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Chapter 9

APPLICATION OF ADVANCED OXIDATION PROCESSES (AOP) TO DYE DEGRADATION - AN OVERVIEW

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ABSTRACT

Advanced oxidation Processes (AOP's) are novel methods for water treatment and are extremely useful in the case of substances resistant to conventional technologies. Organic dyes are a group of those chemicals of special interest which have drawn considerable attention in many industrial processes. However due to their high toxicity and low biodegradability, various approaches have been forwarded concerning the degradation of these dyes by means of AOP's. In this work, an overview of such work is presented and the following approaches are presented: processes based on hydrogen peroxide (H_2O_2 + UV, Fenton, photo-Fenton and Fenton-like processes), photolysis, photocatalysis and processes based on ozone (O_3, O_3 + UV and O_3 + catalyst). Degradation is reviewed and the different mechanistic degradation pathways are taken into account.

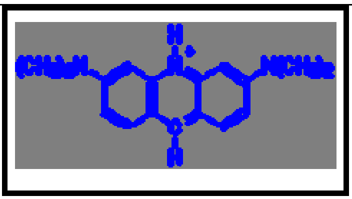
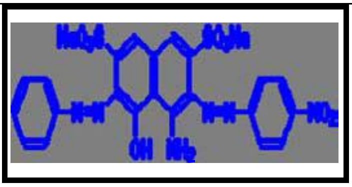
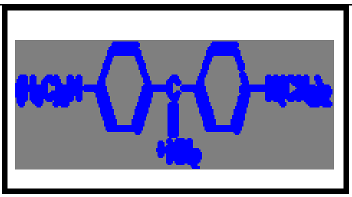
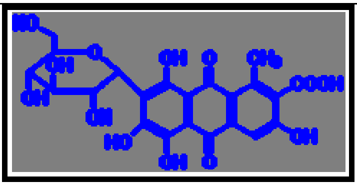
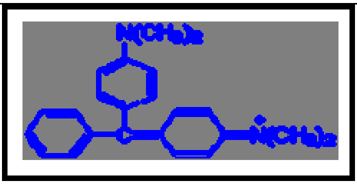
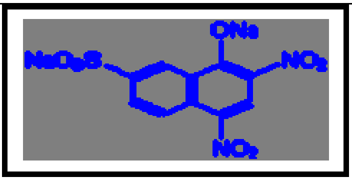
Keywords: Dyes, AOP, Photolysis, Fenton, Photo-Fenton, Ozone, Photocatalysis, Degradation

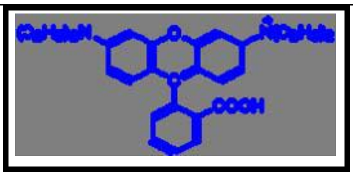
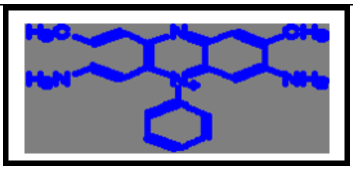
1. INTRODUCTION

With increasing social and political concern on environmental issues, the research activity in the area of water purification has drawn a great deal of attention and has attracted the focus of attention to many workers. Water bodies comprising both polluted wastewaters and groundwater from seas, rivers and lakes are of special concern to people working in water purification and the environment in general. In this regard water quality control standards and regulations against hazardous pollutants have become stricter in many countries.

With increasing revolution in science and technology, there is a bigger demand on opting for newer chemicals which could be used in various industrial processes. Organic dyes come up as one of the many new chemicals which could be used in many industrial activities. Most of these dyes are synthetic in nature and are classified based on their chemical structures into six different classes as azo, anthraquinone, sulfur, indigoid, triphenylmethane and phthalocyanine derivatives. Their general nomenclature along with representative examples is given in Table 1.

Table 1. Different classes of dyes and their structures

Dye	Structure	Class	max
Acridine O		Acridine	497 nm
Amido Black		Azo	618 nm
Auramine O		Diarylmethane	432 nm
Carmine		Anthraquinone	500 nm
Malachite green		Triarylmethane	618 nm
Naphthol Y		Nitro	428 nm

Rhodamine B		Xanthene	555 nm
Safranin O		Quinone-imine	530 nm

Due to the extensive use of these dyes in industries, they have become an integral part of industrial effluent. In fact, of the 450,000 tons of organic dyes annually produced worldwide, more than 11% is lost in effluents during manufacture and application processes [1]. Most of these dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental problem [2].

Various methods have been suggested to handle the dye removal from water; these include the biodegradation, coagulation, adsorption, advanced oxidation (AOP) and the membrane process [3-8]. All these processes have some advantages or disadvantages over the other methods. A balanced approach is therefore needed to look into the worthiness on choosing an appropriate method which can be used to degrade the dye in question. Among these techniques, the advanced oxidation processes (AOP’s) [9] appear to be a promising field of study, which have been reported to be effective for the near ambient degradation of soluble organic contaminants from waters and soils, because they can provide an almost total degradation [10-20]. Among the various AOP’s the main ones taken into account in this work are the following:

(1) Photolysis (UV or VUV)
(2) Hydrogen peroxide (H_2O_2)
- H_2O_2 + UV
- Fenton: $H_2O_2 + Fe^{2+}/Fe^{3+}$
- Fenton-like reagents: H_2O_2 +Fe^{2+}-solid/Fe^{3+}-solid
- photo-Fenton: $H_2O_2 + Fe^{2+}/Fe^{3+}$ + UV

(3) Ozone (O_3)
- ozonation: O_3
- photo-ozonation: O_3 + UV
- ozonation + catalysis: $O_3 + H_2O_2$ and $O_3 + Fe^{2+}/Fe^{3+}$

(4) Photocatalysis
- Heterogeneous catalysis and photocatalysis
- TiO_2 + CdS + combinations

All the above techniques are versatile in nature and can provide the conversion of contaminants to less harmful compounds such as oxygenated organic products and low molecular weight acids [21]. A common denominator in all these techniques is that they produce highly reactive hydroxyl radicals (•OH) at a certain stage which are supposedly the active species responsible for the destruction of pollutants [22]. Due to their high standard reduction potential of 2.8 V, these radicals are able to oxidize almost all organic compounds to carbon dioxide and water. Other simple organic compounds, such as acetic, acid, acetone or simple chloride derivatives are also generated [23]. These smaller molecules can be further degraded by various chemical or photochemical reactions.

2. EXPERIMENTAL METHODOLOGY

Different experimental techniques have been proposed for both qualitative and quantitative analysis of various dyes concerning their degradation. These methods usually involve analysis by instrumental methods such as UV/Vis spectrophotometry [24, 25], GC/MS [26], HPLC [27], Ion chromatography [28], Capillary Electrophoresis [29], Radiometry [30] etc. In this regard, prior procedures of extraction of the aqueous sample with an organic solvent or filtration in case a heterogeneous catalyst or solid reactant is also employed. Since most of the dyes would ultimately breakdown into smaller molecules, an important aspect of this study is also to evaluate the Total organic carbon of the system under investigation [31-33].

3. REACTORS AND LAMPS

3a. Reactors Used for Direct Photolysis and AOPs Based on Hydrogen Peroxide

Most of the papers reviewed [34-36] on this topic have shown that the investigators have generally used the completely mixed batch cylindrical glass vessels for direct photolysis studies. Other methods involve using cylindrical glass flasks [29], glass bottles or glass tubes [37, 38] for direct photolysis, photo-Fenton processes, and processes based on H_2O_2/UV reagent. This is done in order to achieve a good interaction between dyes and radiation.

3b. Reactors Used for AOP's Based on Ozone

Literature review has revealed that semi-batch stirred reactors such as glass bottles or cylindrical vessels are the most commonly used reactor types for ozonation processes [39-42]. Besides this, other configurations used are the bubble columns, and wetted-sphere adsorbers [43,44]. These improve the contact between the gaseous ozone stream and the liquid and polluted stream. An ozone generator is generally located close to the reactor to ensure a continuous supply of ozone gas for the reaction. Ozone is generally generated by either an electric discharge or by irradiating oxygen with UV light. The former technique has been used frequently [45-47].

3c. Reactors Used for AOPs Based on Photocatalysis

The most typical laboratory-scale experimental set up includes a vigorously stirred batch photochemical cell, cylindrical flasks or vessels and glass dishes [48-51]. On the other hand, upflow type, membrane based and coated surfaces have also been reported as photo-catalytic reactors for dye studies [52-55].

3d. General Information for Lamps Used in AOP's

Different types of lamps are used for irradiation purposes in dye degradation studies. The choice depends on the mode of AOP being used, such as UV/H_2O_2, UV/O_3, photo-Fenton's reagents and photocatalysis. A variety of commercial radiation sources are available for this work which includes the high, medium and low-pressure mercury vapor lamp for the generation of UV radiation [56-58] or xenon lamps [59]. The lamps are generally placed in an axial position with respect to the solution container, or in the center of a photolytic reactor in a vertical position.

4. PHOTOLYSIS BY UV LIGHT

UV photolysis is the process by which chemical bonds of the contaminants are broken under the influence of UV light. Products of photo-degradation vary according to the matrix in which the process occurs, but the complete conversion of an organic contaminant to CO_2, H_2O, etc. is not probable, as stronger and more reactive oxidants are normally needed for complete mineralization of bigger organic compounds.

The duration of operation and maintenance of UV oxidation depends on influent water turbidity, contaminant and metal concentrations, existence of free radical scavengers, and the required maintenance intervals on UV reactors and quartz sleeves. A commonly acceptable mechanistic pathway is suggested as follows [60]

$$\text{Dye} + h\nu \rightarrow \text{Intermediates}$$
$$\text{Intermediates} + h\nu \rightarrow CO_2 + H_2O$$

Direct UV-photolysis have resulted in degradation of pollutants, such as dyes, in dilute aqueous solutions [61- 65]. Limitations of UV/oxidation include:

- The aqueous stream being treated must provide good transmission of UV light (high turbidity causes interference). This factor can be more critical for UV/H_2O_2 than UV/O_3 (Turbidity does not affect direct chemical oxidation of the contaminant by H_2O_2 or O_3).
- Free radical scavengers can inhibit contaminant destruction efficiency. Excessive dosages of chemical oxidizers may act as scavengers.

- The aqueous stream to be treated by UV/oxidation should be relatively free of heavy metal ions (less than 10 mg/L) and insoluble oil or grease to minimize the potential for fouling of the quartz sleeves.
- When UV/O_3 is used on volatile organics, the contaminants may be vaporized (e.g., "stripped") rather than destroyed. They would then have to be removed from the off-gas by activated carbon adsorption or catalytic oxidation.
- Costs may be higher than competing technologies because of energy requirements.
- Pretreatment of the aqueous stream may be required to minimize ongoing cleaning and maintenance of UV reactor and quartz sleeves.
- Handling and storage of oxidizers require special safety precautions.

5. HYDROGEN PEROXIDE BASED AOPS

Hydrogen peroxide has been known as an effective oxidant; however it alone is not useful for many organic pollutants such as dyes. It is generally combined with UV light, salts of particular metals or ozone to produce the desired degradation results.

