



CHAPTER II BACKGROUND AND LITERATURE SURVEY

2.1 Wastewater From Textile Industry

The textile industry is well known as a complex and unique operation. It comprises of a diverse group of processes that produces textile-related products such as fiber, yarn, fabric for applications in apparel, home finishing and industry goods (Gohl, 1983).

The four main processes in the textile industry can be classified as yarn formation, fabric formation, wet processing and fabrication. The schematic diagram of each process is shown in Figure 2.1.

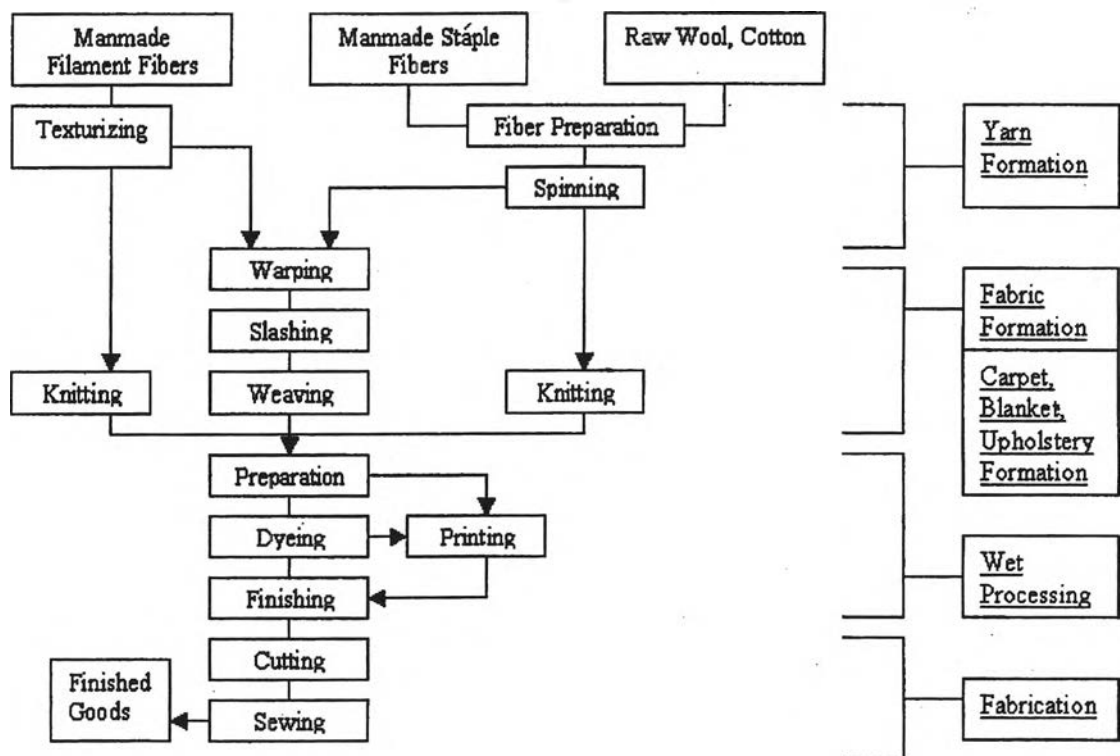


Figure 2.1 Flow chart of textile processing (Gohl, 1983).

Textile establishments receive and prepare fibers, transform fiber into yarn, thread or knit in order to convert yarn into fabric or related products. After the fabric formation process, wet processing is the next process that includes dyeing, printing and finishing. These processes generate a lot of toxic and hazardous wastewater. The final process mainly relates to cutting and sewing.

From the processes mentioned above, each step creates its own air emission and wastewater depending on the chemicals which are used in each operation. Especially in the dyeing process, liquid effluents which come out from dyeing bath have several types of poisonous and harmful species i.e. heavy metal ion residue and acid solvent. Table 2.1 shows the details of these components.

Table 2.1 List of waste streams generated at each level of the textile industry
(Gohl, 1983)

Process	Air Emissions	Waste water	Residual wastes
Yarn Spinning	Little or no air Emissions Generated	Little or no wastewater generated	Packaging waste; sized yarn; fiber waste; cleaning and processing waste
Slashing/Sizing	VOCs	BOD; COD; metal; cleaning waste	Fiber lint; yarn waste; packaging wastes; starch-based sizes
Desizing	VOCs from glycol ethers	BOD from water soluble sizes; synthetic size;lubricants; biocides; anti-static compound	Packaging waste; fiber lint; yarn waste; cleaning materials, such as wipes,rags and filters; cleaning and maintainance wastes containing solvents
Scouring	VOCs from glycol ethers and scouring Solvents	Disinfectants and insecticide residues;NaOH; detergents;fats; oils;pectin;wax; knitting lubricants; spin finishes;spent solvents	Little or no residual waste generated

