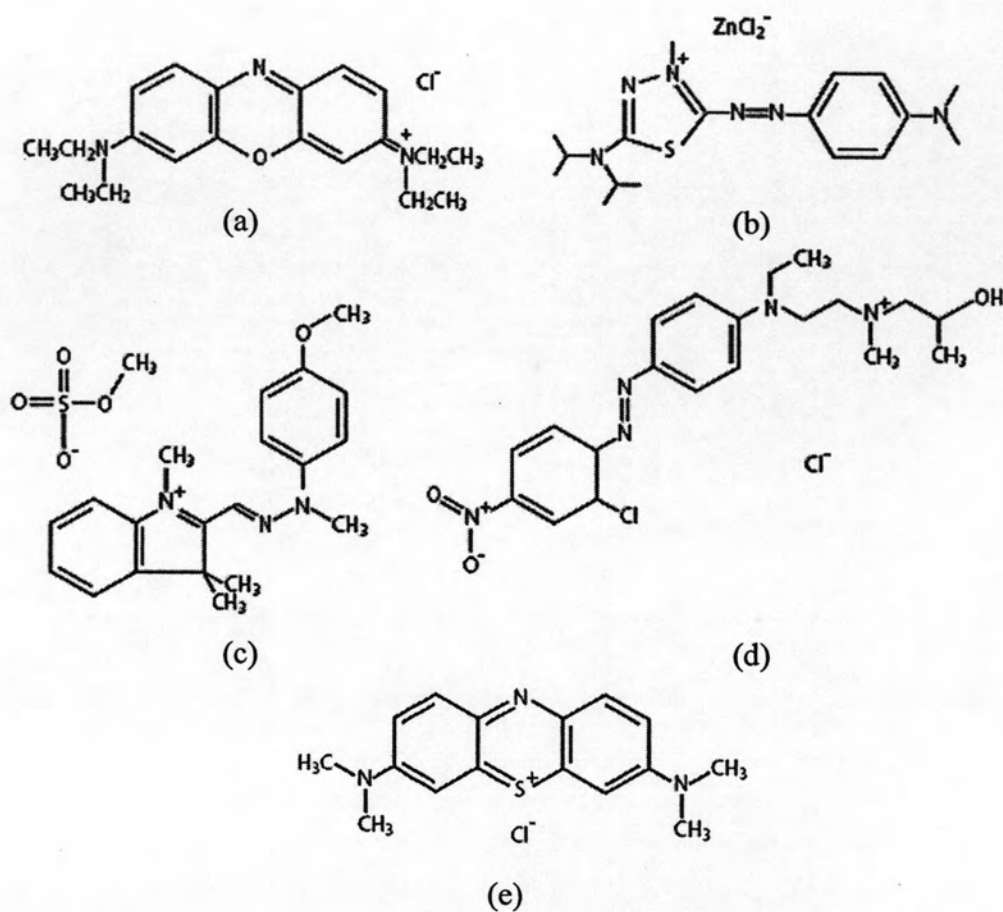


Fig. 2.1 Chemical structures of (a) C.I. Basic Blue 3, (b) C.I. Basic Blue 159, (c) C.I. Basic Yellow 28, (d) C.I. Basic Red 18:1, (e) methylene blue