5a. H_2O_2/UV Reagent

This widely applicable AOP is based on the production of •OH radicals in solution on the photolysis of hydrogen peroxide followed by propagation reactions:

$$H_2O_2 + h\nu \rightarrow 2\ HO\bullet$$

The molar absorptivity of hydrogen peroxide at 253.7 nm is very low (about $20M^{-1}\ cm^{-1}$) and HO• radicals are formed per incident photon absorbed [99]. Since at this wavelength, the rate of photolysis of aqueous hydrogen peroxide is much slower than ozone, the technique demands a higher dose of H_2O_2 or longer irradiation time. On the other hand, the rate of photolysis of hydrogen peroxide has been found to be pH dependent and increases when more alkaline conditions are used, because, at 253.7 nm, peroxide anions HO_2^- may be formed, which have a higher molar absorptivity than hydrogen peroxide [99].

$$HO_2^- + h\nu \rightarrow HO\bullet + O\bullet-$$

The absorptivity of hydrogen peroxide may be increased by using shorter wavelengths. The reaction scheme in this case is proposed as follows [67].

Initiation: $H_2O_2 + h\nu \leftrightarrow 2\ HO\bullet$

Propagation:

$$HO\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O$$
$$HO_2\bullet + H_2O_2 \rightarrow HO\bullet + H_2O + O_2$$
$$HO_2\bullet + HO_2^- \rightarrow HO\bullet + HO^- + O_2$$

Termination:

$HO\bullet + HO_2\bullet \rightarrow H_2O + O_2$
$HO\bullet + HO\bullet \rightarrow H_2O_2 + O_2$

Dye degradation:

$\mathit{dye} + HO\bullet \rightarrow$Intermediates,
$\mathit{dye} + H_2O_2 \rightarrow$ Intermediates + H_2O
$\mathit{dye} + h\nu \rightarrow$ Intermediates
Intermediates + $H_2O_2 \rightarrow CO_2 + H_2O$
Intermediates + $HO\bullet \rightarrow CO_2 + H_2O$
Intermediates + $h\nu \rightarrow CO_2 + H_2O$

In the presence of UV absorbers, the effect will be the same as if there is less radiation intensity available for the photolysis of hydrogen peroxide; also that the amount of radiation transformed into $HO\bullet$ radicals will be lower in the presence of such absorbents.

5a.1. Effect of pH

The pH of the dye solution can have a dramatic effect on the rate of dye decoloration by the UV/H_2O_2 photolytic approach. Our experience with an extensive study of different dyes has shown that some a "pH-profile" must be established for each dye and the effect of acidic or alkaline conditions on dye degradation can not be known a priori. For example, dyes like Auromine O shows 81% decoloration at pH 7, but that cuts into half (47% decoloaration) at pH 2 and falls even lower to 13% at pH 11 (Figure 1). Surprisingly, the % decoloration for Malachite Green doubled from 50% (at pH 7) to 91% or 99% at pH values of 12 and 1, respectively, as shown below (Figure 1). Other dyes such as Safarnin O showed only a marginal effect of pH on dye degradation [60].

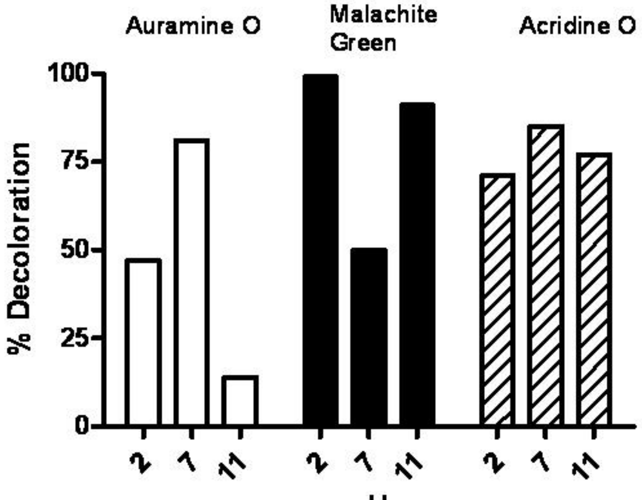


Figure 1. Effect of pH on dye degradation by UV/H_2O_2 photolysis.
[Auramine O] = 20 μM, [H_2O_2] = 1.67 mM; [Malachite Green] = 20 μM, [H_2O_2] = 1.67 ; [Acridine O] = 2 μM, [H_2O_2] = 3.33 mM (unpublished data).

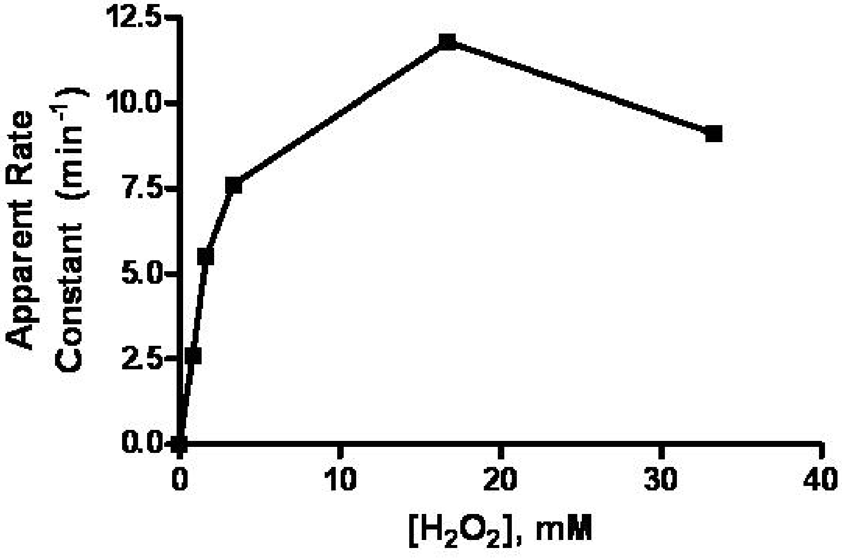


Figure 2. Effect of hydrogen peroxide concentration on dye degradation by UV/H_2O_2 photolysis. Auramine O (20 μM) was exposed to different concentrations of H_2O_2 in the presence of UV light and the apparent rate of dye decoloration was calculated (unpublished data).

5a.2. Effect of Hydrogen Peroxide Concentration [H_2O_2]

As expected, the concentration of hydrogen peroxide plays an important role in dye degradation. Since, hydroxyl radical production depends on the concentration of H_2O_2, it is therefore expected that the higher the hydrogen peroxide concentration, the higher the amount of hydroxyl radicals, and faster the dye degradation. However, it is been reported by various groups (Figure 2) that excessively high concentrations of hydrogen peroxide is in fact, deleterious for efficient dye degradation, as hydrogen peroxide itself reacts with and quenches hydroxyl radicals, as shown below:

$$HO\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O$$

5a.3. Effect of Initial Dye Concentration

Dye concentration is another parameter that is very important for efficient degradation using UV/H_2O_2. It is well established that AOPs, specifically the ones that rely on UV or other source of radiation, generally work well at dilute dye concentrations, since highly colored dye solutions block the penetration of UV light and prevent the production of hydroxyl radicals. In fact, a directly inverse relationship between dye concentration and dye degradation is reported by numerous groups. Figure 3 shows the decrease in the apparent rate of Safranin O decoloration as a function of increasing dye concentration [60].

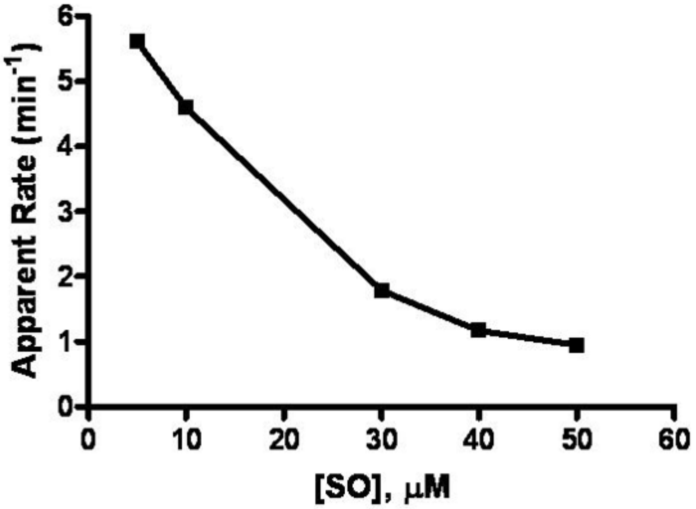


Figure 3. Effect of Safranin O concentration on the apparent rate of degradation by UV/H_2O_2 photolysis. Different concentrations of Safranin O was exposed to 1.67 mM H2O2 and the decoloration rate measured as described elsewhere [60].

5b. Fenton's Reagent (H_2O_2/Fe^{2+})

The Fenton system generates ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals, which are strong oxidizing reagents, and can react with the organic pollutant or dye solution and degrade it [66-69].

$H_2O_2 + Fe^{+2} \rightarrow \bullet OH + {}^{-}OH + Fe^{+3}$

The hydroxyl radical propagates the reaction by reacting with the organic pollutant/dye (RH) to produce further radicals, which can then react in many different steps.

$\bullet OH + RH \rightarrow H_2O + \bullet R$
$\bullet R + H_2O_2 \rightarrow \bullet ROH + \bullet OH$

Additionally many other reactions are also possible, which include the radical-radical reaction or the reaction of the OH radical with H_2O_2

$\bullet OH + \bullet OH \rightarrow H_2O_2$
$\bullet OH + H_2O_2 \rightarrow H_2O + HO\bullet_2$

The peroxide radicals ($HO\bullet_2$) produced in the above case can further oxidize other species present in the solution.

Fenton's reagent has been successfully used to treat a variety of industrial wastes containing a range of organic compounds like phenols, formaldehyde, pesticides, wood preservatives, plastic additives, and rubber chemicals [70-75]. The process has also been applied to wastewaters, sludge, and contaminated soils [76-80].

5b.1. Effect of pH

Change in pH of dye solution has a pronounced effect on dye degradation as shown in many studies [81-83]. The dye decomposition significantly decreases as the pH increases which is attributed to a decreased dissolved fraction of iron species and also formation of colloidal ferric species [84]. On the other hand, at low pH values (around 2 - 4), more $Fe(OH)^+$ is formed and the activity of this species is more than Fe^{+2} in Fenton's oxidation. At low pH values, oxygen concentration remains stable because hydrogen peroxide solvates protons to form oxonium ions ($H_3O_2^+$), which in turn enhances the stability of hydrogen peroxide and reduces its reactivity with ferrous ions [85].