Table 2.1 Continued

Process	Air Emissions	Waste water	Residual wastes
Bleaching	Little or no air Emissions Generated	Hydrogen peroxide, sodium silicate or organic stabilizer; high pH	Little or no residual waste generated
singeing	Small amounts of exhaust gases from the burners	Little or no wastewater generated	Little or no residual waste generated
Mercerizing	Little or no air Emissions Generated	High pH; NaOH	Little or no residual waste generated
Heatsetting	Volatilization of spin finish agents applied during synthetic fiber Manufacture	Little or no wastewater generated	Little or no residual waste generated
Dyeing	VOCs	Meals; salt; surfactants; toxics; organic processing assistance; cationic materials; color; BOD; sulfide; acidity/alkalinity; spent solvents	Little or no residual waste generated
Printing	Solvents, acetic acid from dyeing and curing oven Emissions; Combustion gases; particulate matter	Suspended solids; urea; solvents; color; metals; heat; BOD; foam	Little or no residual waste generated
Finishing	VOCs; Contaminants in Purchased Chemicals; Formaldehyde vapors; combustion gases	BOD; COD; Suspended solids; toxics; spent solvents	Fabric scrapes and trimmings; packaging waste

Not only can the processes inside the textile mill cause the variation of wastes but the diversity of fibers is also the other factor causing different waste streams. Because of the difference in impurity and structure of each fiber, specific pretreatment before yarn formation is typically different. The structure of fibers requires the individual functional groups of dye for dyeing process such as direct and reactive dyes, which are appropriate for cotton and man-made filaments respectively. The characteristics of textile wastes, waste components from preparation processes and the waste concentration from dyeing process are shown in Tables 2.2-2.4 (Callely *et al.*, 1997).

Table 2.2 The characteristics of textile wastes (Callely *et al.*, 1997)

Fibre	Impurities			Process chemicals
	Origin	Main Components	Maximum as percentage of fibre weight	
Cotton	natural	fats, waxes	10	NaOH, Na ₂ CO ₃ bleaching agents
Raw wool	natural	grease, suint, inorganic matter	100	Na ₂ CO ₃ , soap, detergent
Other wool	Natural spinning	grease, oil	10	Na ₂ CO ₃ , soap
Man-made	manufacture	lubricants, anti-static agents	2	Na ₂ CO ₃ , detergents
Cotton Viscose Rayon Polyester	weaving	starch, modified, starch fats, waxes	5	enzymes, acids
Other man-made	weaving	gelatin, polyvinyl alcohol	5	detergents

Table 2.3 Textile Dyeing Processes Waste Concentration (Callely *et al.*, 1997)

Fibers	Dye class	Dye lost (g/kg fibre)	Process chemicals (g/kg fibre)	Total water usage (l/kg fibre)	Effluent concentration (mg/l)	
					dye	process chemicals
Cotton man-made cellulose	direct	1-5	0	40-150	10-50	1000-3000
	reactive	3-20	200-500	50-250	30-200	1500-3000
	vat	1-5	50-200	20-80	20-100	1000-2500
	sulphur	1-10	100-500	50-250	10-100	1000-3000
Wool	acid premetallised	0.5-2.5	100-250	50-250	5-50	1000-2000
Nylon	acid premetallised	0.5-2.5	20-100	30-200	5-50	250-1000
Polyester	disperse	1-5	50-200	50-200	10-50	500-1500

Table 2.4 Textile Wastes Typical Characteristics (Callely *et al.*, 1997)

source	total water usage (l/kg)	pH	Total solids (mg/l)	Suspended solids (mg/l)	COD (mg/l)	BOD (mg/l)
Cotton, woven fabrics	60-500	8-12	500-2000	50-250	200-100	100-500
Cotton /man-made woven fabrics	60-500	6-9	200-2000	50-200	100-1000	50-500
Man-made, knitted fabrics	50-600	4-8	100-1000	20-100	100-1000	50-250
Wool, woven fabrics	80-500	7-10	1000-5000	50-500	200-2000	100-1000

The treatment of textile wastewater has previously been studied and developed by several research groups. Flocculation, sedimentation, adsorption and chemical oxidation are examples of physical and chemical treatments applied to deal with these wastes. Kaurek *et al.* (1989) patented the cation-exchange process, which enables the waste streams to be treated by neutralizing and softening. The regeneration streams are mixed with alkaline wastewater for the precipitation of organic and inorganic impurities.

2.2 Water Soluble Dyes

Dye molecules can be colored so that they selectively absorb and reflect incident light. They mostly are organic compounds and contain at least one each of each radicals called chromophores and auxochromes. In general, the chromophores give the dye molecule a particular color whereas the auxochromes intensify the hue of the dye molecule's color, make the dye more water soluble and improve the color-fastness properties of the dyed or printed fibers. Figure 2.2 shows the examples of chromophore and auxochrome.

Textile materials are colored when dye molecules enter the amorphous regions of the fibers' polymer system. Usually, it is impossible for dye molecules to enter the crystalline regions of the textile fibers because the inter-polymer spaces in the crystalline regions of the fibers' polymer systems are too small for the relatively large dye molecules. There are two forces, which are involved in the interaction between dye, fiber, water and auxiliary. The first one is the force of repulsion, which develops between the dye molecule and water. The other force is the force of attraction, which develops between the dye molecules and fibers.

