



Chapter 2

Theories and Literature Reviews

2.1 Dyes

2.1.1 Dyes Classification

Dyes may be classified according to chemical structure and according to their method of application. Classification of dyes according to chemical structure is most useful to the dye chemist who may be interested dye synthesis and the relationship between chemical structure and properties of in dye. Classification according to method of application is most useful to the technologist concerned with coloration of textile products. Understanding of both of these methods of classification is useful to the textile engineer or textile chemist.

2.1.1.1 Dye Classes According to Chemical Structure

Classification of dyes according to chemical structure into thirteen groups shown in Table 2.1.

Table 2.1 Dyes by structural classes (Waring, cited in Perkins, 1996).

Structural Class	Description	Application Classes
Azo dyes	Containing one or more azo, -N=N-, group	direct, azoic, reactive, acid, basic, disperse
Anthraquinone dyes	9,10- anthraquinone substituted at one or more of four alpha positions (1,4,5, and 8)	vat, reactive, disperse, acid
Benzodifurnone dyes	Contain benzodifuranone (BDF) chromogen	disperse, (maybe others)
Polycyclic aromatic carbonyl dyes	Contain one or more carbonyl groups linked by a quinonoid system	vat
Indigoid dyes	Contain indigoid chromogen	vat (only indigo and tetrabromo indigo are of commercial importance)
Polymethine and related dyes	Contain conjugated system of double bonds not in aromatic rings	basic
Styryl dyes	Contain styryl, C=C, group	disperse
Di- and tri-aryl carbonium dyes	Contain di- or tri-aryl substituted carbon atom	basic, related structures found in direct and reactive classes

Table 2.1 Dyes by structural classes (Waring, cited in Perkins, 1996) (Continued).

Structural Class	Description	Application Classes
Phthalocyanine dyes	Contain metal complex phthalocyanine chromogen	direct, reactive, acid
Quinophthalone dyes	Contain quinophthalone chromogen	disperse
Sulfur dyes	Contain sulfur atoms bridging aromatic ring structures	sulfur
Nitro and nitroso dyes	Contain nitro group on aromatic ring	acid, disperse
Miscellaneous dyes	stilbene, formazen structure	direct, reactive

2.1.1.2 Dye Classes According to Application

(1) Direct dyes

Direct dyes have been used to dye cellulose for over 100 years. Because of the simplicity of application and great choice of products available, direct dyes are popular dye class. Direct dyes range from moderate to poor in washfastness. Lightfastness varies from poor to excellent depending on the particular dye.

(2) Sulfur dyes

Sulfur dyes are widely used on cotton mainly because they are economical to use. They have good to excellent washfastness and good lightfastness in dark shades. Lightfastness of pale shades is poor. Sulfur dyes are usually dull in shade since the molecular structures are complex. As a class, the sulfur dyes are not resistant to chlorine-containing bleaches.

(3) Azoic dyes

Azoic dyeing consists of reacting two components, neither of which itself is a dye, with one another inside the fiber to form an azo pigment. Azoic dyeing is sometimes called naphthol dyeing because one of the components used to make the pigment is often a naphthol.

(4) Reactive dyes

Reactive dyes for protein fibers and nylon have also been offered by dye manufacturers, but dyeing of cellulose is the major use for dyes in the reactive

classification. The reaction between a reactive dye and the fiber produces a covalent bond. By their nature, reactive dyes also react with water.

(5) Vat dyes

Vat dyes are used mainly on cellulosic fibers, but some can be applied to protein fibers. They usually have outstanding color fastness properties. Vat dyes are more expensive and difficult to apply than other classes for cellulose such as direct, sulfurs, and reactives.

(6) Acid dyes

Acid dyes contain acidic groups, usually $-\text{SO}_3\text{H}$, and are used on fibers containing basic groups that can interact with these acidic groups. The fibers that are dyeable with dyes are polyamides containing some free amino, $-\text{NH}_2$, groups. Nylon is the most important synthetic fiber having this characteristic. Wool, silk, and other protein-based natural fibers also have amino groups that can bond with acidic dyes.

(7) Basic dyes

Basic dyes are sometimes called cationic dyes because the chromophore contains a positive charge. Basic dyes are used on fibers containing acidic groups that can interact with these cationic (basic) groups. The fibers that are dyeable with basic dyes contain either carbonyl, $-\text{COOH}$, or more commonly sulfonic acid, $-\text{SO}_3\text{H}$, groups. The color fastness properties of basic dyes vary greatly from one dye to another and depend on what fiber they are used on. As a general rule, wash fastness and particularly light fastness of basic dyes are poor on wool and other protein fibers. On the other hand, wash fastness and light fastness are very good to excellent on acrylic fibers.

(8) Disperse dyes

The disperse dye class is so named because these dyes are almost insoluble in water and are used as finely divided aqueous dispersions. Disperse dyes can be applied to nylon, cellulose acetate, acrylics and occasionally other fibers, but the major consumption is for dyeing of polyester. Wash fastness and light fastness of disperse dye is generally good.

Table 2.2 Dyes by application classes (Barnekart, Barnes and Hussian, cited in Iangphasuk, M., 1997:9-11)

Dyes Class	Characteristics	Typical Fiber	Method of Application
Direct	- highly water soluble - moderate to good light fastness	- cotton - viscose - cotton - wool - other cellulose	- fiber placed in slightly alkaline dyebath - add dye electrolyte (NaCl or Na ₂ SO ₄) to displace dye to fiber, temp. to 96°C
Vat	- insoluble - wet fast	- cotton - viscose - cellulose fiber - wool - rayon - silk - linen - nylon	- fiber placed in dyebath - dye dissolved in alkaline sodium sulfur - dye displaced to fiber with electrolyte -
Sulfur	- insoluble - wet fast - poor resistance to sunlight	- cotton - viscose - rayon - linen - cellulose fiber	- fiber placed in dyebath - dye dissolved in alkaline sodium sulfur - dye displaced to fiber with electrolyte
Azoic or Naphthol	- insoluble pigments - fastness and brightness of shade	- natural and mercerized cotton - rayon - some synthetics	- fiber placed in dyebath - dye chromophore added - boiled to precipitate
Reactive	- high water soluble - good wet fastness	- cotton - viscose - wool - cellulose fiber - silk - linen	- fiber placed in dyebath - add salts to displace dye to fiber - add alkaline to cause reaction between dye and fiber
Acid	- high water soluble - poor wet fastness	- nylon - wool	- dyeing solution must be acid - high temp is used (50-110°C)
Dispersed	- colloid dispersion - very low solubility - good wet fastness	- polyester - nylon - acrylic - cellulose acetate	- fiber placed in acidified dyebath pH 4.5 - dye added - temp to 130°C causes dye migration into fiber
Basis or Cationic	- high water soluble - poor light fastness - poor to moderate wet fastness	- silk - wool - acrylic	- fiber placed in acidified dyebath at pH 4-6 - dye added and temp increase from 100 to 105°C - dye diffuse into fiber

2.1.2 Dyestuff Color Appearance

Witt, cited in Iangphasuk, M. (1997) summarized that dyestuffs appear colored because of chromophores, group(s) of atom, in dye molecules causing wavelength specific light absorption and reflection. Chromophore is an unsaturated functional group in organic compound which can cause the absorption in the ultraviolet visible range. There are seven groups of chromophores in dyestuff as follows:

(1) nitroso group	-NO	or	=N-OH
(2) nitro group	-NO ₂	or	=NO.OH
(3) azo group	-N=N-		
(4) ethylene group	>C=C<		
(5) carbonyl group	>C=O		
(6) carbonyl-nitrogen group	>C=NH	or	>CH=NH
(7) sulfur group	>C=S	or	-C-S-S-C-

Approximately 80% of all reactive dyes are based on the azo chromogen. Azo dyes are compounds containing azo groups (-N=N). The azo groups are mainly bound to benzene or naphthalene rings, but in some cases they are also attached to aromatic heterocycles or enolizable aliphatic group.