5b.2. Effect of Hydrogen Peroxide Concentration [H_2O_2]

The concentration of hydrogen peroxide plays a vital role in dye degradation as shown in many studies [86-90]. The stoichiometric coefficient for the Fenton reaction has been found to be approximately 0.5 mol organic compound/mol H_2O_2 [13]. As concentration of hydrogen peroxide increases, the degradation of dyes also increases, because the amount of oxidant present in the reaction system is higher for the same initial concentration of dye and catalytic ferrous ions. The linear dependence is only achieved when hydrogen peroxide is in excess compared to dye concentration. Like the UV/H_2O_2 photolytic AOP, too much hydrogen peroxide can lead to self-quenching and lead to decrease in dye degradation, as shown in Figure 4 [24].

$$\bullet OH + H_2O_2 \rightarrow H_2O + HO\bullet_2$$

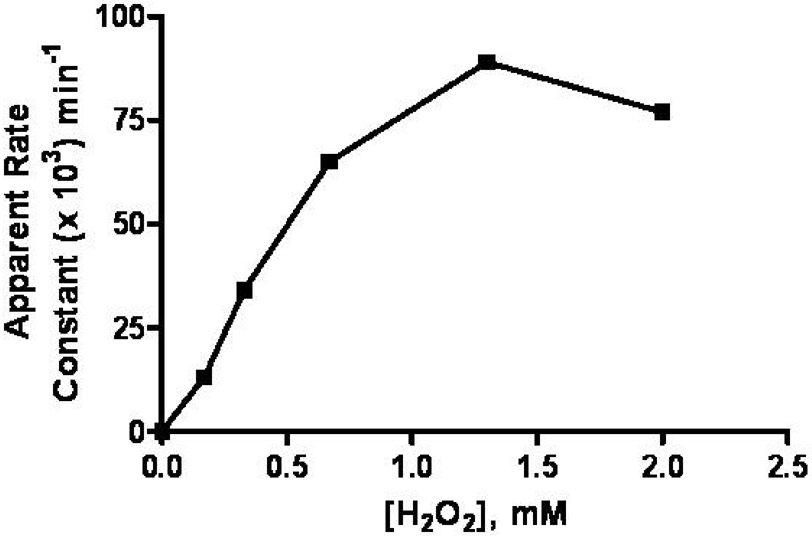


Figure 4. Effect of hydrogen peroxide concentration on Neutral Red degradation by Fenton based AOP. [Neutral Red] = 65 μM, [Fe^{2+}] = 0.34 mM. Apparent rate of dye degradation was measured as described elsewhere [24].

Furthermore, since a number of intermediates are produced in dye degradation, sufficient hydrogen peroxide must be added in order to propagate the reaction. This in fact is seen when pre-treating a complex organic wastewater for toxicity reduction. With increasing amounts of H_2O_2 in solution, chemical oxygen demand (COD) value becomes less and results in little or no change in toxicity until a threshold is attained; further increase of hydrogen peroxide results in a rapid decrease in wastewater toxicity [91].

5b.3. Effect of Ferrous Ion Concentration [Fe^{2+}]

The absence of iron causes no considerable production of any intermediates or active species in solution even in the presence of hydrogen peroxide. With an increase in the concentration of iron, dye degradation increases to a point where further addition of iron becomes inefficient. The optimum amount of iron catalyst is characteristic of Fenton's reagent, although its exact amount varies from dye to dye solution. A typical range of such a solution is 1 part iron per 5–25 parts of hydrogen peroxide (w/w) [13]. A given reaction may be initiated in the presence of either ferrous (Fe^{2+}) or ferric (Fe^{3+}) ions, however when low doses of Fenton's reagent are used (e.g. <10–25 mg/L−1 H_2O_2), ferrous ions are preferred [13].

The influence of ferrous ions in dye degradation is similar to the one for hydrogen peroxide. When Fenton concentration increases, the degradation of dye also increases, because the amount of catalyst present in the reaction system is higher for the same initial concentration of dye and hydrogen peroxide, as shown below in Figure 5 [66].

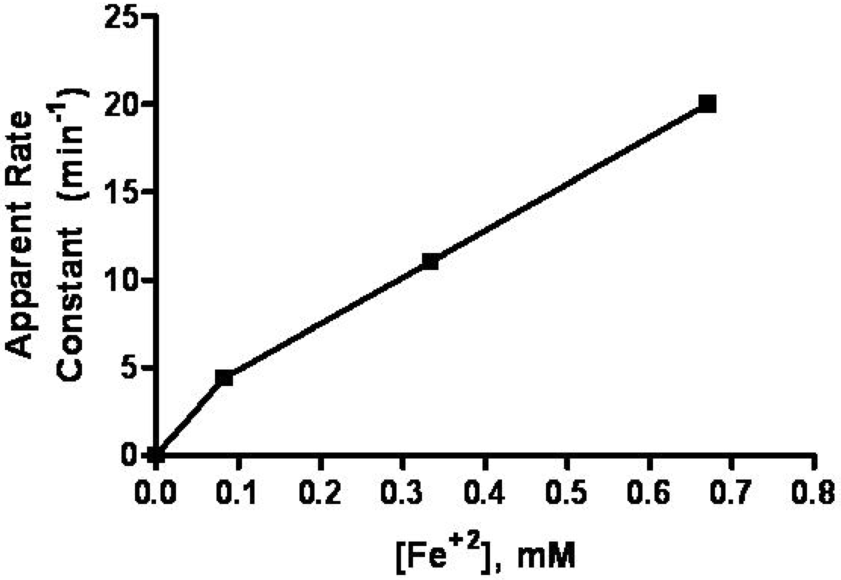


Figure 5. Effect of Fe^{2+} concentration on degradation of Crystal Violet by Fenton based AOP. [Crystal Violet] = 22 μM, [H_2O_2 = 0.34 mM. Apparent rate of dye degradation was measured as described elsewhere [66].

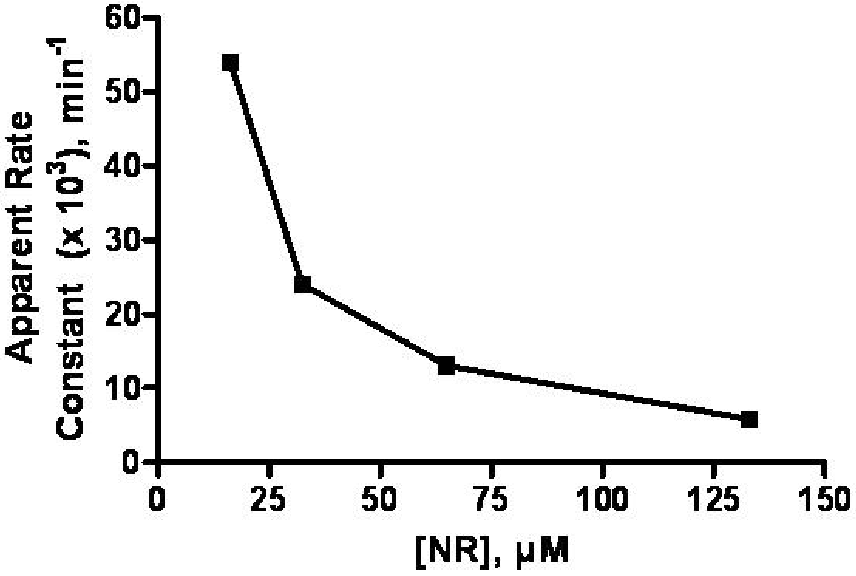


Figure 6. Effect of hydrogen peroxide concentration on Neutral Red degradation by Fenton based AOP. [H_2O_2] = 0.17 mM, [Fe^{2+}] = 0.34 mM. Apparent rate of dye degradation was measured as described elsewhere [24].

5b.4. Effect of Initial Dye Concentration

Increasing amounts of dye in solution also is an important factor in dye degradation. When the other factors of the solution are kept constant and the dye concentration is increased, the degradation of solution becomes less, as shown in Figure 7 [24]. Therefore, at higher dye concentrations, the degradation of the dye will not follow the pseudo-first order kinetics.

5b.5. Effect of Temperature

The studies concerning the effect of temperature have shown that the extent of dye degradation increases with an increase in temperature [67]. However at higher temperatures (around 50^0C), very less increase in the extent of dye degradation is

observed. This has been attributed to the fact that at these temperatures, the efficiency of H_2O_2 utilisation declines because of the rapid decomposition of H_2O_2 into oxygen and water at high temperatures.

5c. Fenton-like Reagent's (H_2O_2/Fe^{2+}-solid)

Although Fenton reaction has shown promising results in dye degradation, its biggest disadvantage still remains the unavailability of homogeneous catalyst in solution. In many cases the disadvantage has been countered by introducing heterogeneous supported metals [50, 92-95]. In this case the hydroxyl ions are activated by iron ions which are released from the support material. Some common materials used in this regard are *goethite*, *Nafion membranes*, and *iron powder*. Geothite (α-FeOOH) is considered to be a suitable alternative for Fenton-like degradation of dyes and has been used by various investigators to remove hazardous pollutants [96]. The reaction mechanism involves the production of ferrous ions from the reductive dissolution of the compound [97].

$$\alpha\text{-FeOOH}(s) + 3H^+ + e^- \leftrightarrow Fe^{2+} + 2H_2O$$

whereas the electrons are produced via the following reaction

$$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$$

On combination of the above two equation gives the following

$$2\alpha\text{-FeOOH}(s) + 4H^+ + H_2O_2 \leftrightarrow 2Fe^{2+} + O_2 + 4H_2O$$

The Fe^{2+} ions produced in the reaction then react with H_2O_2 to produce the •OH radicals which can subsequently take part in a series of reactions to degrade the organic species.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + {}^-OH$$

Geothite is also known to interact chemically with H^+, ^-OH, cations, and anions, followed by a series of dissolution reactions. The reaction is more feasible under reducing conditions [97,98].

5d. Photo-Fenton's Reagent ($H_2O_2/Fe^{2+/}UV$)

Photo-Fenton reaction scheme is well known in the literature and has been employed for wastewater and soil treatment [100-105]. The method has shown better results as compared to Fenton or Fenton-like reagents, as it involves interaction of radiation (UV/Vis) with Fenton's reagent [100]. The technique has shown promising results in removing pollutants from natural and industrial waste water and increasing the biodegradability of dyes. It is being used as a pre-treatment method to decrease the toxicity of waste water [106-107]. The dye degradation using this technique in general depends on the initial dye concentration, hydrogen peroxide and ferrous ion and the intensity of radiation. Generally speaking, the pseudo-first kinetic constants obtained in a photofenton reaction are higher than those obtained in the single photolytic process [108]. This can be attributed to the additional contribution of the hydroxyl radicals produced as a result of the photolytic reaction of the overall solution which contains hydrogen peroxide.

In a photfenton reaction, the overall dye degradation is more when compared to Fenton's reaction or H_2O_2/UV technique because of the production of OH radicals by multiple pathways. All initial, propagation, termination and dye degradation steps are the same as the ones for reactions with Fenton's and UV/H_2O_2 reagents. However, another step for initial reactions must be added [100,108,109], which does not take place in Fenton reaction, because there is no radiation.

6. AOPS BASED ON OZONATION

6a. Ozone (O_3)

Ozonation has been widely used for drinking water disinfection—bacterial sterilization, odor, algae, and organic compound degradation [89,110-113]. It is more efficient in pollutant degradation and is not harmful for most organisms, because no new compounds are added to treated waters. Ozonation of dissolved compounds in water can constitute an AOP by itself, as hydroxyl radicals can be generated from the decomposition of ozone, which might be catalyzed by hydroxyl ions or initiated by the presence of traces of other substances [114]. The ozone decomposition increases at high pH values. Literature review has shown the use of ozonolysis could be applied to many different compounds. [110,115-117]. The specific application of ozonation to degrade dyes has been reported by many investigators [118-120]. The dye degradation in this case also follows the pseudo-first order kinetics [121]. The degradation of dyes via ozonolysis is reported to be higher at higher pH values and is due to the production of more HO• radicals in alkaline media and the dissociation of dyes to ionic form that can react with ozone easily than the non-dissociated species [121,122]. At low pH values, ozone exclusively reacts with compounds with specific functional groups through selective reactions such as electrophilic, nucleophilic or dipolar addition reactions [123].

