Dyes and Pigments

New Research

Arnold R. Lang
Editor

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PREFACE

Chapter 1 - Photodynamic therapy (PDT) is a cancer treatment based on activation of a drug by light. The drug, called photosensitizer, absorbs the energy of light of the proper wavelength and transfers it to surrounding molecules, mainly oxygen, forming reactive oxygen forms like radicals and singlet oxygen. These highly reactive species are responsible for destruction of targeted cells. Besides the direct effect on the cells, vascular shutdown develops as well and immune response is activated, both being important for long-term control over the tumor. Most of the photosensitizers are recruited from the group of porphyrins and related compounds like chlorins, bacteriochlorins, porphycenes, texaphyrins, and phthalocyanines. However, other dyes also entered the trials for photodynamic evaluation, e.g. some tricyclic dyes or hypericine. We discuss in this chapter, the history, photophysical and photochemical principles of PDT, as well as the biological effects of the photosensitizers. The main structural groups of photosensitizers are discussed and the most important drugs, either approved or in trials are described. Also, other approaches closely connected with PDT (catalytic therapy, sonodynamic therapy, photothermal therapy, and photochemical internalisation) are mentioned in this chapter.

Chapter 2 - Phthalocyanine analogues containing alkyl-substituted benzenoid rings and pyridine rings are interesting compounds, because quaternation of the pyridine nitrogen is expected to form cationic amphiphilic compounds.

Non peripheral long alkyl substituted zinc phthalocyanine derivatives, zinc bis(1,4-didecylbenzo)-bis(3,4-pyrido)porphyrazine and zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine were reacted with dimethyl sulfate and monochloroacetic acid to give their quaternary products. Also the zinc phthalocyanine derivatives reacted with diethyl sulfate to afford the sufo-substituted products. All reacted compounds showed amphiphilic character.

Regio isomers of zinc bis(1,4-didecylbenzo)-bis(3,4-pyrido)porphyrazine were also quaternized with dimethyl sulfate.

Identical peaks in cyclic voltammograms appeared for these products before and after quaternization.

Zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido)porphyrazine was evaluated the the photo-dynamic therapy of cancer efficacy by cancer cell culture.

The light exposed dimethyl sulfate quaternized zinc bis(1,4-didecylbenzo)-bis(2,3-pyrido) porphyrazines in IU-002 cells produces cell disruption that can be detected as a decrease as fluorescence.

Chapter 3 - The textile industry uses large amounts of water in its dyeing processes. Due to environmental problems the supercritical dyeing process has been developed. In this process supercritical carbon dioxide is used as the solvent for dyes.

On the other hand, pigments, used in the formulation of paints, inks, toners and photographic emulsions can be micronized by supercritical antisolvent process. Their production in form of micrometric particles with controlled particle size distribution can largely improve their characteristics.

For these reason, in the last years, supercritical fluids more and more have been proved as environmentally benign media for dyeing processes and as antisolvent to control the formation of micrometric particles.

The physico-chemical properties of supercritical fluids are halfway between those of gases and liquids; more these properties can be easily modified by a simple variation of pressure or/and temperature. Therefore, supercritical fluids can be used to develop solventless or solvent reduced processes and their mass transfer properties are useful to produce micronized particles with controlled size and distribution.

In this field, the publications appeared over the past years could be reviewed under two groupings, one involving the measurements of solubilities of dyes in supercritical carbon dioxide, with and without co-solvent, and supercritical CO_2 dyeing of fibre, and the other involving the micronization of dyes with narrow particle size distribution using a supercritical antisolvent process. In the following, a lot of recent papers will be cited, which should give an overview of actual results on solubility and precipitation of dyes in supercritical carbon dioxide.

Chapter 4 - Photochromism refers to a reversible phototransformation of a chemical species between two forms having different absorption spectra. Photochromic compounds reversibly change not only the absorption spectra but also their geometrical and electronic structures. The molecular structure changes induce physical property changes of the molecules, such as fluorescence, refractive index, polarizability, electrical conductivity, and magnetism. When such photochromophores are incorporated into functional molecules, such as polymers, host molecules, conductive molecules, liquid crystals, the properties can be switched by photo irradiation. Among of all kinds of photochromic compounds, the spirooxazine dyes (SPO) are well-known photochromic compounds that show their high fatigue resistance and excellent photostability, which is one of the most promising candidates for applications in molecular electronics such as optical memory, molecular switching devices. In this review, we describe the recent development of spirooxazine dye as photo-controlled molecular switches in molecular materials, especially photochromism of spirooxazine in single crystal phase, spirooxazine dye polymer materials as fluorescence molecular switches, electrical conductivity switches, and viscosity switches, liquid crystal switches, gel switches and so on. In addition, layer by layer self–assemble spirooxazine dye in supermolecular chemistry as a photoswitching unit is described. We mainly present specific examples from our own research, which highlight our research group's contribution.