2.1.3 Reactive dyes

Reactive dyes are colored compounds which have suitable group capable of forming covalent bonds between a carbon or phosphorus atom of the dye ion or molecule and an oxygen, nitrogen or sulfur atom of hydroxyl, an amino or a mercapto group, respectively, of the substrate.

The characteristic structural features of a reactive dye are shown below. In some cases the reactive group is attached directly, i.e. without a bridge, to the chromogenic system. (Fig 3.1) and (Table 3.3)

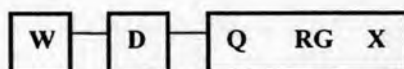


Figure 2.1 Structure of reactive dyes (Johnson, 1989)

- RG = reactive group; components of hydroxyl or amino groups
- Q = bridge link, i.e. -NH-, -NHCO-, -SO₂-, -NHSO₂-, -NCH₃-
- X = leaving group
- D = chromogen, coloring substrate
- W = water-solubilising group

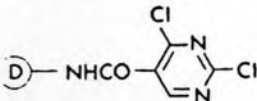
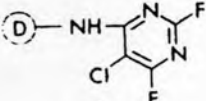
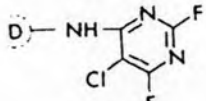
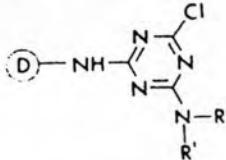
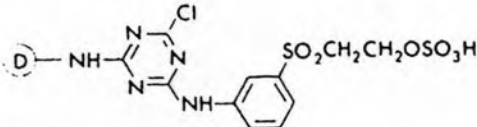
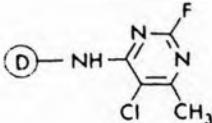
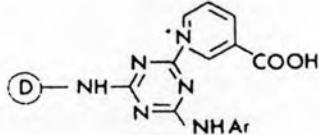
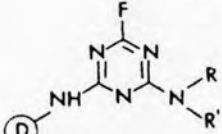
Table 2.3 Reactive groups in reactive dyes of the major dye manufacturers of the world (Johnson, 1989).

Reactive group	First sold	Trade name and original manufacturer ^a	Used for
$\text{D}-\text{SO}_2\text{CH}=\text{CH}_2 \cdot \text{D}-\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$	1952	Remalan (HOE)	Wool
$\text{D}-\text{NHCOCH}_2\text{CH}_2\text{Cl}$ and $\text{D}-\text{NH}-\text{N}(\text{Cl})\text{N}(\text{NHR})$	1954	Cibalan Brilliant (CIBA) (now Irganol, CGY)	Wool
$\text{D}-\text{NH}-\text{N}(\text{Cl})\text{N}(\text{Cl})$	1956	Procion MX (ICI)	Cellulose
$\text{D}-\text{NH}-\text{N}(\text{Cl})\text{N}(\text{R})$	1957	Cibacron (CIBA)	Cellulose
ditto	1957	Procion H (ICI)	Cellulose
$\text{D}-\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$	1958	Remazol (HOE) †Remalan Fast (HOE)	Cellulose Wool
$\text{D}-\text{NHCH}_2-\text{CH}(\text{OCH}_2)-\text{CH}_2$ and others (disperse dyes)	1958	Procinyll (ICI)	Polyamide
$\text{D}-\text{NH}-\text{N}(\text{Cl})\text{N}(\text{Cl})$	1960	Drimarene Z and X (S)	Cellulose
ditto	1960	Reactone (Gy) (now Cibacron T, CGY)	Cellulose
$\text{D}-\text{SO}_2\text{NHCH}_2\text{CH}_2\text{OSO}_3\text{H}$	1960	Levafix J (BAY)	Cellulose
$\text{D}-\text{NHCO}-\text{C}_6\text{H}_3(\text{Cl})_2-\text{N}(\text{Cl})\text{N}(\text{Cl})$	1961	Levafix E (BAY)	Cellulose
$\text{D}-\text{NHCOCH}_2\text{CH}_2\text{Cl}$	1961	Primazine (BASF)	Cellulose
$+\text{D}-\text{NHCOCH}_2\text{CH}_2\text{OSO}_3\text{H} \cdot \text{D}-\text{NHCOCH}=\text{CH}_2$			
$\text{D}-\text{SO}_2\text{NHCH}_2\text{CH}_2\text{SSO}_3\text{H}$	1962	†Wool Fast Turquoise Blue SW (HOE)	Wool
$\text{D}-\text{CH}_2\text{NHCOC}(\text{Cl})=\text{CH}_2$	1962	Lanasyn Pure Blue FBL (S)	Wool
$\text{D}-\text{NHCO}-\text{C}_6\text{H}_3(\text{Cl})_2-\text{N}(\text{Cl})\text{N}(\text{Cl})$	1963	Reatex (Fran) (now Elisiane)	Cellulose
$+\text{D}-\text{NHCO}-\text{C}_6\text{H}_3(\text{Cl})-\text{S}-\text{N}(\text{Cl})$			

Table 2.3 Reactive groups in reactive dyes of the major dye manufacturers of the world (Johnson, 1989) (Continued).