6a1. Mechanism of Ozonation

This is divided into two main types, Direct and Indirect:

6a2. Direct Ozonation

In acidic media (pH ≈ 2) the decomposition of ozone is initiated by the action of HO^- ions is too low and consequently the concentration of hydroxyl radicals is small in solution [122]. This results in smaller rate constant values in the range of $1–1000 M^{-1}\ s^{-1}$. At higher pH values, $HO^\bullet$ concentration increases, thereby increasing the dye degradation [121]

6a3. Indirect Ozonation

In this reaction, ozone is first decomposed and the resulting species then react in the system with HO^- ions to form HO• radicals, which can then enter in several reactions to degrade the dye molecule.

The mechanism can be divided in three different parts [124];

Initiation reactions:

$O_3 + HO^\bullet \rightarrow O_2^{\bullet-} + HO_2^\bullet$ $\quad k_1 = 70\ M^{-1}\ s^{-1}$

Propagation:

$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2$ $\quad k_2 = 1.6 \times 10^9\ M^{-1}\ s^{-1}$

$O_3^{\bullet-} + H^+ \leftrightarrow HO_3^\bullet$

$HO_3^\bullet \rightarrow HO^\bullet + O_2$ $\quad k_3 = 1.1 \times 10^8\ M^{-1}\ s^{-1}$

$HO^\bullet + O_3 \rightarrow HO_4^\bullet$ $\quad k_4 = 2.0 \times 10^9\ M^{-1}\ s^{-1}$

$HO_4^\bullet \rightarrow HO_2^\bullet + O_2$ $\quad k_5 = 2.8 \times 10^4\ s^{-1}$

$HO_2^\bullet \leftrightarrow O_2^{\bullet-} + H^+$

Dye degradation:

$dye + HO^{\bullet} \rightarrow$ Intermediates,
$dye + O_2 \rightarrow dye\text{-}OO^{\bullet} \rightarrow$ Intermediates + $HO_2^{\bullet}$
Intermediates + $HO^{\bullet} \rightarrow CO_2 + H_2O$
Intermediates + $O_2 \rightarrow CO_2 + H_2O$

6b. O_3/UV Reagent

Photolytic ozonation (O_3/UV process) is another of AOP and is an effective mode for the destruction of toxic organics present in water [120,125-127]. The method has a significant potential as a wastewater treatment method. The final products of degradation in this case are merely CO_2, H_2O and low molecular weight organic compound if complete mineralization is achieved [128]. The aqueous systems is saturated with ozone and then irradiated with UV light at 253.7 nm. Since the extinction coefficient of ozone at this wavelength is $3300 M^{-1} cm^{-1}$, its decay rate is higher than that of hydrogen peroxide [129].

6b1. Reaction Mechanism

The degradation of organic molecules by O_3/UV reagent follows a similar mechanism to the one described for simple ozonation. However some additional steps are involved in the overall reaction scheme. These are outlined below [125].

$H_2O + O_3 + h\nu \rightarrow H_2O_2 + O_2$
$H_2O_2 + h\nu \rightarrow 2HO\bullet$

The decomposition of H_2O_2 is enhanced in the presence of O_3

$2O_3 + H_2O_2 \rightarrow 2HO^{\bullet} + 3O_2$

6b2. Ozonation + Homogeneous/heterogeneous Catalysis

O_3/H_2O_2, O_3/Fe^{2+} and $O_3/Fe^{2+}/UV$

The photodegradation of some organic compounds by ozone and UV radiation, alone or combined with hydrogen peroxide or ferrous and ferric ions, has also been reported by several authors [89,110,130]. A combination of AOP's has shown considerable increase in dye degradation than the single processes. In the case of ozone + H_2O_2, in addition to the general pathway for ozonation, ozone reacts with H_2O_2 when it is present as HO_2^-.

Other propagation reactions include the following

$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+$
$O_3 + HO_2^- \rightarrow HO\bullet + O_2^- + O_2$
$O_3 + HO\bullet \rightarrow HO_2^{\bullet} + O_2$

The chain reaction may be terminated by a radical- radical reaction such as
$HO\bullet + HO_2\bullet \rightarrow H_2O + O_2$ $k = 3.7 \times 10^{10} M^{-1} s^{-1}$

On the other hand, experiments which involve the Fenton reagent and are subjected to ozonolysis have shown improved mineralization of organic compounds. Besides an increase in the rate of degradation, total oxygen content (TOC) have also shown to increase from 21 to 43% by using this method instead of single ozonation.

7. PHOTOCATALYSIS

Photocatalytic degradation has proven to be a promising technology for degrading organic compounds [50,54,131-140]. The technique is more effective as compared to other techniques because semiconductors are inexpensive and can easily mineralize various organic compounds [141].

7a. Mechanistic Pathways

The photocatalytic decolouration of a dye is believed to take place according to the following mechanism. When a catalyst is exposed to UV radiation, electrons are promoted from the valence band to the conduction band. As a result of this, an electron-hole pair is produced [50]

$$\text{Catalyst} + h\upsilon \rightarrow e^-_{cb} + h^+_{vb}$$

where, e^-_{cb} and h^+_{vb} are the electrons in the conduction band and the electron vacancy in the valence band respectively. Both these entities can migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In most cases h^+_{vb} can react easily with surface bound H_2O to produce OH radicals, whereas, e^-_{cb} can react with O_2 to produce superoxide radical anion of oxygen [55]

$$H_2O + h^+_{vb} \rightarrow OH^{\cdot} + H^+$$

$$O_2 + e^-_{cb} \rightarrow O_2^{-\cdot}$$

This reaction prevents the combination of the electron and the hole which are produced in the first step.

The $OH^{\cdot}$ and $O_2^{-\cdot}$ produced in the above manner can then react with the dye to form other species and is thus responsible for the decolouration of the dye

$$O_2 \cdot\text{-} + H_2O \rightarrow H_2O_2$$

$$H_2O_2 \rightarrow 2\ \cdot OH$$

$$OH^{\cdot} + \text{Dye} \rightarrow \text{Dye}_{ox}\ (k = 10^9 - 10^{10}\ M^{-1}\ s^{-1})$$
$$\text{Dye} + e^-_{cb} \rightarrow \text{Dye}_{red}$$

Direct and Indirect photocatalytic pathways are the two suggested mechanisms for a given photocatalytic reaction. These are discussed below

7a1. Direct photocatalytic Pathway

Two different approaches have been suggested for this type of mechanism

(i) Hetrogeneous Photocatalysis - The Langmuir–Hinshelwood Process

The Langmuir–Hinshelwood process is applied to heterogeneous photocatalysis and can be explained on the basis of production of electrons and holes by the photoexcitation of the catalyst. The hole is then trapped by the adsorbed dye molecule on the catalyst surface to form a reactive radical state which can decay as a result of recombination with an electron. The catalyst is regenerated as a result. Langmuir-Hinshelwood (L-H) expression in its simpler form is given by [142]

$$1/r = 1/k_r + 1/(k_r k_a C)$$

where, r is the reaction rate for the oxidation of reactant (mg /l.min), k_r is the specific reaction rate constant for the oxidation of the reactant (mg /l.min), k_a is the equilibrium constant of the reactant (l / mg) and C is the dye concentration. Numerous examples of dye degradation adhering to such a process are reported in the literature [50,141-143].

(ii) The Eley–Rideal Process

In this process, the free carriers are initially photo-fragmented followed by subsequent trapping of the holes by surface defects. The surface active centers(S) can then react with the dye (chemisorption) to form an adduct species such $(S\text{–dye})^+$ which can further decompose to produce products or can recombine with electrons. The reaction scheme is outlined below [144].

$\text{Cat} + h\nu \rightarrow e^- + h^+$ (photogeneration of free carriers)
$S + h^+ \rightarrow S^+$ (hole trapping by surface defects)
$S^+ + e^- \rightarrow S$ (physical decay of active centers)
$S^+ + \text{dye}^+ \rightarrow (S\text{–CP})^+$ (chemisorption)
$(S\text{–dye})^+ \rightarrow S + \text{products}$

7a2. Indirect Photocatalytic Mechanism

In this process, electron–hole pairs are photogenerated on the surface of the catalyst. The hole is then trapped by the water molecules leading the formation of HO• radicals and H^+ and the electrons allow the formation of H_2O_2 which further decomposes in more OH^- radicals by means of its reaction with the oxygen supplied in the medium. Finally, the radicals formed during this mechanism are responsible for the oxidation of the organic molecule producing intermediate and end products [48]

The stepwise mechanism is illustrated below

$h\nu \rightarrow e^- + h^+$
$h^+ + H_2O(\text{ads}) \rightarrow HO(\text{ads})\bullet + H^+(\text{ads})$

$O_2 + 2e^- \rightarrow O_2 \bullet- (ads)$
$O_2 \bullet- (ads) + H^+ \leftrightarrow HO\bullet_2 (ads)$
$HO\bullet_2 (ads) \rightarrow H_2O_2 (ads) + O_2$
$H_2O_2 (ads) \rightarrow 2HO\bullet (ads)$
$HO\bullet + dye \rightarrow Intermediates \rightarrow CO_2 + H_2O$

7b. Degradation Studies of dyes

With the advancement of AOP techniques, various semiconductors have been tested for their efficiencies towards dye degradation. Some of these include TiO_2, V_2O_5, ZnO, WO_3, CdS, ZrO_2 and their impregnated forms [50,100,145-149]. Generally, any semiconductor doped with a secondary dopant would increase its activity. Several metals have been used for doping; these include Pt, Li^+, Zn^{+2}, Cd^{+2}, Co^{+3}, Cr^{+3}, Fe^{+3}, Al^{+3} etc.[150-152]. The presence of transition metals increase the photocatalytic activity either by scavenging electrons that reduce the recombination of charges and therefore favors the $HO^\bullet$ formation, or by modifying the surface properties of the material regarding the active sites, presence of defects etc., which could increase the adsorption and favour the interfacial reactions. Titanium dioxide mediated photocatalytic oxidation has been applied more extensively for dye studies [153-156]. This is mainly because of its low cost, stable nature and its optical absorption in the UV region. The use of TiO_2 has also guaranteed good results in detoxification of water samples loaded with molecules like anilines, alcohols, and organochlorides [157-160]. A quick comparison between TiO_2 and other semiconductors such as ZrO_2 reveals that the photocatalytic efficiencies are quite different. Although the bandgap energies for both TiO_2 and ZrO_2 are the same (3.1 eV), the higher activity of TiO_2 could be attributed to a higher efficiency in the separation of the photogenerated charges (less e^-/h^+ recombination rate) due to the structure of the material. On the other hand ZrO_2 presents a low absorbance in the UV range due to intra-band gap surface states, thereby causing its low activity.

7.b.1. Effect of pH

The pH has a great effect on the photodegradation efficiency of dyes. The variation in solution pH changes the surface charge of TiO_2 particles and shifts the potentials of catalytic reactions. As a result, the adsorption of dye on the surface changes thereby causing a change in the reaction rate. Acid yellow 17 (an anionic dye) has shown to be more degraded at pH 3 [161], whereas, Orange II and Amido Black 10B showed maximum degradation at pH 9 [162]. Similar results have been reported for TiO_2 mediated photolytic reactions for the removal of chlorophenols in [163].

7.b.2. Effect of the Dose of Semiconductor

Dye degradation is also influenced by the amount of the photocatalyst. The dye degradation increases with increasing catalyst concentration, which is characteristic of heterogeneous photocatalysis. The increase in catalyst amount increases the number of active sites on the photocatalyst surface thus causing an increase in the number of $HO^\bullet$ radicals which can take part in actual decoloration of dye solution. Beyond a certain limit of catalyst amount, the solution becomes turbid and thus blocks UV radiation for the reaction to proceed and therefore percentage of the degradation starts decreasing [50, 164,165].