Dye molecules are organic molecules that can be classified into three main types: anionic dye, cationic dye and disperse dye. The color from an anionic dye is caused by the anionic part of the dye molecule while the color from cationic dye is caused by cationic part. On the other hand, the color from disperse dye comes from the whole molecule. The first two dye molecule types are applied for an aqueous solution while the third one is applied for an aqueous dispersion.

In addition to their solubility in water, dyes can also be classified by the method of application of the dyes.

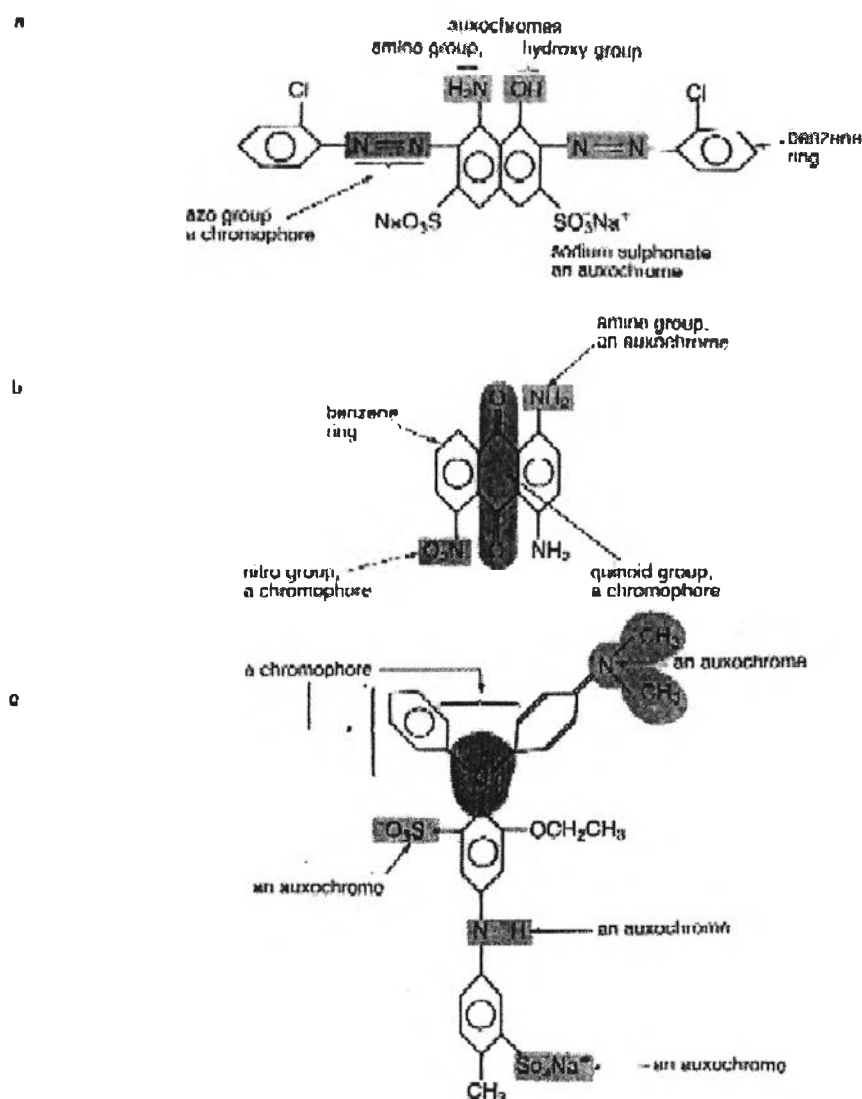


Figure 2.2 Structural formulae of various dye molecules.(the shading indicates chromophores (dark) and auxochromes (light))

- C.I. Acid Blue 86, 44075
- C.I. Disperse Violet 8, 62030
- C.I. Acid Violet 15, 43525

2.2.1 Acid Dyes

Acid dyes are so called because they are usually applied under acidic conditions. These water soluble dyes can be applied for man-made, synthetic, nylon fibers and natural protein fibers i.e. wool, silk, modified acrylic fiber and leather. The molecules of acid dyes are anionic type that commonly contain a sodium salt of sulphonic acid groups, (-SO₃Na). The adsorption of acid dyes on fibers results from an ionic or salt link between the dye molecules and the fiber polymer. The sites on the fiber mostly are amino groups, which are in protonated form; as a result, these functional groups can adsorb the acid dye molecules. The adsorption of dye onto the fiber site is shown in Figure 2.3. Hence, an acid condition is necessary in order to connect the fibers and dye molecules together. Figure 2.4 shows the examples of chemical structure of acid dye, which is used in the textile industry.