Reactive group	First sold	Trade name and original manufacturer*	Used for
$\text{D}-\text{NHCOCH}=\text{CH}_2$ (metal complexes)	1964	Procilan (ICI)	Wool
$\text{D}-\text{NHCOCH}_2\text{CH}_2-\text{N} \begin{array}{c} \diagup \text{N} \\ \diagdown \text{C} \\ \text{O} \\ \text{Cl} \end{array}$	1964	†Primazine P (BASF)	Cellulose
$\text{D}-\text{NHCO}-\text{C}_5\text{H}_2\text{N}_2$ (with Cl substituents)	1964	Solidazol (Fran)	Cellulose
+ $\text{D}_2-\text{NHCOCH}_2\text{CH}_2\text{SO}_2\text{R}$			
$\text{D}-\text{SO}_2\text{CH}_2\text{CH}_2\text{NR}_2$	1965	Remazol H (HOE)	Cellulose
$\text{D}-\text{NH}-\text{C}_5\text{H}_2\text{N}_2$ (with NHCH_2OH substituents)	1965	†Calcobond (ACY)	Cellulose
$\text{D}-\text{NHCO}-\text{C}(\text{Br})=\text{CH}_2$	1966	Lanasol (CIBA)	Wool
$\text{D}-\text{CH}_2\text{NHCOCH}_2\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$	1967	†Lanafix (NSK)	Wool
$\text{D}-\text{NHCO}-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}(\text{HSO}_2)-\text{CH}=\text{CH}_2$	1967	Solidazol N (Fran)	Cellulose
$\text{D}-\text{NH}-\text{C}_5\text{H}_2\text{N}_2$ (with SO_2CH_3 , Cl , and CH_3 substituents)	1967	Levafix P (BAY)	Cellulose
$\text{D}-\text{NH}-\text{C}_5\text{H}_2\text{N}_2$ (with SO_3H , Cl , and Cl substituents)	1967	Procion Supra (ICI)	Cellulose
$\text{D}_2-\text{NH}-\text{C}_5\text{H}_2\text{N}_2$ (with SO_3H , OCH_3 , and SO_2CH_3 substituents)	1967	Procion SP (ICI)	Cellulose
+ $\text{D}_2-\text{NH}-\text{C}_5\text{H}_2\text{N}_2$ (with Cl and SO_2CH_3 substituents)			
$\text{D}-\text{NH}-\text{C}_5\text{H}_2\text{N}_2$ (with OCH_3 and Cl substituents)	1968	Cibacron Pront (CIBA)	Cellulose

Table 2.3 Reactive groups in reactive dyes of the major dye manufacturers of the world (Johnson, 1989) (Continued).

Reactive group	First sold	Trade name and original manufacturer ^a	Used for
	1968	†Reactofil (Gy)	Cellulose
	1970	Verofix (BAY)	Wool
ditto	1970	Levafix P-A (BAY)	Cellulose
ditto	1970	Drimalan F (S)	Wool
$\text{D}-\text{SO}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$	1970	Hostalan (HOE) ^b	Wool
	1971	Drimarene R and K (S)	Cellulose
$\text{D}-\text{PO}_3\text{H}_2$	1978	Procion T (ICI) ^c	Cellulose
	1978	Cibacron F (CGY)	Cellulose
	1980	Sumifix Supra (NSK)	Cellulose
	1981	Levafix PN (BAY)	Cellulose
	1984	Kayacelon React (KYK)	Cellulose
	1988	Cibacron C (CGY)	Cellulose
modified vinyl sulphone			

^a C.I. abbreviations of presently existing manufacturers, old abbreviations only for companies no longer existing as such. Dyes marked † are no longer produced.

^b Most Hostalan dyes contain, however, one of the reactive groups $-\text{SO}_2\text{CH}_2\text{OSO}_3\text{H}$ or $-\text{SO}_2\text{CH}_2\text{CH}_2\text{Cl}$.

^c Now marketed in mixtures with disperse dyes as Procilene dyes.

2.1.4 Textile Production Process

The textile industry involves in the manufacture of fabrics from both natural and man-made fibers. There are various types of manufacturing processes depending on the raw materials and textile products. The wet processes can be briefly described as follows (Hussian, US-EPA and Yanumate, cited in Iangphasuk, M.,1997:6-7)

(1) Desizing

Desizing is a process in which starch-based wrap size is hydrolyzed by acid or digested by enzymes to render it soluble in water and therefore readily removable by washing. Polyvinyl alcohol and acrylic sizes are usually removed directly in scouring.

(2) Scouring

Scouring consists of a hot alkaline treatment in which oily, waxy or greasy material or acquired impurities as well as some ash, pectins and protein, if present, are removed from fibers. The action can involve saponification and emulsification as well as simple solution of the impurities in the alkaline liquor. Scouring with chlorinated hydrocarbon solvents is also use to some extent.

(3) Bleaching

Bleaching is used to destroy residual natural color in fibers remaining after the scouring process. It is an oxidation process usually effected with hydrogen peroxide or sodium hypochlorite.

(4) Mercerizing

Mercerizing is the treatment of cotton yarn or fabric, while under tension to prevent shrinkage, with sodium hydroxide solution in the concentration range of 16 to 25 percent.

(5) Dyeing

The function of dyeing is to anchor dyestuff molecules to textile. Dyeing solutions are prepared by using many kinds of dyestuff and auxiliary chemicals. Chemical loading varies widely depending on the weight of fabrics being dyed and the color desired. After dyeing, 5-50% of dyestuff and 90% of auxiliary chemicals

remain in the dyebaths. Although the dyebath can be reused many times, finally when the impurities in dyebaths exceed acceptable values, they must be discharged. Other wastewater is obtained when dyed products are rinsed to remove excess dye and other chemicals. These dye chemicals present problems for traditional wastewater treatment because many cannot easily be biodegraded.

(6) Printing

Printing, like dyeing, is a process for applying color to fabric. Instead of coloring the whole cloth, as in dyeing, print color is applied only to specific areas of the cloth to achieve a planned design. The chemicals used are not only printing pigments but also some auxiliary chemicals such as binder, latex, emulsifier, solvent and thickener.

(7) Finishing

Finishing is the treatment of fabric to give a desired surface effect, such as calendared, embossed, lacquered, or napped.

2.1.5 Textile Wastewater Treatment Processes (Cooper, 1995)

2.1.5.1 Coagulation, flocculation and precipitation

- **Inorganic coagulants** – lime, magnesium and iron salts – have been used for coagulation of dye waste over many years. With changes in dyes, and with the dye consents proposed, these no longer give completely satisfactory treatments.

- **Organic polymers** have been developed for color removal treatments and, in general, they offer advantages over inorganic: sludge production is much less and color removal was significantly improved. It was found, however, that color consent conditions were not reliably met.

- **Cationic polymers**, despite low mammalian toxicity, are toxic to freshwater fish at low concentrations and care must be taken that the flocculation condition ensure low residual polymer. Consideration also has to be given to the sensitive sewage treatment processes, such as nitrification.

Certain polymers may inhibit this process, giving rise to increased levels of ammonium in the river.

In considering this treatment processes the cost concentration must be taken into account, sludge disposal costs are growing rapidly.

2.1.5.2 Oxidation techniques

A variety of oxidizing agents can be used to decolorize dye waste, and are described in turn below.

- **Chlorine:** Chlorine, in the form of sodium hypochlorite, decolorizes many dyebaths efficiently, though not all. It is low-cost technique, but there is concern about any excess chlorine forming adsorbable organohalides (AOXs) with organic material in the effluent and the watercourse. In some countries, legislation on AOXs levels is already in place.

- **Chlorine dioxide:** Chlorine dioxide (ClO_2) is less reactive than chlorine. It did not decolorize dye waste efficiently to consent conditions, as it has no effect on some dye classes (such as vat dyes). Nevertheless, chlorine dioxide is highly effective against reactive, direct, disperse and anionic pre-metallised dyes. It could be used as polishing treatment.