7.b.3. Effect of the Initial Concentration of Dye

The initial concentration of dye in a given photocatalytic reaction is also another factor which needs to be taken into account. In this case it was found that percentage degradation decreased with increasing amount of dye concentration, while keeping a fixed amount of catalyst in these studies [50,165]. This can be rationalized on the basis that as dye concentration increases, more organic substances are adsorbed on the surface of TiO_2, whereas less number of photons are available to reach the catalyst surface and therefore less $HO^{\bullet}$ are formed, thus causing an inhibition in degradation percentage.

7.b.4. Effect of Additives

The photocatalytic degradation of dyes is also effected by the presence of additives in solution matrix [50,161,162,166-168].These additives are generally present as ions which are initially added to the dye solution as ionic compounds to improve the industrial process. However on release of wastewater, the ions become an integral part of the effluent. Many common ions present in dye wastewater are Fe^{+2}, Zn^{+2}, Ag^{+}, Na^{+}, Cl^{-} , PO_4^{-3}, SO_4^{-2}, BrO_3^{-}, CO_3^{-2} , HCO_3^{-} and persulphate ions. Each of these added ions causes a certain decrease in percentage degradation of the dye solution, as shown in Table 2. The change in dye degradation in the presence of some selective ions is explained below on the basis of their chemical reactions in solution. For example, Fe^{+2} ions most likely undergoes the following chemical reaction in solution with $HO^{\bullet}$ radicals already produced in solution

$$HO^{\bullet} + Fe^{+2} \longrightarrow OH^{-} + Fe^{+3}$$

The above reaction has an appreciably high rate constant value of $3.5x10^{8}\ M^{-1}sec^{-1}$ [169]. Thus in the presence of Fe^{2+}, $HO^{\bullet}$ radicals are easily converted into OH^{-}, thereby decreasing their concentration and thus less degradation of dye solution is observed.

Likewise, the presence of CO_3^{-2} and HCO_3^{-} ions are usually added to the dye bath to adjust the pH of the dye solution. In the presence of these ions, dye degradation also decreases. This can be explained on the basis that the presence of these ions scavenge the $HO^{\bullet}$ radicals according to the following reactions thus causing a decrease in percentage degradation.

$$CO_3^{-2} + HO^{\bullet} \longrightarrow CO_3^{\cdot -} + OH^{-} \qquad k = 3.9\times10^{8}$$

$$HCO_3^{-} + HO^{\bullet} \longrightarrow CO_3^{\cdot -} + H_2O \qquad k = 8.5\times10^{6}$$

Similarly, a decrease in degradation value in the presence of Cl^{-} is due to its hole and hydroxyl radical scavenging effect, which occurs as follows [50]

$$Cl^{-} + h_{VB}^{+} \longrightarrow Cl^{\cdot}$$

$$Cl^{-} + Cl^{\cdot} \longrightarrow Cl^{\cdot -}$$

$$HO^{\bullet} + Cl^{-} \longrightarrow HOCl^{\cdot -}$$

$HOCl^{\bullet -} + H^+ \longrightarrow Cl^{\bullet} + H_2O$

The presence of sulphate ions in solution also causes a decrease in percentage degradation because these ions can react with $HO^{\bullet}$ radicals in solution and result in their depletion as follows [170]

$SO_4^{-2} + HO^{\bullet} \rightarrow SO_4^{\bullet -} + OH^{-}$

Addition of a strong oxidizing agent such as persulphate ions ($S_2O_8^{-2}$) also decreases the degradation percentage because it can produce sulphate ions in solution;

$S_2O_8^{-2} + e^{-}_{cb} \rightarrow SO_4^{\bullet -} + SO_4^{-2}$

The sulphate ions can then react with $HO^{\bullet}$ radicals as shown above. The sulphate radicals can further react with water molecules to produce more sulphate ions as follows:

$SO_4^{\bullet -} + H_2O \rightarrow HO^{\bullet} + SO_4^{-2} + H^+$

Since $SO_4^{\bullet -}$ is less reactive than $HO^{\bullet}$ radicals, therefore SO_4^{-2} concentration increases in solution which leads to less dye degradation.

The addition of bromate ion (BrO_3^{-}) can also decrease percentage degradation. This can be explained on the basis that this species is an efficient electron scavenger and can react in the solution as follows [50]

$BrO_3^{-} + 6\ e^{-}_{cb} + 6\ H^+ \rightarrow Br^{-} + 3\ H_2O$

The bromide ions produced in the reaction can react with $HO^{\bullet}$ radicals in solution (rate constant value = $1.1 \times 10^{9}\ M^{-1}sec^{-1}$) thus decreasing their concentration which result in less degradation

$Br^{-} + HO^{\bullet} \rightarrow {}^{\bullet}Br + OH^{-}$

Likewise the addition of ethanol can inhibit the photodegradation of a dye solution. This is because of the reason that ethanol can quench hydroxyl radicals which are the main source of dye degradation chemistry [161].

Photocatalytic degradation is also influenced by the presence of oxygen or air [171 -176]. The degradation becomes less in the absence of oxygen and this has been attributed to the recombination of photogenerated hole–electron pairs. Oxygen adsorbed on the surface of a semiconductor prevents the recombination process by trapping electrons according to the reaction [177, 178]:

$O_2 + e^{-} \rightarrow O_2^{\bullet -}$

Table 2. Change in percent decoloration of three different dyes in the presence of various ions (ion concentration = 50 mg/L, irradiation time = 20 min)[a]

[Ions]	% decoloration		
	TB	***SO***	***CV***
–	40	21	17
Fe^{2+}	6	3.5	8.5
Zn^{2+}	11	–	7.5
Ag^{+}	23	7.5	10
CO_3^{2-}	23	7	10
HCO_3^{-}	23	12.5	10
Cl^{-}	11	9	15
BrO_3^{-}	29	–	9.5
$S_2O_8^{2-}$	12	11	12
SO_4^{2-}	38	9	12.5
PO_4^{3-}	33	17	9
NO_3^{-}	24	10	13

[a] TB = Toludine Blue, SO = Safranin Orange, CV = Crystal Violet. The studies correspond to [TB] = 80µM, V_2O_5/TiO_2 = 20 mg/20 mL;[SO] = 80 µM, V_2O_5/TiO_2 = 25 mg/20 mL; [CV] = 40µM, V_2O_5/TiO_2 = 30 mg/20 mL.(This table taken from our work, ref [50])

It is known that the reaction rate is a function of the fraction of adsorption sites occupied by dissolved oxygen which makes it a limiting factor towards the photoxidative process [177].

CONCLUSION

All the AOP's based on H_2O_2 (Fenton, photo-Fenton and H_2O_2-UV) have been reported to achieve the degradation of dyes. These techniques are of interest because they are less expensive than ozonation. A combination of AOP techniques such as O_3/UV and photo-Fenton techniques has been reported to achieve higher degradation of dyes. The photocatalytic processes have shown higher degradation of dyes than the rest of the AOP's for the treatment of most of the dyes. Photocatalysis is advantageous with respect to the other AOP's as the catalyst is not consumed during the reaction.

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Chapter 10

First Steps to a Deductive Classification System of Colorants from the Point of View of Structural Chemistry[*]

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Dedicated to my wife

Abstract

Beginning with well known building blocks and putting them together by using noncovalent bonds of the type 1) intermolecular H-bonds and 2) intramolecular π…π-bonds and 3) inorganic metal-complexes, the deductive classification system of colorants is derived. The building blocks are called 1) 'chromogens' and 2) 'tetrahedral' respectively 'octahedral' metal-complexes.

There are three 'classes' of colorants: 1) 0.4 nm structures, 2) sheets structures, 3) 3-dimensional networks.

The dichotomy soluble-insoluble is due to quality and number of bonds between the building blocks, forming the crystal lattices of colorants. A view on their entirety and characteristics is opened.

This paper makes use of the stack principle of organic molecules of dyestuffs in order to create the deductive classification system of colorants. Important but nevertheless in the second position in the order of rank are solubility/insolubility, stability, counteractions of light with colorants (absorption/reflexion). The author hopes for intriguing queries by colour chemists.

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a) [*] Revised and extended version of a lecture "Organic crystals with π…π -intrastack forces ("0,4 nm structures". Part 2, "A new Classification System of Colorants", held on 16th of January 2004 in Optiva Inc., Musskaya pl. 1, Moscow (Russia).

The author is of the opinion that the deductive classification of colorants points to an axiomatic wording. Perhaps therefore colorants become more understandable and interesting for students of chemistry?

Keywords: Colorants; classification system; building blocks; one-,two- and threedimensional networks

'With this you have started a novel classification system on pigments. Sorry, I can't take your paper into consideration for my monograph 'Color Chemistry'.[1]

The longest way starts with a first step.
Konfuzius (551-479 v. Chr.)

1. PREFACE

Always classification comes after experimental results and therefore it is the fundament of scientific endeavours. Many times colorants (colorant materials) have been arranged.

To set the scene studying good textbooks of the last decades referring to inorganic and organic chemistry onto specialist terms as "dyestuff" and "pigment" is charming.

Textbooks are *interlocutors,* because they codify the knowledge of their time and therefore they are very informative. The author has studied nine textbooks of organic chemistry, written between 1950 and 2003. The result:

Fieser 1950 [1,I]; Karrer 1963 [1,II]; Klages 1967 [1,III]; Christen + Vögtle (1989) [1,IV]; Beyer + Walter (1991) [1), V]. The textbooks [I-V] are old fashioned and deal with dyestuffs at some lenght. However, from 1980 on textbooks take up new features and do not pay much attention to dyestuffs [VI -X].

The state-of-the-art and best book comes from H. Zollinger [2] . In every respect it is worth reading and a future pointing monograph. Professionel chemists look for monographs like [2] or [3]. They arrange to different aspects of colorants. Usually dyes and pigments are treated well in textbooks and/or monographs [2], [3] with introducing syntheses. That is undoubtedly necessary and correct.

Schulze's "Farbentabellen" [4] are predecessors of the most authoritative leading and volumineous work in the field of colorant classification, the 'Colour Index' [5]. It is earmarked only for specialists but is the comprehensive compendium of all colorants.

The index forms to 1) hues; 2) chemical constitution, 3) generic names; 4) solubility; 5) syntheses; 6) organic or inorganic origin; 7) application and dyeing techniques; 8) trade names; 9) patents and others. Already this enumeration catches a glimpse on this collection [5].

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b) [1] Answer to the author's off-print [D&P, 59 (2003), p. 1-24] written by H. Zollinger, prof. emer. ETH Zürich (08.09.03). Original Swiss German: "Vielen Dank für Ihren Sonderdruck. Sie haben damit ein neuartiges Klassifizierungssystem auf Pigmente begonnen. Leider kann ich Ihre Arbeit für mein neues Buch "Color Chemistry" nicht mehr berücksichtigen. Es ist jetzt in den Händen der Druckerei und ich werde es erst nach Druck und Buchbinderei wieder sehen".

Up till now the entirity of inorganic pigments never had been a subject in inorganic textbooks. Therefore the inorganic counterpart to Herbst/Hunger [3] is written by Buxbaum [6].