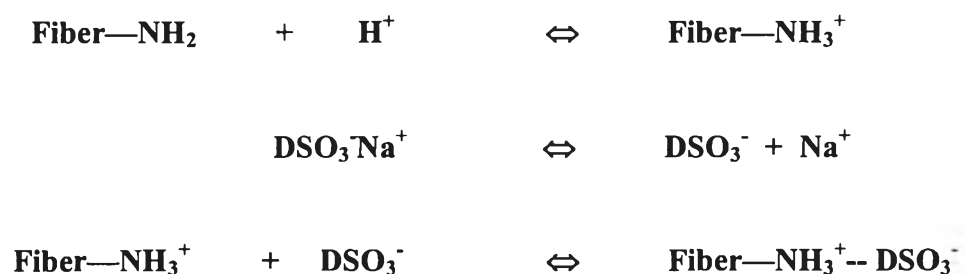


Figure 2.3 Adsorption of dye onto fiber site.

where Fiber—NH₂ is the fiber polymer

Fiber—NH₃⁺ is the fiber polymer in protonated form

DSO₃Na⁺ is the dye molecule

DSO₃ is the dye anion

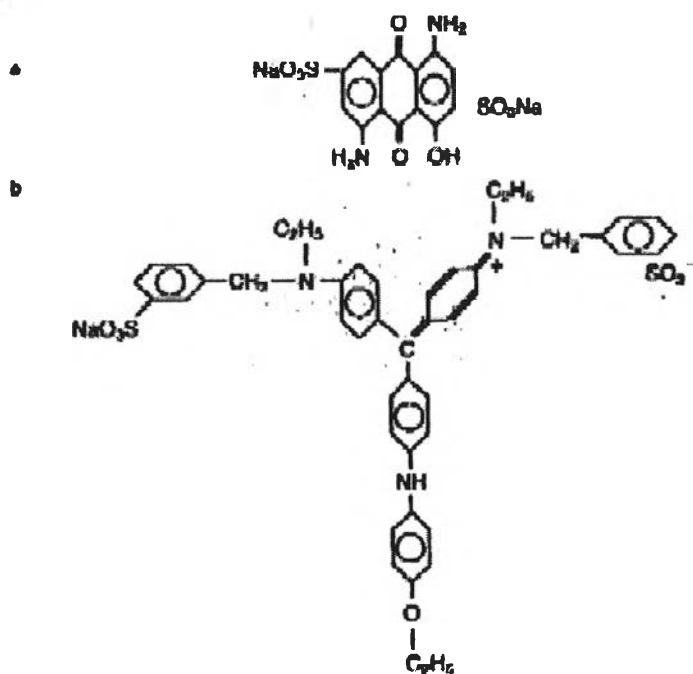


Figure 2.4 Nature of acid dye molecules.

(a) C.I. Acid Blue 45

(b) C.I. Acid Blue 83

2.2.2 Direct Dyes

Direct dyes have an excellent substantive property particularly for cellulosic textile materials. These water soluble anionic dye molecules can be applied for man-made and natural cellulose fiber i.e. cotton and viscose fibers. Because of the negative charges on the cellulose fiber surface, the addition of electrolyte (NaCl) to the dye liquor is substantial to attain the adequate exhaustion of the dye molecule by the fiber polymer system. The molecular structure of direct dyes mostly have the azo groups, $-N=N-$, and generally in the form of $R_1-N=N-X-N=N-R_2$. These are similar to the acid dyes. However, they have a larger molecule than the acid dyes. Their attachment is through both hydrogen bonds and van der Waals forces, and the intensity of the latter increases with increasing of the molecular size. Figure 2.5 shows the example of the direct dyes.

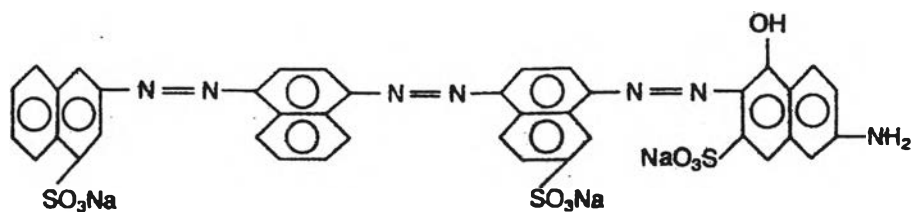


Figure 2.5 The nature of direct dye, C.I. Direct Blue 71, 34140.

2.2.3 Reactive Dyes

They are so called reactive dyes because their molecules react chemically with the fiber polymer. The fibers most readily colored with reactive dyes are the man-made and natural cellulose fibers, synthetic nylon and natural protein fibers.

These dyes have a very stable electron arrangement and provide very good resistance to the degrading effect of the ultraviolet component of sunlight as a result from the very stable covalent bond that exist between dye molecule and fiber polymer. The textile materials colored with reactive dyes have a very good wash-fastness especially in the usual laundering and dry-cleaning washing condition. Figure 2.6 demonstrates the example of chemical structure of reactive dye.

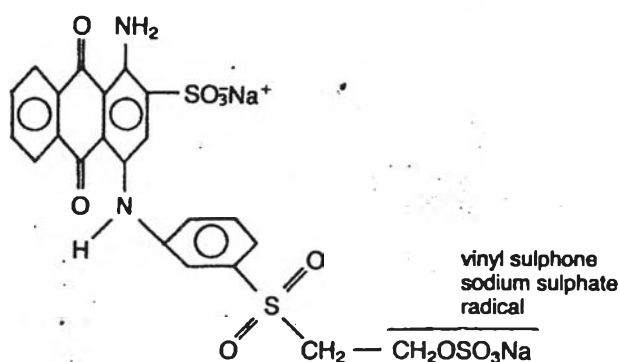


Figure 2.6 Structural formula for a vinyl sulphone derivative reactive dye (C.I. Reactive Blue 19,64200).