- **Hydrogen peroxide:** Hydrogen peroxide, alone, is insufficiently powerful to decolorize dye waste at a normal temperature and pH. In acid solution, however, with iron(II) (Fenton's reagent) as a catalyst, the peroxide forms the vigorous hydroxyl radicals and may be used to decolorize dye wastes.

Ultraviolet light/hydrogen peroxide oxidation involves the single-step dissociation of hydrogen peroxide to form hydroxyl radicals. Hydroxyl radicals ($\text{OH}\cdot$) can oxidize organics compounds such as dyes by abstraction of protons producing organic radicals ($\text{R}\cdot$) which are high reactive and can be further oxidized.

Fenton's oxidation is capable of treating both soluble dyes, such as reactive dyes, and insoluble dyes, such as vat and disperse dyes. The vigorous oxidation also reduces the COD of the effluent. Neutralization of the effluents

after treatment causes precipitation of the iron oxide and hydroxide, which removes any remaining insoluble dye from the effluent by adsorption and/or flocculation.

- **Ozone:** Ozone is a very powerful oxidizing agent which will decolorize dye wastes. A high COD significantly reduces the effectiveness of the color removal, but is not itself reduced. Ozone must be generated on site and its toxicity to operating personnel must be taken into consideration. The main advantage of ozonation is no sludge production.

Ozone in combination with hydrogen peroxide or ultraviolet irradiation provides an effective supply of hydroxyl radicals for complete degradation of most pollutants.

2.1.5.3 Adsorption

The most commonly activated carbon is the original adsorbent used to adsorb dye molecules and remove color. The activated carbon can be granulated (GAC) or powdered (PAC). Not only activated carbon, but other adsorbents such as silica gel, fly ash, fired clay, baggasse pith and activated alumina have also been used for dyestuff adsorption. Silica gel is good adsorbent for basic dyes. After a period of time, regeneration will be required. The efficiency of regenerated activated carbon is much lower than for fresh material.

2.1.5.4 Biological treatment

- **Aerobic:** During the standard biological effluent treatment color is not destroyed, but considerable amounts may be adsorbed on to the biomass. This is dependent on the loading, and some breakthrough may be observed. As mentioned previously, this adsorption does not occur with reactive dyes or with some acid dye; with these dyes, therefore, further treatment will be required.

- **Anaerobic:** Preliminary work on anaerobic degradation of effluent has indicated that it is not efficient for color removal. Moreover, there is some

concern that the presence of sulfates in the dye waste may give rise to hydrogen sulfide under anaerobic conditions.

2.1.5.5 Membrane Techniques

The research investigated various types of membrane techniques that are currently commercially available. There are:

- Microfiltration
- Ultrafiltration
- Nanofiltration
- Reverse osmosis

2.1.6 Taiwan's Effluent Standard

The discharge standards of 1998, textile industries are required by Environmental Protection Administration of Taiwan to comply with the COD and color less than 100 mg/l and 400 in American Dye Manufacturer Institute (ADMI) unit, respectively. (Environmental Protection Administration, ROC., 1998).

Table 2.4 Taiwan's Effluent Standard (Environmental Protection Administration, ROC., 1998).

Effluent characteristics	Effluent limits
Water temperature	1. For effluents discharged into surface water bodies other than the ocean: # Below 38°C (from May to September) # Below 35°C (from October to April) 2. For effluents discharged directly into marine waters, the temperature at the discharge point shall not exceed 42°C; and the temperature difference should not exceed 4°C for surface water at 500 meters from the discharge point.
pH	6.0–9.0
Fluorides (not including complex ions)	15
Nitrate nitrogen	50
Ammonia nitrogen	10
Orthophosphates (calculated as trivalent phosphate radicals)	4
Phenols	1
Anionic surfactants	10
Cyanide	1
Oil and grease (n-hexane extract)	10
Soluble iron	10
Soluble manganese	10
Cadmium	0.03
Lead	1
Total chromium	2
Hexavalent chromium	0.5
Organic mercury	not detectable
Total mercury	0.005
Copper	3
Zinc	5
Silver	0.5

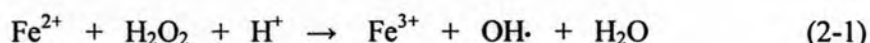
Table 2.4 Taiwan's Effluent Standard (Environmental Protection Administration, ROC., 1998). (Continued)

Effluent characteristics	Effluent limits
Nickel	1
Selenium	0.5
Arsenic	0.5
Boron	1
Sulfide	1
Formaldehyde	3
PCBs	not detectable
Total organophosphorous compounds (such as Parathion, Diazinon, Tamaron, Azodrin, EPN, etc.)	0.5
Total aminomethyl-carbamate (such as Mipcin, Carbofuran, Lannate, Unden, BPMC, etc.)	0.5
Herbicides (such as Butachlor, Paraquat, 2,4-D (sodium), Lasso, CNP-MCPA, Glyphosate, etc.)	1
Endosulfan	0.03
Endrin	0.0002
Lindane	0.004
Heptachlor and its derivatives	0.001
DDT and its derivatives	0.001
Aldrin, Dieldrin	0.003
Pentachlorophenol and its salts	0.005
Toxaphene	0.005
Pentachloronitro-benzene	not detectable
Folpet phaltan	not detectable
Captafol	not detectable
Captan	not detectable
Biological oxygen demand (BOD)	30
Chemical oxygen demand (COD)	100
Suspended solids	30
True color	400

2.2 Fenton Processes

Advanced oxidation processes (AOPs) have shown a potential for treating refractory compounds in water. Among various AOPs, Fenton's ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) has effectively treated various organic contaminants. The combination of hydrogen peroxide and a ferrous ion has been referred to as "Fenton's reagent". The reactivity of this system was first observed in 1876s by its inventor H.J.H. Fenton, but its application as an oxidizing process for destroying toxic organics was not applied until the late 1960s. Today, Fenton's reagent is used to treat a variety of industry wastes containing a range of toxic organic compound (wastes derived from dyestuffs, pesticides, wood preservatives and rubber chemicals).

Fenton's reagent is a mixture of H_2O_2 and ferrous ion under acidic pH condition (3-5), which generates hydroxyl radicals according to the reaction.

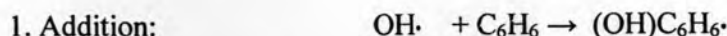


Fenton oxidation can be carried at normal temperature and at atmospheric pressure. Fenton reactions exploit the reactivity of the hydroxyl radical ($\text{OH}\cdot$), which has a very high oxidation potential and is able to oxidize almost all organic pollutants quickly and non-selectivity, produced in acidic solution by the catalytic decomposition of H_2O_2 . Its position is second in the oxidation potential series next to fluorine.