The author of this work makes a strong plea for reading J. Shore's "Classification and general properties of colorants", chapter 1 in [7]. Shore outlines many items of colorants classification systems. [2], [3], [6] and [7] compile the knowledge of our time.

Might be correlated organic and inorganic pigments?

- A simple and practical answer give standards like DIN 55944 [8]. This standard gives a *short* survey of colorants. Together with DIN 55943 it introduces immediately into the technical world of colorants. The author draws the reader's attention to the recent editions DIN 55943, 2001-10 and DIN 55944, edition 2003-11, [8]. DIN 55944 classifies colorants *according to coloristic and chemical aspects.* Standards are dedicated right straight for the use of industrial personnel and introduces immediately into the technical world of colorants. They are used for definition of terms, are enumerating, describing and amazingly complete. Without a doubt standards of DIN are important, however, sometimes rather general. DIN 55944 (european norm) specifies ‚colorants' as general term with respect to colouring materials. This standard defines dyes as 'soluble' and pigments as 'insoluble' in the application medium.
- Another answer gives Erk: "Although there are some fundamental differences between organic and inorganic pigments which originate from the different bonding situations in the solids, many of the principles outlined here for organic pigments may be applied to inorganic pigments as well" [9].
- A further answer gives the author of this paper, which is interested in the precise meaning of the dichotomy soluble/insoluble in context with colorants. He destinates the target by studying their transitions and trying to find correlations with structural chemistry. By introducing the term "building block" [~ building unit] the author of this paper evades tedious discussions between *different bonding situations in the solids,* Erk [9]. The author's 'building blocks' are closely connected with the colorants according to chemical aspects (DIN 55944).

The author classifies the entirity of colorants by introduction of building units (molecules/ions) and the

- *inter*molecular (*non-covalent*) bonds
- dichotomy soluble/insoluble
- the connections of building units to one-, two- and three-dimensional entities
- size of colorant
- thermal stability.

Every chemist knows the connection of monomers to plastics and man-made fibres as a general principle and about the correlation of cross-linking and solubility. Kind and density of the networking at the same time is the crucial point and is a valid one for inorganic pigments too. Networking of chemical building blocks (units) is the basic topic of the structural chemistry and their connection reveals bonding rules of solid states.

Some experts will ask for the application and importance of Kitaigorodskii's epoch-making theory (bump-in-hollow-principle) of organic molecules within this classification [10]. Kitaigorodskii's theory however, is complemented by the chloro-rule of G.M.J.Schmidt, see the summary in Desiraju's monograph: [11, p.179-194] "The chloro group may therefore easily identified as a good *steering group* in crystal engineering", [11 p.192] and soon after Desiraju enlarges on to all hetero atoms: " These effects are not specific to sulfur and suggests that all hetero atoms are important in determining 4-Ang. structures of planar aromatics" [11, p. 216]. The early papers of Desiraju (1984-1986) [12, p. 99], [13, p. 160] and [14, p. 222] applicate the chloro-rule of G.M.J.Schmidt.

The publication presented here begins very consciously with finished molecules/ complexes, the above mentioned building blocks (units). They crystallise to lager molecule associations [15] or infinite complexes [16], [17]. The author draws the attention to one- two- or three dimensional network architecture with building blocks, an usual procedure with crystal engineering. From this point of view common characteristics and boundaries of colorants emerge. They are the topic of this publication. The common grounds contain also inorganic pigments whose building blocks are introduced as metal-complexes. The studies of the stability of inorganic crystals formed by coordination polyhedrons, s. Pauling [16] and [17] are exemplary.

The herewith submitted publication is restricted to organic π…π- intrastack bonds, intermolecular H-bonds and ionic-covalent bonds (metal complexes). Up to now the entirety of "colorants" (dyes, pigments) has not been arranged with regard to networking. Indeed the chemist knows inorganic pigments (carbon black, iron oxide, chromium oxide, titanium oxide and other ones). However, for colouring paints, plastics and building materials they lead an individual existence in the field of the inorganic chemistry. Evaluating organic pigments under the view of crystalline character is a field for specialists still today, almost unknown, however. But also the opposite, seeing dyes as a borderline case of crystalline colorants, seems to be absurd.

This is due to the unusually broadly scattered application fields of colorants. Finally it has to be reminded of that pigments are in some respect an unknown technical field (printing inks, enamels, paints, pickles, plastic, fibres). They exist in a technological niche. So phthalocyanine blue is an important example of a pigment, which is an "insoluble" dye. The author designated this as 'road signs blue'. The unsolubility of phthalocyanine blue and the kind of its application are known only to specialists, although chemists nevertheless are working continuously at the change of soluble to insoluble and vice versa. That is valid from the lab up to application technique and production.

The relation soluble-insoluble is the breath of chemistry.

The several application techniques of dyestuffs and pigments (fibres, paint printing ink etc.) are using the basic difference of insoluble pigment to soluble dye. From the viewpoint of university chemists they have the odour of crafts, trade, small industry, technique and shift into low wage countries.

2. INTRODUCTION

In this contribution the author attempts to present a deductive survey of all "colorants" from the viewpoint of *structure chemistry*. Chemists will recognize fast formal similarities to plastics. However, with plastics dominates the covalent bonds between the molecular building blocks. For their deductive arrangement colorants require the principle of bonds between building blocks of ionic, metal-complex like or non-covalent kind. Those ones are in the first place intermolecular H-bridges and intramolecular π…π- stacks. Furthermore the essential groups "dyes", "organic pigments" and "inorganic pigments" must remain recognizable and their common basis becomes understandable.

Anyway, it is a deductive representation anyway possible? Fortunately “dye-chromonics” [18] have become known since 2000 as state-of-the-art "dyes" [19]. They are important as liquid crystals(!) in the field of modern π-functional dyes. According to the opinion of the author they fill exactly the gap between dyes and pigments.

3. DYES

One is astonished again and again as the molecular thinking dominates strongly at chemists. Beyond doubt the success of the textile dyes, which stood at the evolution of the chemical industry, is responsible for that. The dye industry synthesized new molecules (chromogens) continuously and successful, see Zollinger [2] and Herbst/Unger [3]. That led to an abundance of various dyestuffs, having a muddling effect on external chemists (and students).

Among technical knowledge the chemistry of *soluble* molecules suffices for dyeing.

For the author’s point of view that seems to be an essential cause for understanding the 3-dimensional arrangement of organic molecules in the field of pigments as a special subject. The chemistry of dyes has developed advanced colouring procedures and has come to reliable findings since 150 years.

Every colour chemist knows about dye aggregate in the dyeing bath [2, p. 379, 386, 406] and [20]. Also herringbone structures [18, 19] or T-structures may be formed in this moment [11]. Both are allied and point at liquid crystals.

The following items indicate the start of crystallization of vat dyestuffs in the fibre:

- Even around 1970 Kratky had been able experimentally by X-ray small angle scattering to prove the agglomeration as “stacks” of up to four dye molecules in the firm cellulose fibre [21, 22].
- Zollinger [2, p. 417] argues in a similar way: "dyes are usually present as single molecules or small clusters". Zollinger also evaluates the relation vat dyestuff to pigment [2, p. 313]: "because of their low solubility in organic solvents and in water, vat dyes are natural candidates for pigments".
- Zollinger writes about vat dyestuffs: "Vat dyes, for instance, even become pigments after their application" [2, p. 2]. One can turn round the last two sentences: The ability of the molecules of vat dyestuffs for the formation of π…π-intramolecular

> stacks is not only an essential condition for the formation of crystals of carbonyl pigments, but also for the formation of molecule piles in the fibre.

In the scientific literature many items to this subject are found, e.g. [23-32]. The author recommends the review [20] with excellent references to dye structure and aggregation of textile dyestuffs. The results were obtained by using microscopy, x-rays and spectra. Especially many vat dyes crystallize after absorption onto the fibre as a result of post-treatment [25-28].

Furthermore papers point to the direction of crystallization [26-28]. Sumner et al. [26, p. 186, fig. 3 B] wrote “the molecules are then free to migrate and combine with one another to form crystals. Vat dye crystals are usually needle-shaped, and (…..) the molecules are arranged across the length of the needles”. Wegmann [28] points out changes in hue in the case of vat dyes in fabric caused by soaping. This results in clearer hues and often in improvements in fastness.

But also advices for the textile industry are helpful, for example the BASF brochure [30]. It is written from the chemical aspect and uses the term “aggregation”, that is the polydisperse state, up to the re-oxidation of leuko vat dyes. Only in connection with soaping the terms ‘crystals' and ‘crystallizing' are introduced. Crystallization is presented as a result of soaping and therefore taken as a cause of the improved fastnesses (wet fastness, chlorine fastness, light fastness). Stack formation is not mentioned anywhere.

Associations of dyes forming crystals are mentioned in [31, p.148]: “Dimers are probably formed first and these grow by addition of further molecules to give lamellar micelles in which the dye molecules are stacked up like cards in a pack”.

And “The changes which take place during soaping are essentially those of crystallisation of the vat dye into a more stable crystal habit” [31, p.514]. Already the pioneering monograph of Vickerstaff is to be mentioned [32]. From a contempory point of view (2002) the mechanism to explain what happens during soaping, see [7, vol. 2, p. 909].

The author is of the opinion that stack formation of vat dyestuffs has to be accepted as the final state of soaping because this is the common feature of *all* pigments (pile rule) [33]: In the cellulose, fibres are arranged as tiny stacks of vat dyestuff molecules, due to the energetically promoting step of *intra*molecular $\pi \ldots \pi$ forces.

Which function do those carbonyl groups now have jutting out from the piles at the side? Two diffusion models for dyes in fibres, the pore model and the free-volume model, both developed by dye chemists, give the answer. If we follow the summary explanations of Zollinger [2], p. 403, p. 404, fig.11.8], best suitable will be the “pore model” for cellulose and the “free-volume model” for polyesters.

Obviously the carbonyl group works at cellulose fibres (pores) about intermolecular H-bridges of the type dye-unit-C=O … HO-Cellulose. In the pores piles take over the function of struts then, which means, pores filled with water are penetrated with piles of vat dyestuffs. Instead of the intermolecular H-bridges of the type

dye-unit-C=O … HO-cellulose then such of the type
dye-unit-C=O … H_2O … HO-cellulose

have to be assumed.

The dyeing process with vat dyestuffs about all steps of operation is absolutely understood. With respect to chemical-physics stack formation (crystallization) could make understandable the fourth operation step “soaping”. Too strong soaping leads to a lack of rub resistance [30, p. 30]. The interpretation by stack formation is: When too large “stacks” arise, they are not anymore optimally adjusted to the pore diameter of the fibres (intermolecular H-bonds). Using tissues demands not only flexible fibres, but also flexible stacks, for example in the area of knees, at pressure points, seams. Covalent bonds are rather inflexible (with regard to distance and angle), non-covalent bonds (π…π- intrastack- and H-bonds) are by far more mobile (with regard to distance and angle).

Might small stacks be nuclei of “liquid crystals”?

Berndt mentions the difficulty of re-vatting after soaping [30, p. 30]. In the course of the publication presented one can say: Soaping of vat dyestuffs forms molecule stacks, positions them in the fibre and leads to a lower energy state.

Soaping as a crystallization process and stabilization of vat dyestuffs at cellulose surface becomes understandable as a synergistic effect (cooperation) of two non-covalent bonds.