The process of applying reactive dye can be considered as a few steps. The first step, dye liquor is prepared by dissolving reactive dye into water followed by adding an electrolyte (mainly alkali solution) in order to assist exhaustion of the dye. The acid condition may be required depending on the type of fibers. The textile will be introduced to the dye batch in the next step *in situ* with heating the system where the reactions between dyes and fibers occur. Figure 2.7 shows how the reactive dye attaches itself onto the fiber.

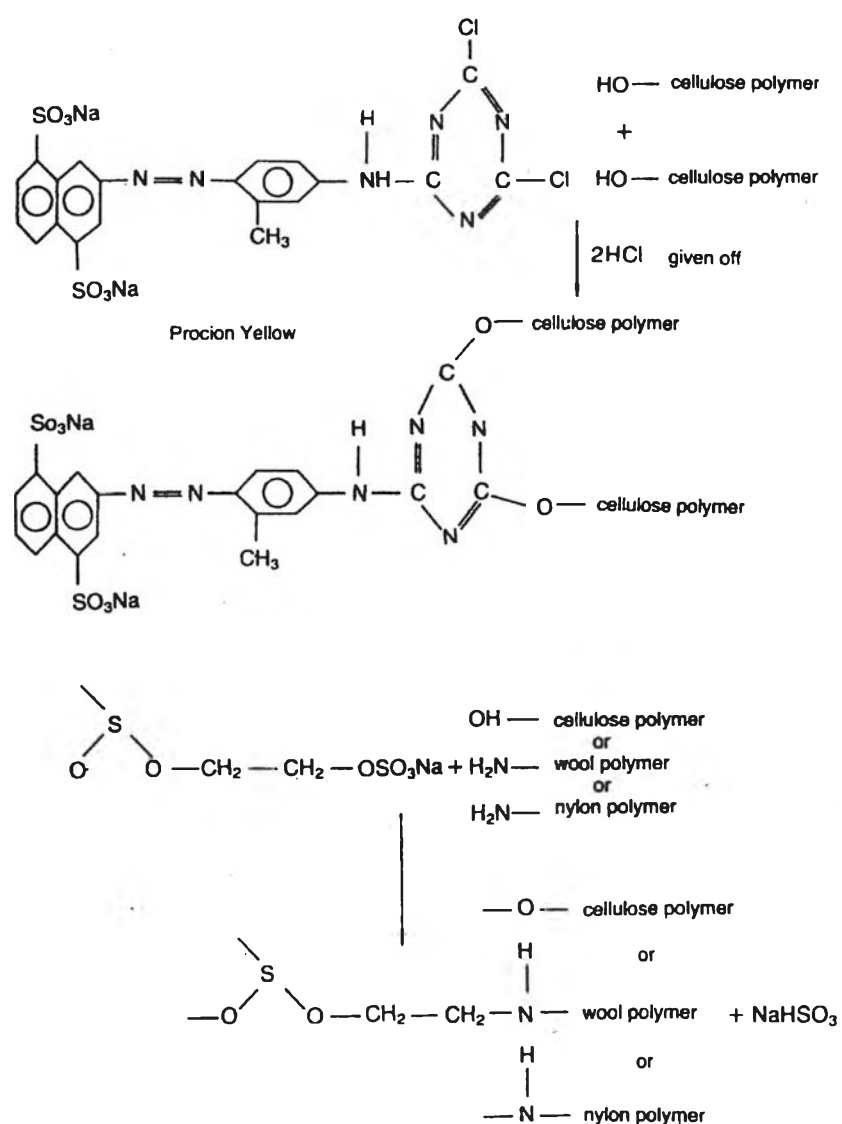


Figure 2.7 The reactive dye molecule and how it attaches itself, by way of covalent bonding, to fiber polymers.

2.3 Heavy Metals

Heavy metals, which have been defined as (1) elements with atomic number greater than iron, and (2) metals with densities greater than 5.0 g/cm^3 , are of high environment concern because of their toxicity.

In general, heavy metals used in a variety of processing techniques throughout the textile industry, including oxidizers for water insoluble dyes, aftertreatment of direct dye, heavy metal catalyst used for curing resins, finishes (i.e. flame retardant, soil release, and water repellent), dye stripping agents, and various classes of dyes. Table 2.5 lists various dye categories which contain heavy metals that are controlled via the new water quality criteria. Among these heavy metals, copper has reported as the highest concentration specie from textile wastes stream.