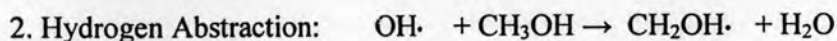
Table 2.5 Oxidation potential of common species (US Peroxide, 2005)

Reactive Species	Oxidation Potential (V)
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine	1.36

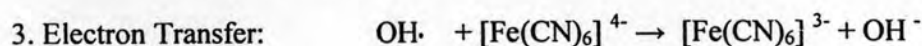
The chemical reactions of the hydroxyl radical in water are of four types (US Peroxide, 2005):



where the hydroxyl radical adds to an unsaturated compound, aliphatic or aromatic, to form a free radical product (cyclohexadienyl radical shown above).



where an organic free radical and water are formed.



where ions of a higher valence state are formed, or an atom or free radical if a mononegative ion is oxidized.



where the hydroxyl radical reacts with another hydroxyl radical, or with an unlike radical, to combine or to disproportionate to form a stable product.

In applying Fenton's Reagent for industrial waste treatment, the conditions of the reaction are adjusted so that first two mechanisms (hydrogen abstraction and oxygen addition) predominate. Typical rates of reaction between the hydroxyl radical and organic materials are $10^9 - 10^{10} \text{ k (M}^{-1} \text{ s}^{-1}\text{)}$.

The key Fenton's reagents, H_2O_2 and iron salts, are relatively inexpensive. Iron is highly abundant (and may be naturally occurring in the system being treated) and is non-toxic. H_2O_2 is relatively easy to transport and handle, as well as being environmentally benign in diluted form.

Use of Fenton processes can lead to the complete mineralization of some organic compounds, converting them to CO_2 , H_2O and inorganic ions. However, this would usually involve a large excess of chemicals which the production of substantial amounts of sludge is the major drawback of Fenton reaction.

2.2.1 Hydrogen Peroxide

2.2.1.1 General Information

Hydrogen peroxide was discovered by Therald, L.J. in 1818. Hydrogen peroxide is a ubiquitous compound present in natural water. Although pure hydrogen peroxide is fairly stable, it decomposes into water and oxygen when heated above about 60°C. One benefit of decomposition of hydrogen peroxide is that the released oxygen can stimulate aerobic biological activity. Hydrogen peroxide also decomposes in the presence of numerous catalysts, e.g., most metals, acids, bases, salt of metals, reducing agents, oxidizable organic materials, or flammable substances. Hydrogen peroxide is prepared commercially by oxidation of alkylhydro-anthraquinones or by electrolysis of ammonium bisulfate. It can also be prepared by reaction of barium peroxide with sulfuric acid or is prepared (with acetone) by oxidation of isopropanol.

Aqueous solution of hydrogen peroxide is mainly used for oxidation reactions, including bleaching process, chemical syntheses, and for water and wastewater treatment. In drinking water purification, hydrogen peroxide is used to pre-oxidize organic constituents and to eliminate iron and manganese ions.

2.2.1.2 Physical and Chemical Properties

An aqueous solution of hydrogen peroxide is clear, colorless, water-like in appearance and nonflammable. It is miscible with cold water and is soluble in alcohol and ether. At high concentration, it has a slightly pungent or acidic odor. The chemical formula for hydrogen peroxide is H_2O_2 and its molecular weight is 34.015 g/mole.

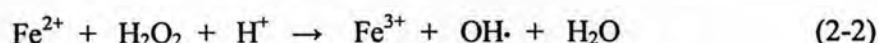
2.2.1.3 Toxicology

According to the US regulation, no concentration of H_2O_2 is listed as the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) regulated substances (i.e., a persistent environmental hazard). Nor is the standard industrial strength hydrogen peroxide (those < 52% wt.%) covered under the Federal Risk Management guidelines. However, a hazardous material permit-termed a Hazardous Materials Inventory Statement (HMIS) – may be required by local

response agencies, depending on the concentration, volume, and location of hydrogen peroxide stored. If released to the environment, hydrogen peroxide will decompose to oxygen and water with concurrent generation of heat.

2.2.2 Fenton Reaction

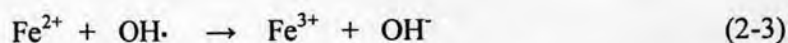
In Fenton process, H_2O_2 is decomposed by Fe^{2+} to produce highly reactive hydroxyl radical as expressed by equation (2-2)



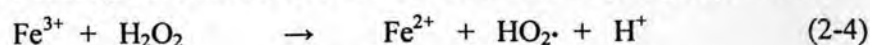
The hydroxyl radical can non-selectivity attack the C-H bonds of organic molecules and is capable of degrading many solvents, haloalkanes, esters, aromatics, and pesticides (Haag and Yao, cited in Sakulkittimasak, P., 2004:8). Huang et al., cited in Sakulkittimasak, P. (2004) summarized the major advantages of using Fenton's process over other oxidation processes to treat hazardous wastes:

- (1) There are no chlorinated organic compounds formed during the oxidation process as in chlorination.
- (2) Both iron and hydrogen peroxide are inexpensive and non-toxic.
- (3) There are no mass transfer limitations because the reaction is homogeneous.
- (4) No light is required as a catalyst and, therefore, the design is much simpler than ultraviolet light systems.
- (5) Hydrogen peroxide can be electrochemically generated in situ, which may further increase the economic feasibility and effectiveness of this process for treating contaminated sites.

Under acidic conditions and with an excess of ferrous ion, the hydroxyl radical generated can further react with ferrous ion to produce ferric ion:

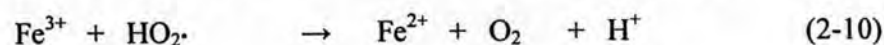
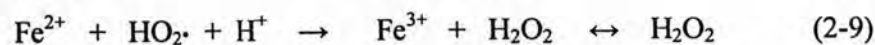
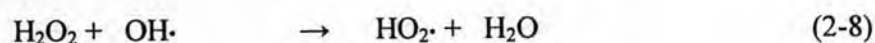
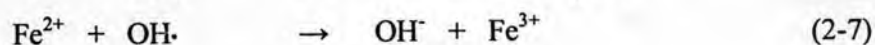
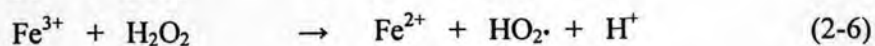
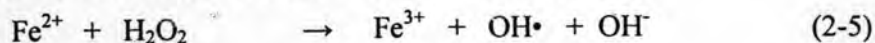


By properly controlling experimental conditions, ferric iron can be regenerated back to ferrous iron a subsequent reaction with another molecule of hydrogen peroxide:



The HO₂[•] radicals produced have been shown to also participate in oxidation of some organic compounds, although they are much less reactive than hydroxyl radical.