Clusters may be also T-structures [11], [18], [19]. Everyone chemically trained can recognize post-treatment with soap and water at 100°C between 30 s and 60 min as a suspicious operation for dyes. The dye molecules could transform from the T- over herringbone- to the most stable stack-structure while soaping. Dye manufacturer and dye consumer depend on each other by industrial type-precise dyeing. For that the statements [34] are important.

It is essential to the author to point out at the stable *final state* of dye molecules (fastnesses) in the fabric.

The next step on the way to stacks is the expanded crystallization of dye molecules to large piles. In the first place the molecules aggregate with themselves to “supramolecules”. These are called lyotropic liquid crystals (LLC). Already Edwards et al. include some remarks on key physical steps associated with textile dying [18, p. 103 – 104]. They have opened completely new industrial perspectives, see chapter 5 "Dye-chromonics". Because already dyes of the type of pseudoisocyanines belong to the “dye-chromonics” (see there), also aggregation of other dyes (s. azoic dyes, [2, p. 200-202] is probable.

Further and important are ‘solvent dyes’ and ‘disperse dyes’, the first ones are insoluble in water, but soluble in organic solvents [34], the second ones are almost but not completely insoluble in water, [2, p. 195]. Both are ‘non-ionic dyestuffs’ and solvent dyes are often classified under pigments as well as dyes.

What think chemists about the formation of stacks in the course of their application? Experiments and evaluations should be seen with respect to this view point, especially the free-volume model [2], p. 403]. Do adopt dyeings of polyester fibres with disperse dyes ‚molecular stacks’ and are these the start (begin) of ‘recrystallisation’ ? What is about the comment of Zollinger: “in recent years, it was found, that combinations of two or more disperse dyes gives rise to higher dying rates on polyester as compared to individual dyings. In the best of our knowledge, this phenomenon has not been investigated scientifically” [2, p. 403]. Are stack formed bymolecules of two or more distinct disperse dyes?

Both, anionic and cationic (basic) dyestuffs forms stacks, [35, 36, 37-40].

4. CLASSICAL ORGANIC PIGMENTS, (COP’S)

In the course of the deductive classification of colorants the non-covalent bonds must be emphasized.

In the shadow of previous dye research Pararot (in 1885) was synthesized as the oldest organic pigments, just like CI pigment Red 49:1, (1899), mentioned above. Then Hansa Yellow (in 1909) and Toluidine Red followed, see [4]. *All* these molecules form ‘stacks' with the aromatic (flat) part (pile rule) [33]. At the same time they form the typical distance of ~ 0.35 - 0.42 nm, named also ‘0.4 nm-structures’ by Desiraju [2, p. 160-162, 212-222].

Therefore the “π … π- intramolecular stack”-principle of structure is clear and responsible also for the *technological* properties. π…π- intrastack forces are decisive for stability, however obviously limited by classical organic pigments. At times of the syntheses of Hansa Yellow and Toluidine Red only few application technicians knew the industrial use of the pigments, i.e. unsolubility, recognized it as important. Questions about the cause of the unsolubility, crystallization and 3-dimensional structure were without technical importance and therefore uninteresting. Soluble dyes dominated thinking and action, for example with A. v .Baeyer's indigo synthesis. After that resonance questions of *single dye molecules* came to the fore on the part of basic research.

The fact that two qualified crystallographic researchers during the discussion of crystal structures of important pigments disregarded the existence of π…π- intrastack forces is until today designating for the small interest in the causes to unsolubility of organic pigments.

In this contribution the relationship between structure and unsolubility is placed in the foreground and is the arranging principle of the classification system. A new chromogen (unit, building block) has similarity with a new material permitting to build novel houses. In fig. 2 of the publication [33, p.6] pigment properties are compared with distinct masonries. An addition explanation could give the comparison between houses with pigment crystals: Modern technical evolutions make higher demands on both.

In order to meet these demands, unsolubility had to be increased for example already in the time from 1910. Larger molecules of the BON type (*b*eta*o*xy*n*aphthoic acid-anilide) and disazocondensation pigments (in 1955) were synthesized, see [33, fig.1, p.5]. Also Zollinger mentions in his monograph, that "azoic colorants and pigments can be regarded as a borderline case of dyes and pigments" [2, p.201]. Thus vat dyestuffs became an interesting source for carbonyl pigments [4, p. 313]. The preceding quotations show the narrow gearing of dyes and pigments.

The chromogens mentioned are construction principle for characteristic groups of pigment classes. *Pigment chemistry in the origin sense is architecture with molecules*, and the destination is a ‘building', is the (pigment)-crystal.

5. DYE-CHROMONICS, (LLC’S)

A modern survey for the term "chromonics" is given in [19]. Accordingly "chromonics" are known also as medicines (drugs) and are not only limited to dyes. However, only these are of interest in this chapter, which is called therefore dye-chromonics. Speaking in modern terms they are called lyotropic liquid crystals, LLC’s.

The earliest experimental investigation goes back to Scheibe [37]. In [37] also indications of preceding literature are contained. Hoppe’s publications [38], [39] are of interest likewise. Early as Scheibe Jelley recognized the pseudoisocyanine dyes as ‘polymers’ [40]. Modern speaking π…π- *intrastack* forces between the flat dye molecules and with it self-aggregation to supramolecular piles (stacks) are the uniform building principle for “dye-chromonics”. This increases the *viscosity* of aggregated dyes and causes the name “polymer”. However, the “dye-chromonics” have nothing common with polymeric plastics. Scheibe-polymers were the first “chromonics” in modern sense. Their technical importance for sensitization of silver chloride emulsions of photographic films was recognized fast.

Chemically speaking “dye-chromonics” are polyaromatics, which are related to carbonyl dyes and with them to vat dyestuffs. They are attaining industrial importance in coating of glass or plastics by nanofilm crystallisation. These coated substrates (glass or plastic) are suitable for the production of “polarizers”, “retarders” and liquid crystal display cells. The first commercial application of this new material technology is creating optical films for the flat panel display market. Today “dye-chromonics” are investigated intensively [41-44]. Probably there are even further technical applications [44].

The chemical constitution of the single molecules (chromogens ~ building blocks) used successfully for polarizers and retarders are essential. Those ones are

- indanthroneblue (!) substituted with sulfonic acid, a sulfonation product of a dibenzimidazoles derivative of
  a) perylenetetracarboxylic acid (cis and trans) and
  b) naphthalinetetracarboxylic acid,
- 2.9-disulfonic trans-quinacridone [45].

The combination of hydrophilic and hydrophobic properties is characteristic for this type of the “dye-chromonics”: *‘With certain modification of hydrophilic-hydrophobic balance”, are capable of self-assembly to large supramolecules that act as the major structural element'* [41, p.5]. Self-aggregation is observed also in thinned aqueous solution.

“Dye-chromonics” show a remarkable ability to π…π- intrastack forces, which form supramolecules. For other dyes π…π- intrastack forces may be subordinate perhaps, but they are the supporting scaffold for “dye-chromonics”. Polarizers are produced by shearing an aqueous solution of the “dye-chromonics” (supramolecules) using a metal stick (Mayer wire-wound rod) being moved electronically over a glass or plastic substrate in a small distance in parallel. Now the “molecular stacks” (~ rods) have minimal shear-resistance by orientating parallel and in coating direction. The long rod structures align along the shear force direction in a wet layer. After water has evaporated, the layer of parallel supramolecules must be converted to a water insoluble form. Due to sulphonic acid groups, which protrude laterally from the side (edges) of every molecule in the “stack”, this is done by immersion in a $BaCl_2$-solution, 15%, acting for 1-2 seconds. In this treatment Ba^{2+} -ions displace NH_4^+-counter ions and cross-link sulfonic acid groups of parallel stacks. Therefore many Ba^{2+} -ions tighten mechanically the film [44, p.319]. The “dye-chromonics” are precipitated, (made insoluble) by Ba^{2+}-ions and remain in unchanged positions on the glass substrate. *That is 2-dimensional chemistry.* 1-dimensional π…π- “stacks” are vertically cross-linked by inorganic O ---Ba^{2+}---

O-groups. The endless (infinite) 2-dimensional (flat) network is a chemically bonded by aromatic π-electrons and Barium^{2+}-ions.

This chemical procedure reminds of the syntheses of toners. In order to make them insoluble dyes substituted with sulphonic acid groups are precipitated by Me^{2+}-ions. Every chemist knows, that for this purpose particularly Ba^{2+}-, Sr^{2+}-, Ca^{2+} -, Mn^{2+} -ions are used [33, p.5]. This precipitation is designated also as a partial fitting of (or with) barium sulphate. Zollinger [2, p. 413] designates the Ba^{2+}-ions in this connection as “counterions”. The procedure led to the production of an early azopigment. It was synthesized first by Julius: Lithol Red 1899, CI pigment Red R, 49:1, BASF/Ludwigshafen (Germany). See also chapter 4, ‘classical organic pigments '.

Syntheses of 2-dimensional molecular lattices with industrial-physical importance are left to the High Technology (nanotechnology) of our time. The Ba^{2+}-crosslinked dye-chromonics can be understood easily as ‘pigments’ having expanded 2-dimensionally on a glass substrate. In the ideal case these are slices of single crystals, crystallographically seen. Since *two* chemical bonds (*p*eriodic *b*ond *c*hain vectors, that is PBC-vectors) are effective in the crystal plane, F-faces are possible and according to Hartman and Perdok these are morphologically most stable in the respective crystal [46]. The publication uses the expression “building blocks”.

“Dye-chromonics” molecules have large similarity to those of vat dyestuffs. “Dye-chromonics” aggregate (via π…π- intrastack forces) with consequences for the technical use, and like this the same aggregation influences vat dyestuffs during dyeing (diffusion, soaping), see Zollinger [2, p. 288-302] or Berndt [30, p. 8-9].

However “dye-chromonics” do not have colour strength (tinctorial strength) in comparison with dyes and pigments. However, they show properties of π-functional dyes, see *10 (conclusion).*

6. HIGH PERFORMANCE PIGMENTS (HPP'S)

The author has compiled all published organic crystal lattices of pigments up to the year 2000 in [33]. In this enumeration high performance pigments play an essential role.

The principle of stack-formation is a major aspect again. At the same time every pile from molecule to molecule (intermolecular) is occupied by lateral NH- and CO-groups a million times. These get in touch with neighbouring piles about intermolecular H-bridges in the sense of the formation of –NH…OC- groups. Many millions of piles, parallel to each other, form sheets from molecules through cross-linking. The building principle resembles that of Ba^{2+}-crosslinked “dye-chromonics”. Quinacridones [47], Diketopyrrolopyrroles (DPP's) [48b], Benzimidazolones [48a] and Thiazines [48c] have a reputation for these sheet structures.

With reference to Quinacridones, Lincke proposed a 2-dimensional mesomeric structure within crystal lattice in order to interpret their extremely increased stability [49].

Phthalocyanine pigments are characterized by π…π- intrastack bonds, the Cu-containing grades additionally by $\{CuN_6\}$-octahedrons. They are π…π- intrastack/ metal-complexes [33, p. 13].

7. CARBON BLACKS

Carbon blacks are typical HPP-pigments, assembled in "*stacks of sheets*". Speaking in the terms of this paper, the cores of benzene are the "building blocks" of the sheets. However, as each chemist knows, they are of excellent stability by *'intrasheet'* (covalent) $\pi \ldots \pi$-conjugation. They are precursors of today's supramolecules. The position of carbon blacks in tab.1 is exactly the borderline of HPP's and CICP's. Carbon blacks are children of graphite and this is a typical F-face substance. Strictly speaking, carbon blacks are half organic and half inorganic pigments, i.e. they are transitions from organic to inorganic pigments. The "scope of 0.4 nm – structures" includes carbon blacks [50].