Table 2.5 Average metal content of selected dyes (ppm) (Karen and Michael, 1994)

Metal	Dye Class					
	Acid	Basic	Direct	Disperse	Reactive	Vat
Arsenic	<1	<1	<1	<1	1.4	<1
Cadmium	<1	<1	<1	<1	<1	<1
Chromium	9	2.5	3	3	24	83
Cobalt	3.2	<1	<1	<1	<1	<1
Copper	79	33	35	45	71	110
Lead	37	6	28	37	52	6
Mercury	<1	0.5	0.5	<1	0.5	1
Zinc	<13	32	8	3	4	4

Copper can cause a lot of illness and lethal diseases. The high amount of copper can cause liver and kidney damage and effects on the blood. Skin contact with copper can result in an allergic reaction in some people. This reaction is usually skin irritation or a skin rash. Moreover, animal studies have shown effects on the stomach and abnormalities in development when animals were fed a diet high in copper.

2.4 Chitin and Chitosan

2.4.1 Structure and General Applications

Chitin is the natural carbohydrate polymer which contains unique characteristics. It was first discovered by Braconnot in 1823. The name “Chitin” comes from the Greek word “Chiton” which means the shell (Foster and Webber, 1960, Shahidi *et al.*, 1999.). Since chitin is the second most abundant biopolymer in nature next to cellulose (Muzzarelli, 1997), there are a lot of research groups studying its properties and applications. Inside the living organism such as fungi, algae, protozoa, annelid, mollusk and arthropod, chitin acts as an important function by maintaining the strength of cell wall particularly in arthropod shell i.e. crab, shrimp and lobster. The structure of chitin is a long, linear polysaccharide molecule which is similar to the molecule of cellulose. The monomer unit in chitin is N-acetyl-D-glucosamine (2-acetamido-2-deoxy-D-glucose). These units are linked by $\beta(1, 4)$ -2-acetamido-2-deoxy-D-glucose ($C_8H_{13}NO_5$)_n.

In general, three types of chitin can be observed by difference molecular conformation. β -chitin, which is found mostly in the crab and shrimp shell, has the parallel molecular pattern while α -chitin, in mollusk, has the anti-parallel pattern. Unlike β and α type, γ -chitin has the disorder pattern and hardly to find in the nature. Mostly can be divided the preparation of chitin from nature sources in three steps which are the deproteinization by NaOH or enzyme protease, the demineralization by HCl and the decolorization by alcohol or ether respectively. Chitin is insoluble in many solvents, for example water, diluted acid, both of concentrated and diluted base, alcohol and other organic solvent. It can be dissolved in concentrated HCl, H₂SO₄, H₃PO₄, formic acid and DMAc-LiCl (N,N-Dimethylacetamide lithium chloride). Molecular weight of chitin is over 1×10^6 with around 200-4000 degree of polymerization.

Chitosan is the one of derivative form of chitin. It was accidentally found by Rouget in 1859 by boiling chitin with concentrated NaOH (Li *et al.*, 1992). By this accident, the acetamino groups (-NHCOCH₃) were transformed to be the amino groups (-NH₂) by removing acetal radicals (-COCH₃) in which this process was

called “N-Deacetylation process”. Alike the molecular unit of chitin, chitosan’s monomer is D-glucosamine (2-amino-2-deoxy-D-glucose). The degree of deacetylation can imply to the total amount occurring amino groups. These amino groups are the main useful function of chitosan because, for example, they can be protonated in the form of NH_3^+ as a result in altering chitosan to be the cationic polyelectrolyte. Chitosan can be solubilized by organic solvent which $\text{pH} < 6$, mostly using acetic acid and formic acid, and some of inorganic acid in the moderate temperature i.e. nitric acid, hyperchloride acid, perchloride acid and phosphoric acid. It cannot solubilize in water and all basic solvents.

In addition, chitin and chitosan are inexpensive and environmental benign, harmless to humans and plentiful by product from food industry. They are very effective as a purifier and separator for industry works, as an immobilization support of biocatalysts in food and pharmacy processes, as a flocculant and coagulant in wastewater treatment, and as a film application in agriculture, and are used for another application (Kawamura *et al.*, 1997). In some applications, the ability of chitosan can be improved by modifying chitosan flake as porous bead form. This modification has been done by dissolving chitosan flake with a suitable solvent, typically in acetic acid, and spraying dropwise into the caustic casting solution to solidify the spherical chitosan beads. As the beads are dissolved in an aqueous acid solution, they need some further chemically improvement by the cross-linking agent so that the acid resistance and mechanical strength properties of the beads can be increased significantly. Cross-linked chitosan gel beads also increase the internal surface area, however, they reduce the saturation adsorption capacity because of the decreasing of free amino groups (Hsien and Rorrer, 1995). Figure 2.8 shows the molecular structure of cellulose, chitin and chitosan.