Major reactions involved in Fenton process (Parsons, 2004):



The factors affecting the efficiency of Fenton's reaction are wastewater characteristics, dosage of H₂O₂ and Fe²⁺, pH, reaction time and temperature. The most important factors are pH and dosages of H₂O₂ and Fe²⁺. The optimum pH range of Fenton's reaction is between 3 and 4. The optimal H₂O₂ dosage to COD removal is calculated based on the disproportion of H₂O₂ to provide 0.5 mole O₂ per mole H₂O₂.

$$\text{COD removal} : \text{H}_2\text{O}_2 = 1 : 2.1 \text{ (weight concentration) (Chou et al., 2003)}$$

2.2.3 Types of Fenton processes (Parsons, 2004)

2.2.3.1 Homogeneous processes

When all the reactants are present in the dissolved phase, the process is said to be homogeneous. These processes may still, however, lead to the precipitation of some insoluble species, such as metal hydroxides, but this is not part of the main process. The example of homogeneous Fenton processes are: Fenton processes (Fe(II)/ H₂O₂/dark), Photo-Fenton Processes (Fe(II)/ H₂O₂/light), Fenton-like reagent (Cu(I), Co(II), Ti(III))

2.2.3.2 Heterogeneous processes

The source of iron used as a catalyst for the Fenton process can be a solid surface, including iron-containing minerals or iron-coated silica particles (sand), as well as iron adsorbed onto zeolites.

A major disadvantage of wastewater treatment by homogeneous Fenton processes is that the iron must usually be removed from the water after treatment is complete. This can usually be achieved by raising the pH the solution, however this can lead to the production of large volumes of iron-containing sludge. Heterogeneous Fenton processes are of particular interest, since most of the iron remains in the solid phase. The solid phase is usually granular (iron oxides, sand or zeolites), hence the treated water is easily separated from the iron. The example of homogeneous Fenton processes are: Iron oxide catalyst (mineral oxide catalyst; goethite, lepidocrocite, hematite, limonite and magnetite).

2.2.4 Fluidized-bed Fenton process

Fluidized-bed Fenton process lets ferric ion (Fe^{3+}), produced in the Fenton reaction, be transformed into iron oxide (FeOOH) onto the carrier surface via the crystallization or sedimentation. This process combines the functions of homogeneous chemical oxidation ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), heterogeneous chemical oxidation ($\text{H}_2\text{O}_2/\text{FeOOH}$), fluidized-bed crystallization, and reductive dissolution of FeOOH . This process not only attains high COD removal efficiency but also reduces the large amount of iron sludge being produced. Furthermore, FeOOH synthesized from the reaction of H_2O_2 and Fe^{2+} can also be used as the heterogeneous catalyst of H_2O_2 .

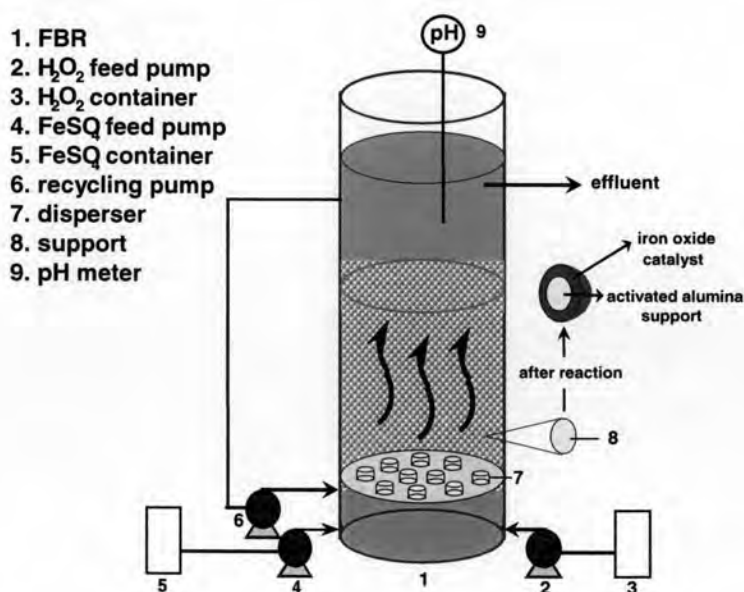


Figure 2.2 Fluidized-bed Reactor (Chou et al., 2003)



Figure 2.3 Fluidized-bed Fenton reactor in full-scale.

Comparison of various advanced treatment technologies are listed in Table 2.6.

Table 2.6 Comparison of various advanced treatment technologies of industry wastewater (Chou et al., 2003)

Items	Membrane Separation	Activated Carbon Adsorption	Chemical Coagulation	Ozone Oxidation	Fenton Method	Fluidized-bed Fenton Method
COD removal efficiency (%)	90-95	20-75	20-50	30-60	65-85	70-90
Capital cost (US \$/m ³)	50-1100	260-430	60-140	570-1100	60-140	60-200
Operating cost (US \$/m ³)	0.4-1.0	0.3-1.1	0.1-0.4	0.7-1.0	0.3-0.7	0.25-0.4
Operating cost (US \$/kgCOD)	4-10	3-11	1-4	7-10	3-7	2.5-4
Note	Concentration must be treated	Activated carbon must be regenerated	Sludge must be treated	Wasted O ₂ must be treated	Sludge must be treated	Sludge is reduced 70%, compared to Fenton method

* Based on the COD reduction from 200 to 1000 mg/l.

2.2.5 Effect of system position and process condition

2.2.5.1 pH

The reaction rate of the Fenton process tends to be highest at around pH 3 and decrease with increasing pH. The pH tends to change during the Fenton process; hence pH control is important in most processes.

In a study by Chou et al., cited in Parsons (2004), studied iron oxyhydroxide and Fenton's reagent in a fluidized-bed reactor (FBR), the pH was found to strongly affect the efficiencies of mineralization and Fe^{3+} precipitation rates. When treating benzoic acid, they found that the degradation efficiency decreased with increasing pH, while the removal efficiency of total iron increased with pH in the pH range 2.8-4.5.

Hsueh et al. (2005) studied the degradation of azo dyes using low iron concentration of Fenton system, the optimum pH is about 2.5-3.0.

2.2.5.2 Temperature

The rate of reaction with Fenton's reagent increases with increasing temperature, with the effect more pronounced at temperatures $< 20^\circ\text{C}$. However, temperatures increase above $40\text{-}50^\circ\text{C}$, the efficiency of H_2O_2 utilization decline. This is due to the accelerated decomposition of H_2O_2 into oxygen and water. As a practical matter, most commercial applications of Fenton's reagent occur at temperatures between $20\text{-}40^\circ\text{C}$. Applications of Fenton's Reagent for pretreating high strength wastes may require controlled or sequential addition of H_2O_2 to moderate the rise in temperature which occurs as the reaction proceeds. This should be expected when H_2O_2 doses exceed $10\text{-}20\text{ g/L}$. Moderating the temperature is important not only for economic reasons, but for safety reasons as well. (Parsons, 2004)

Merric et al. (2004) investigate color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process, the experiments were conducted on the dye solutions at $30, 40, 50$ and 60°C temperature ranges. The COD removal increased with increasing temperature until 40°C . Highering temperature up

to 60°C affected COD removal negatively at dye concentrations due to the destabilization of flocs resulting in increased ferrous ions which scavenged OH radicals during Fenton reaction.

2.2.5.3 Reaction time

The time needed to complete a Fenton reaction, most notably catalyst dose and wastewater strength. For simple phenol oxidation (less than 250 mg/L), typical reaction times are 30 - 60 minutes. For more complex or more concentrated wastes, the reaction may take several hours.