8. EFFECT PIGMENTS

Bronzes are an old group of inorganic pigments, produced of aluminum and/or copper metal, s. Pfaff [48e]. By crushing and sizing of above metals bronzes become the desired thin metal flakes, i.e. pigments. One can understand bronzes as '2-dimensional' metals'. "Building blocks" are metallic Al and/or Cu/Zn. The metal atoms (spheres) are closely packed in layers (111). Bronzes are essential raw material for metallic coatings.

Modern effect pigments (pearlescent or interference pigments) interfere with visible light. For this purpose flat platelets or sheets of aluminium oxide (Al_2O_3) or mica or titanium dioxide (TiO_2) or silica (SiO_2) are selected or synthezised by inorganic preparative chemistry and covered with one or several thin layers of other inorganic oxides (inorganic complexes).

Building blocks are inorganic coordination polyhedrons of the types $\{SiO_4\}$, $\{TiO_6\}$, $\{FeO_6\}$ and $\{AlO_6\}$. After all, effect pigments use the flat-face principle [46]. These are examples of 2-dimensional preparative inorganic chemistry in industrial scale. The author takes the production of 2-dimensional crystals (pigments) as HighChem Syntheses. The here mentioned coordination polyhedrons are used too in [48e].

For effect pigments and "sheets" weak cohesion (easy cleavability) between the flakes is necessary.

9. COMPLEX INORGANIC COLOUR PIGMENTS (CICP)[2]

In the field the colorants, 2-dimensional connections of coordination polyhedrons to 'effect pigments' (s. chapter 8) are exceptions. 3-dimensional connection is the rule and pronounced subject of inorganic structural chemistry. CICPs consist of close densely packed spheres of oxygen and the more electropositive ions, which are nearly all smaller than oxygen, are found in the interstices between the close-packed oxygen ions, see for example [48d]. Due to the electronic charges of coordination polyhedrons, their bonds are shared 3-dimensionally. Especially, if strong O…Me…O bonds are acting between the sequence of close-packed layers, these result in very stable crystals. However, the layers of close densely

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c) [2] The abbreviation 'CICP' is not in accord to DIN. However, the interested reader is referred to the term 'CIC' in DIN 55943:2001-10, p. 6

packed oxygen- and metal ions are not “sheets”. *Every CICP consists of sequences of such layers of atoms, ions or complex ions.* This is the basis of the crystallography. [48d, p. 43] shows two illustrations of TiO_2-rutile and [48d, p. 44] of spinel. One can see clearly the layers of the closed packed ions.

Connecting metal complexes of the type $\{MeO_6\}$, $\{MeO_4\}$ or $\{MeS_4\}$ 3-dimensionally, so particularly oxide complex bonds $\{MeO_6\}/\{MeO_4\}$ achieve highest stability.

Additionally, some sulphide complexes have to be mentioned. Characteristic S…Me…S-bonds are the cause of maximum stability. Besides some of them are brought to a given particle size and -form by burning in presence of salts. Frequently spherical shape is approximated. That’s why the particle diameter of TiO_2-pigments is synchronized with the exact wavelength of the visible light and their frequency distribution corresponds to the global solar radiation [51]

CONCLUSION

Table 1 summarizes the colorants in 7 rows:

1) From tiny dye stacks (row 1, chapter 3),
2) over π…π- stacks, comprising millions of molecules, however still weak (row 2, chapter 4),
3) over strong π…π- stacks comprising millions, Ba^{2+}- cross-linked (row 3, chapter 5),
4) to strong π…π- stacks comprising millions, with lateral networking through intermolecular H-bridges (sheet structures) (row 4, chapter 6),
5) to carbon blacks, known to every chemist, (sheet structures) (row 5, chapter 7),
6) to effect pigments (inorganic sheet structures) (row 6, chapter 8).
7) Finally the 3-dimensional networking to oxide pigments is a qualitative jump and necessary for understanding highest stability (row 7, chapter 9).

Line ‘class' arranges the colorants according to the aspects “stack” (1-dimensional), “sheet” (~ F-face; 2-dimensional) and/or “sphere” (3-dimensional). Summing up, one is able to remark an overlap of the groups (1) to (7).

All other lines are self-explanatory.

The characteristics of fabrics are the confusing amounts of dyes, fibres and dyeing techniques. These led to the development of a very special, technical language. The same refers in an adapted manner to porcelain, ceramics, enamels as well as lacquers and printing inks. Coloration of varied objects (substrates) with different basic (primary) materials seem to be insuperable barriers between differing technical fields. The employees of producers and suppliers have their own technical languages. The "high performance final products" demand for skilled people, which have developed a skilled language in the course of time, fitting exactly to their products.

Additionally, the differences between colorants in the fields (1) to (7) are controlled by the substrates 'clothes' and other ones like 'paper', 'car bodies', 'cans', 'furniture', 'tableware' or mass pigmented pieces of 'plastics' or 'man-made fibres'. However, the author supposes, that substrates like glass/plastic for 'dye-chromonics', at least, create a functional unit with 'dye-chromonics', a sandwich-structure. Keyword: adhesion/cohesion.

The author wants to draw the reader's attention to typical drawbacks of dyes and pigments, see tab.1. Strictly speaking they are characteristics of non-covalent bonds of all colorants:

- Dyestuffs tend to agglomerate in the dyeing bath.
- Dispersing of organic and inorganic pigments is always difficult. However, the most stable organic pigments like phthalocyanines, quinacridones, peryleneimides etc. are *bad* with respect to their dispersibility.
- Organic pigments/inorganic pigments tend to absorb many additives and solvents from the liquidly medium (in preparations).
- After some weeks or months pigments in many liquid lacquers tend to settle down or to form sediments at the bottom of the can. In order to avoid these drawbacks, technicians are engaged in it and therefore working steadily.
- Perhaps, there is a further drawback with non-covalent bonds and “dye-chromonics”. Seed growth defects in crystalline structure tend to destroy the crystal long range order.

Readers searching for threedimensional figures, which demonstrate connnectivities between colorants , shall have a special look at the papers [33, 47, 49].

11. SUMMARY

Strictly speaking “dye-chromonics” do not appertain to “colorants”, since they do not have any coloring strength, but they perform their function as coloring substances under influence of electric current on substrates (glass/plastic) of flat panel displays. Furthermore inorganic oxides within the coated interior of monitors are not colorants either.

Already the monograph of Zollinger [4] exceeds the field of dyes,

- the boundaries between dyes and pigments are emphasized as leaky and
- in several chapters “π-functional systems” [2, p. 3, 13, 429ff] are stressed,
- for example dichroitic dyes for liquid-crystal displays [2, p. 522- 526].

Therefore, at the end of this classification system the previous definition of colorants by Zollinger [2, p.1] is:

"An even more important criterion is the following: colorants are either *dyes* or *pigments*", which might be expanded by: "Up to 1990 colorants had been either dyes or pigments. Soon after 1990 liquid crystals (thermotropic or lyotropic) became bridges between dyes and pigments and they point also to biologically important colorants like hemin, chlorophyll and others.

Modern colorants include functional π-electron systems".

“Dye-chromonics” are bridges - also for understanding - between dyes and organic pigments. They appertain already more to the π-functional systems.

Desiraju writes with respect to “Chemistry – The middle kingdom” [52]: “ Much of this chemistry was built with concepts and models like electronegativity/electropositivity, oxidation/reduction, hardness/softness, enthalpy/entropy, kinetics/thermodynamics, reactivity/ selectivity, electrophilicity/nucleophilicity and chirality/achirality”. And some sentences below: ” Chemistry is oceanic with respect to factual information, but it has always been contained with respect to the number of concepts and models that were required to understand all these facts”.

The author of this paper concludes:

All the colorants are small in comparison with the whole of material sciences. Therefore *technological* dichotomies like ‘soluble/insoluble’, ‘stability/instability’, ‘cheap/expensive’, ‘toxic/ nontoxic’ are of decisive practical importance and at the very core of our life.

CONCLUDING REMARKS

Only few datas across the whole of colorants are compiled (summarized) in table 1. Apparently there are *intermolecular* contacts with influences the crystal structure of organic molecules, i.e. ‘steering groups’ or pi...pi-charge-transfer forces. The range ‘soluble-insoluble’ corresponds with the wealth of dying techniques and mass colorations (mutual correspondence).

In our life there are many dichotomies ‚soluble’ and ‚insoluble’, however, application of colorants is the most aesthetical one. This will be confirmed by famous great painters like Hokusai:

Someone interested in the the life of the Japanese illustrator and printmaker Hokusai may study Francois Places’ tale “The old man mad about drawing”. The tale ends with:

> “From the age of six I started drawing all sorts of things. At fifty I had already drawn a great deal, but nothing that I did before my seventieth year was worth any great note.It was at seventy-three that I began to understand the true shape of animals, insects, and fishes, and the nature of plants and trees.
>
> Therefore, at eighthy-six I will have made more and more progress, and at ninety I shall have penetrated even further into the essence of art. At a hundred I will certainly have reached a marvelous stage, and at a hundred and ten each dot and each of my drawings will have a life of its own. I would like to ask those who survive me to ascertain whether I have not spoken without reason”.

Table 1. Classification of Colorants from the view of structural chemistry (building blocks)

Chemical starting products selectively and variably synthesised to intermediate products and these to chromogens or to selected metal oxides/sulfides								
only a few become a member of					**C** **Graphite**	**Al, Cu, Fe**	**{SiO$_4$},** **{TiO$_6$},** **{FeO$_6$}**	**{MeO$_6$},** **{MeO$_4$},** **{MeS$_4$}**
	(1)	(2)	(3)	(4)	(5)	(6)		(7)
Colorant	Dyestuff	classical organic pigment (COP)	dyestuff-chromonic (LLC)	High performance pigment (HPP)	Carbon black	bronze, flakes, metallic pigments	pearlescent pigments	**C**omplex **i**norganic **c**olor **p**igment (**CICP**)
Bond type	$\pi \ldots \pi$- intrastack + laterally connected bonds by				Intrasheet covalent π-bonds	metallic bonds	silicate and metaloxide complexes	Metal oxide/sulfide complexes
	dyebath + pores of tissue	furthermore van der Waals bonds	Ba^{2+}- ions	Interstack H-bonds				
Size of colorant	single mol. or tiny stacks	stacks of hundreds of molecules			sheets one on the other	~ 1000 layers (sheets, platelets) of atoms or inorganic complexes		exact adjustment of particle size
Correlation colorant/substrate	dyestuffs in pores of tissue	COP in resins	selfaggregation on substrate + Ba^{2+}- ions	HPP + plastic, resin, fibres	carbon black in resin	metal oxides, coated sheets of mica, titanium dioxide, hematite		CICP + resin, plastic, plaster, mortar, ceramic
Class	← scope of (1-dimens.) 0.4 nm structures →					✕ ✕ ✕ ✕ ✕ ✕		**3-dim. Networks** (spheres)
	✕ ✕ ✕ ✕ ✕		← scope of (2-dimens.) F-faces →					
Thermal stability (°C)	~ 120	~ 150	~ 240	~ 400	~ 800	different		~ 1300

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