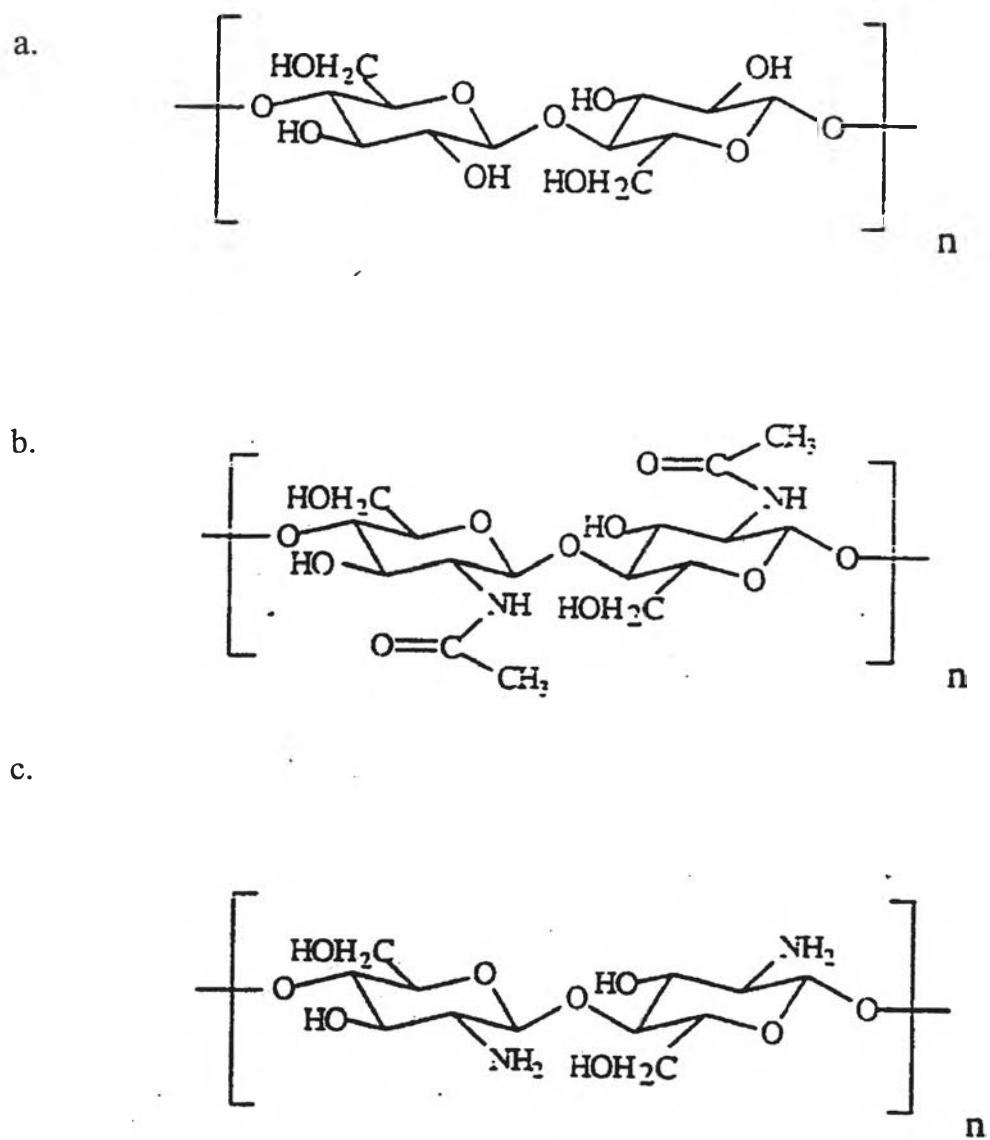


Figure 2.8 Chemical structure of (a) cellulose, (b) chitin and (c) chitosan.

2.4.2 Physical and Chemical Properties of Chitosan

Two important properties of chitosan relevant to this research work are degree of deacetylation and molecular weight. Both of them affect directly mechanical properties and adsorption capacity of chitosan. Degree of deacetylation and molecular weight depend on many variables in which occur during the synthesis process through the final purification processes.

2.4.2.1 Degree of Deacetylation

Degree of deacetylation is the factor which is used to identify the difference between chitin and chitosan. Since chitin and chitosan are copolymer of N-acetyl-D-glucosamine and D-glucosamine, degree of deacetylation is the ratio between these two monomers. The more D-glucosamine groups, the higher of degree of deacetylation can be observed in which representing more chitosan properties and vice versa. In general, the degree of deacetylation is more than 70% for chitosan. Several techniques are used for determining degree of deacetylation such as IR-spectroscopy, CHN analysis or elemental analysis and ¹H-NMR Proton analysis. The higher degree of deacetylation, the more units of chitosan are cross-linked, which increases its solubility because the free amino groups on chitosan unit can be protonated to form cationic amine group (-NH₃⁺) which is dissolvable in some electrolytic organic solvent i.e. acetic acid and formic acid.

2.4.2.2 Molecular Weight

The molecular weight of native chitin is usually larger than 1×10^6 while that of the commercial chitosan product is between 2×10^5 to 1.2×10^6 . Several methods are used to determine molecular weight of chitosan ; for examples, light scattering, gel-permeation chromatography (GPC), high performance liquid chromatography (HPLC), and viscosity measurement. The viscometry method is one of the simplest and most rapid methods, or which are based on the well-know Mark-Houwink equation.

$$[\eta] = K * \overline{M}_w^a \quad (2.1)$$

where; a and K are the constant
 \overline{M}_w is the weight-average molecular weight

Since 1974, several reports have dealt with the determination of the values of K and a for chitosan. However, each of these results was different although the determining conditions, such as solvents, and temperature, were very similar.