Swaminathan et al. (2003) investigated for the decolorization and degradation of commercial dyes wastewater summarized that COD removal increased when contact time was increased. Nearly complete removal of COD could be achieved when the contact time between 60 and 120 minutes.

Xu et al. (2004) studied degradation of dyes in aqueous solutions by the Fenton process. The reaction in this investigation is 120 minutes. The experiments of TOC and color removal almost became steady after 60 minutes.

2.2.5.4 H₂O₂ and Fe²⁺ concentration

The reaction rate tends to increase with H₂O₂ concentration. However, the ferrous ion and H₂O₂ not only react to form hydroxyl radicals, but are also scavengers of hydroxyl radicals. The ratio of H₂O₂ to Fe²⁺ should affect the rate of hydroxyl radical production and scavenging. Hence it is important to use the optimum H₂O₂ and Fe²⁺ concentration. (Parsons, 2004)

Powell et al., cited in Viphanphong, W. (1997) investigated the removal of color and TOC from segregated dye using ozone and Fenton's reagent suggested that the ratio of H₂O₂ and Fe²⁺ should be 10:1.

2.2.5.5 Type of dyes

Gregor, cited in Viphanphong, W. (1997) who studied the oxidation decolorization of textile wastewater with advanced oxidation process reported that vat and disperse dyes should not be treated by Fenton's reagent.

Xu et al. (2004) investigated the degradation of dyes in aqueous solutions by the Fenton process. These include 6 dyes types: acidic, reactive, direct, cationic, disperse and vat dyes. The former four types of dyes were decolorized and their TOC values were decreased greatly, while the color and TOC removals of the latter two types were lower. The color removal was easier than the TOC removal indicating that the chromophoric groups were destroyed during the degradation of dyes, and were partly mineralized to CO_2 and H_2O .

2.2.5.6 Inorganic anion concentration

Degradation rates by Fenton process can be decreased due to the presence of certain anions that either scavenge hydroxyl radicals or form unreactive complexes with Fe^{3+} .

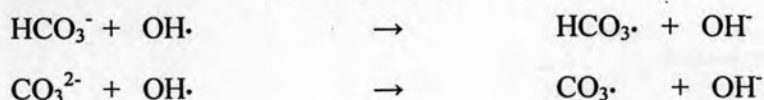
Pignatello, cited in Parsons (2004) studied the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ found that the inhibition of 2,4-D degradation followed the order $\text{SO}_4^{2-} \approx \text{Cl}^- \gg \text{NO}_3^- \approx \text{ClO}_4^-$, whereas the inhibition of Fe^{3+} -catalysed decomposition of H_2O_2 followed the order $\text{SO}_4^{2-} \gg \text{Cl}^- > \text{NO}_3^- \approx \text{ClO}_4^-$. It was concluded that sulfate ligands reduced the reactivity of Fe^{3+} , while chloride was responsible for hydroxyl radical scavenging.

Lu et al., cited in Parsons (2004) found that anions suppressed the degradation of dichlorvos by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ in the order $\text{H}_2\text{PO}_4^- \gg \text{Cl}^- > \text{NO}_3^- \approx \text{ClO}_4^-$. The inhibition by H_2PO_4^- was attributed to the formation of unreactive Fe^{3+} complexes.

Malik and Saha (2003) investigated the oxidation of direct dyes with H_2O_2 using Fe^{2+} as catalyst found that chloride ion range from 0 to 600 mg/l, dye degradation decreased with increasing chloride ion concentration. The reason is may be due to loss of hydroxyl radical.

2.2.5.7 Alkalinity

The presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ alkalinity reduces the degradation of dye due to scavenging of hydroxyl radicals. The carbonate radicals ($\text{HCO}_3^\cdot / \text{CO}_3^\cdot$) form under high alkalinity conditions (Buxton et al., cited in Parsons, 2004) follow this reactions:



Dye decomposition may not be inhibited by carbonate/bicarbonate radical scavenger system as a consequence of the bicarbonate radical formation at pH 7 and the presence of carbonate radicals at pH 12 (Arslan et al., cited in Parsons, 2004). At low pH, HCO_3^- reacted H^+ to form H_2CO_3 and be converted to H_2O and CO_2 therefore, alkalinity was not affected Fenton reaction.

Lin S. and Gurol M.D., cited in Parsons (2004) studied the mixture of H_2O_2 and iron oxide (goethite, $\alpha\text{-FeOOH}$) particles for treatment of water contaminated with synthetic organic pollutants summarized that bicarbonate ions (0-30 mM) seem to be unable to inhibit the oxidation of BuCl in this heterogeneous process most likely because the oxidation reaction takes place on the iron oxide surface rather than the solution phase, and bicarbonate ions cannot compete successfully with BuCl for adsorption on the surface.

2.3 COD and color removal kinetics

Integrated forms of the rate law are useful for analyzing rate data to determine reaction rate constants and reaction order. Let us first consider the irreversible reaction as;



The rate law is used to estimate the kinetic parameters (k and n), an n th-order rate equation of the form;

$$d[\text{A}] / dt = -k[\text{A}]^n$$

To determine the behavior of $[A]$ as a function of time, we must integrate the rate expression with respect to time. We will do this for several values of the reaction order, n . The reaction is zero order as follows this equation;

$$d[A] / dt = -k[A]^0 = -k$$

and upon integrating, we obtain

$$[A] = [A]_0 - kt$$

that $[A]_0$ = the concentration of A at $t=0$, that is the initial concentration of A. When $n=1$, the reaction is *first order*, both with respect to A and overall, and we can write;

$$d[A] / dt = -k[A]$$

Rearranging this equation and solving the integral,

$$\int_{[A]_0}^{[A]} (d[A] / [A]) = - \int_0^t k dt$$

$$\ln [A] = \ln [A]_0 - kt$$

$$[A] = [A]_0 e^{-kt}$$

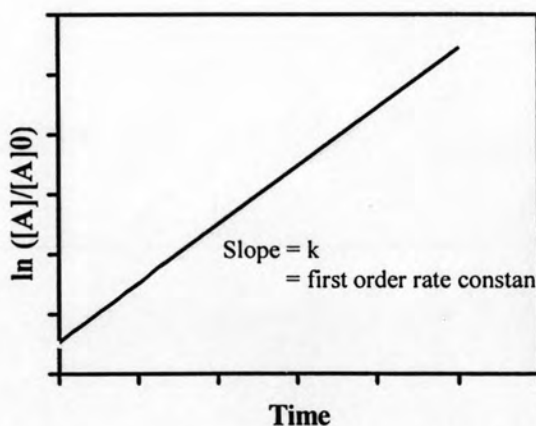


Figure 2.4 The first order reaction rate constants.