Wang *et al.*, (1991) obtained the following equation to determine a and K .

$$\begin{aligned} K &= 1.69 * 10^{-30} * DD^{14.0} \quad (r = 0.996) \\ a &= -1.02 * 10^{-2} * DD + 1.82 \quad (r = 0.998) \end{aligned}$$

2.5 Adsorption by Chitin and Chitosan for Dye Removal

Reactive dye is one of the most usage water soluble dyes in the textile plant. After dissolved, its molecule can separate into two parts, cationic and anionic groups. Mostly the anionic groups come from sulfonic acid residue that acts as a site for adsorption by ion-exchange with the protonated amino groups ($-\text{NH}_3^+$) of chitosan unit as shown in Figure 2.3.

Muzzarelli (1977) reported the kinetic of the reaction of Procion yellow RS with the amino groups of chitosan. Dichlorotriazine dye reacts with the amino groups of chitin and chitosan in both alkaline and acidic media whereas the hydroxyl groups take part in the reaction in alkaline media only.

Shimizu *et al.*, (1995) studied the effect of added metal ions on the interaction of chitin and partially deacetylated chitin with azo dye carrying two hydroxyl groups. The metal ions used were Zn^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+} . It was observed that the degree of adsorption increased with increasing Cu^{2+} . This might be attributed to the formation of the polymer-copper-dye coordination linkage. The other group determined the effects of degree of deacetylation (DD) of chitin with the variation of pH on dye removal from textile effluents. It was found that the dye adsorption capacity increased with increasing of DD of deacetylated chitin for each pH.

Moreover, the other researcher studied the capability of chitosan to remove vinyl sulfone and chlorotriazine reactive dyes from aqueous solutions. They found that the amount of adsorbed dye decreased with increasing particle size of the chitosan.

Wu *et al.*, (2000) investigated the comparative adsorption of metal and dye on flake and bead types of chitosans. They found that chitosan in the bead form had a higher capacity for reactive red 222 (RR222) than the flake type by a factor 2.0-3.8 and also higher in adsorption rate. Thus, chitosan beads provide the possibility for industrial pollution control, especially for high-molecular-weight pollutants.

2.6 Adsorption by Chitin and Chitosan for Metals Removal

Another attractive application of chitosan is the adsorption of metal cations. Many research groups studied this behavior by which the variation of metal cations and the formation of chitosan are altered as the important parameters. Muzzarelli (1976) had made an extensive review on this issue.

Muzzarelli (1976) gave the collection rates of metal ions onto chitosan as $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$ as the same as the Irving and Williams series, and there was a relation between the order and the second ionization potentials.

Guibal *et al.*, (1995, 1998) studied the kinetic behavior of adsorption of the radioactive isotopes and heavy metal ions by chitosan both in flake and bead form. They found that the adsorption rate was controlled by the diffusion of metal ions and the kinetic data depending on type of metal can be well fitted by Langmuir or Freundlich isotherm.

Hsien and Rorrer (1995) investigated the effect of cross-linking on chitosan beads and cadmium ion adsorption capacity. It was found that the cross-linking may have reduced the crushing strength of the beads by shifting the void fraction from macropores to mesopores as the internal surface area increased. As a result, the mechanical strength was improved, is progressively suitable for column applications.

The mechanism of complex formation of metals with chitosan is manifold and is probably dominated by different processes such as adsorption, ion-exchange, and chelation under different conditions. The mechanisms for the binding of metal

ions to chitosan have been proposed by Park and Choi (1983) based on the acid-base equilibria and related properties.

While studying the use of chitosan in removal of heavy metal and radioactive isotope and in recovery the valuable metals, Muzzarelli *et al.*, (1989) concluded that the favorable sorption may be achieved by buffering condition. It was found that, when chitosan was contacted with an unbuffered aqueous metal solution, it resulted in a shift to higher pH which can cause the metal hydroxide precipitations. Thus, the pH of the metal solutions after contact should be kept below the pH at which the metal hydroxide can be formed in order to confirm that the removal of metal ions was only due to the chitosan and not due to the precipitation.

Fixed-bed operation is a promising technique for textile waste treatment. Wastes stream, normally, consists mainly dyestuff and heavy metals component. Ruiz *et al.* (2001) studied the sorption of palladium ions on glutaraldehyde-crosslinked chitosan flake in fixed-bed systems. The sorption performance were dominantly controlled by the presence of competitor anions in the solution depending on mass transfer characteristic of each anion. In general, the breakthrough curve of fixed-bed system can be controlled by several parameters such as the column depth, the superficial flow velocity, the metal concentration and also the size of adsorbent particles. They found that although the effect of these parameters cannot be neglected, the difference was not influence as in other sorbent/sorbate systems. The sorption of molybdate ions by using chitosan gel beads, for example, the influence of intraparticle diffusion on kinetic control was more marked, and the breakthrough curves were more sensitive to those operating conditions i.e. flow velocity, column height and particle sizing.