If the reaction is greater than first order, then we can write;

$$d[A] / dt = -k[A]^n$$

and integrating, we obtain

$$\int_{[A]_0}^{[A]} (d[A] / [A]^n) = -\int_0^t k dt$$

or

$$[-1/(n-1)][1/[A]^{n-1}] - [-1/(n-1)][1/[A]_0^{n-1}] = -kt$$

or

$$[1/(n-1)][(1/[A]_0^{n-1}) - (1/[A]^{n-1})] = -kt$$

If $n=2$, for example, the reaction is *second order*, both with respect to A and overall, we can write as follow;

$$(1/[A]) = (1/[A]_0) + kt$$

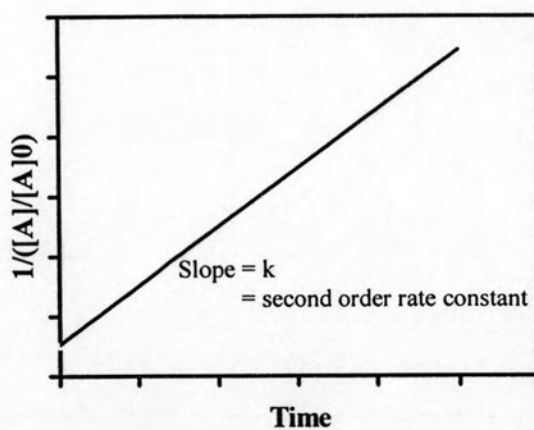


Figure 2.5 The second order reaction rate constants.

2.4 Literature reviews

2.4.1 Fluidized-bed Fenton Process

Chou et al. (1999a) investigated on the effect of Fe^{2+} on the catalytic oxidation in the FBR applying supported $\gamma\text{-FeOOH}$ as the carrier. They found that both mineralization of organics and crystallization of Fe^{3+} were simultaneously well performed under properly condition. Moreover, the reductive and the crystallization of $\gamma\text{-FeOOH}$ as well as the oxidation of BA was proposed based on the experiment results.

Chou et al. (1999b) demonstrated that the treatment efficiency of benzoic acid at an initial pH of 3.2 was higher than at initial pHs of 6.0 and 10.0 which could be partly explained by reductive dissolution of $\gamma\text{-FeOOH}$. Beside, the majority of oxidation occurred on the catalyst surface, with some occurred in the solution due to iron dissolution of the catalyst.

Chou et al. (2004) applied a novel supported iron oxyhydroxide (FeOOH) catalyst to treat benzoic acid by hydrogen peroxide using a fluidized-bed crystallization reactor. By controlling the internal circulation of the FBR, the upflow superficial velocity was maintained normally at 48 m/h with 50% bed expansion. The crystallization reached the maximum between pH 3.0 and 4.0 and the crystallization increased with increasing $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio, and then attained a plateau.

2.4.2 Textile wastewater treatment by Fenton process

Kang et al. (2002) evaluates the Fenton process, involving oxidation and coagulation, for the removal of color and chemical oxygen demand (COD) from synthetic textile wastewater containing polyvinyl alcohol and a reactive dyestuff, R94H. This study reported that the removal of color by Fenton process requires relatively lower dosages of H_2O_2 and Fe^{2+} , whereas, much higher dosages of both H_2O_2 and Fe^{2+} are necessary to obtain the same level of COD removal. The four

reaction modes at same iron dosage, the color removal follow the decreasing order: Fenton oxidation > Fenton-like oxidation > ferric coagulation > ferrous coagulation. The color removal is more sensitive to deteriorate at relatively low and high levels of COD, but not at medium COD level. It is concluded that Fenton process for the treatment of textile wastewater favors the removal of color rather than COD.

Hsueh et al. (2005) investigated Fenton and Fenton-like reactions at low iron concentration ($\leq 10 \text{ mg l}^{-1}$) to oxidize three commercial azo dyes, namely Red MX-5B, Reactive Black 5 and Orange G. Concentration of 0.1mM dyes was used because it corresponded to the level of pollution found in strongly colored polluted waters located close to textile manufacturing sites. The optimum pH for both Fenton and Fenton-like reactions in this study are about pH 2.5–3.0. The optimum H_2O_2 concentration is about 200 mg/l for 0.1mM dyes (varying H_2O_2 100, 200, 350 and 500 mg/l). In the initial stage of reaction ($\leq 30 \text{ min}$), the dye decolorization rate of Fenton reaction exceeds than that of Fenton-like one. However, when the reactions time over 60min, there shows almost no difference of the dye decolorization efficiencies between Fenton and Fenton-like reaction. The experiment conditions: pH fixed 2.5, H_2O_2 dose of 100 mg/l, ferric nitrate dose in the form of Fe^{3+} , varied from 0 to 10 mg/l, there is almost no difference between 1 and 10 mg/l of Fe^{3+} for the dye decolorization during a 1h reaction time. Additionally, the results show that dye decolorization can occur at very low iron concentrations (1 mg/l) in both Fenton-like and Fenton reactions. The decolorization of azo dyes undergoes a fast reaction rate than the mineralization of azo dyes under the same conditions.

Meric et al. (2004) investigated the color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process. This study was performed in a systematic approach searching optimum values of FeSO_4 and H_2O_2 concentrations, pH and temperature. Optimum pH and temperature for 100 mg/l of RB5 were observed as 3.0 and 40°C, respectively, using 100 mg/l of FeSO_4 and 400 mg/l of H_2O_2 resulted in 71% chemical oxygen demand (COD) and 99% color removal. For 200 mg/l of RB5, 84% COD removal was obtained using 225 mg/l of FeSO_4 and 1000 mg/l of H_2O_2 yielding 0.05 molar ratios at pH 3.0 and 40°C. Color

removal was also more than 99%. It is concluded that the H_2O_2 requirement seems to be related to initial COD of the sample. $\text{FeSO}_4/\text{H}_2\text{O}_2$ ratios found were not changed for both concentrations. When slow mixing time increased up to 30 min COD removal decreased to 55% for 100 mg/l of RB5 due to floc destabilization. Color was removed higher than 99% for all mixing times.

Meric et al. (2005) who studied the effectiveness of Fenton's oxidation (FO) process and ozone (O_3) oxidation compared with a coagulation-flocculation (CF) process to remove effluent toxicity as well as color and COD from a textile industry wastewater. The FO process removed COD at high rate (59%) than O_3 (33%) while color removal was similar (89% and 91%, respectively). The CF process removed both COD and color at rates similar to the FO process. The FeSO_4 concentration of 300 mg/l and H_2O_2 concentration of 800 mg/l at 40°C and 3.0 pH was defined as optimum condition for FO process. COD and color removals reached 59% and 84%, respectively, at the end of 10 minutes.

Xu et al. (2004) who studied the degradation of dyes in aqueous solutions by the Fenton process. These dyes include 6 types: acidic, reactive, direct, cationic, disperse and vat dyes. The former four types of dyes were decolorized and their TOC values were decreased greatly, while the color and TOC removals of the latter two types were lower. The color removal was easier than the TOC removal indicating that the chromophoric groups were destroyed during the degradation of dyes, and were partly mineralized to CO_2 and H_2O . The catalytic activities of four metal ions on the degradation efficiencies of Vat Blue BO, which was chosen as a model dye because of its lowest color and TOC removals. The sequence of catalytic ability for metal ions alone was $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ag}^+$.