Chapter 5 - Dyestuff in water introduces several environmental problems and should be removed for clean water system. Fenton oxidation can be as an effective technique for the water treatment. In this report, homogeneous and heterogeneous catalysis in Fenton oxidation was examined for two dyes with acidic (Naphthol blue-black, NBB) and basic (Methylene Blue, MB) properties. The behaviour of these dyes under different experimental conditions (temperature, pH, peroxide concentration, Fe concentration) was studied using Fenton (Fe^{2+})

and Fenton-like (Fe^{3+}) reactions for the following processes: 1) normal Fenton oxidation, 2) Fenton oxidation combined with sonication effect, 3) Fenton oxidation combined with a solid catalyst (activated carbon). The main Fenton oxidation reactants, Fe^{2+}, Fe^{3+} and H_2O_2 were used in small quantities in order to observe closely the reaction kinetics for decolourisation of these dyes. It was found that both sonication and heterogeneous catalysis offer improvements to the Fenton oxidation under optimised conditions, with Fe^{2+} being faster than Fe^{3+} initially but Fe^{3+} ending up with a higher overall efficiency. 90-95% decolourisation was achieved in some optimised runs after 2 hours; however the general decolourisation was completed for all batch runs after a period of 24 hours, except in conditions where the reaction did not proceed at all. Chemical oxygen demand (COD) removal also occurred during the decolourisation process of both dyes, in maximum efficiencies of about 80% after 48 hours. Methylene blue also showed greater decolourisation efficiency in comparison with Naphthol blue-black for most of the experimental runs under the same experimental conditions. The reaction kinetics was mainly pseudo-first order for majority of the homogeneous reaction, as determined by non-linear regression or a combination of first order kinetics for heterogeneous reactions.

Chapter 6 - Water is an important natural resource for sustainable ecosystems, human life and economical development. The control of water pollution has become of increasing importance in recent years. Dyes make the world more beautiful through colored products, but cause a lot of problems in the environment. For decoloration and degradation of textile wastewater many applicable methods have been developed, but because of the composition complexity of the textile wastewater the use of universal procedures seems to be impossible. So, there is a need to find an efficient and cost-effective wastewater treatment for the decoloration of textile wastewaters. In this chapter a survey of the most widely used and, according to many researches, the most promising textile wastewater decoloration methods are presented.

Chapter 7 - Synthetic dyes that are extensively used in various industrial branches represent a serious environmental problem when they are emitted into the effluents as they are hardly biodegradable in conventional wastewater treatment plants. Therefore, alternative methods for decolouration of the wastewaters are developed, among them adsorption on solid sorbents is one of the most effective ones. Because the conventional sorbents such as activated carbon are rather expensive for large-scale applications, various low-cost materials have been tested as alternative non-conventional sorbents for the dye removal from waters. Numerous natural materials (zeolites, clays), industrial wastes (fly ash, iron slag), agrowastes or biosorbents exhibit a sufficient ability to retain various kinds of dyes from aqueous solutions and are available (locally and sometimes also globally) in great quantities and at low prices, and thus they can be used potentially for the treatment of the dye-containing effluents. A brief review of the non-conventional sorbents for the dye removal is given in this article together with selected applications. It should be emphasized that the dye sorption onto non-conventional sorbents is a rather complex process in which several mechanisms may be effective simultaneously. Effects of principal operational parameters on the dye sorption are discussed in the article, such as an effect of pH (governing both the dissociation/protonation of the active groups on the sorbent surface as well as side equilibria in solution), the presence of inorganic salts or surfactants. Basic equations describing the sorption equilibria (sorption isotherms) are presented. The results of kinetic measurements that allowed (in some cases) to identify a rate-limiting step of the overall sorption process are also mentioned in this chapter.

Chapter 8 - Laboratory investigations, pilot-plant experiments and an industrially established technology illustrated that electron beam (EB) treatment can efficiently destroy textile dyes in aqueous solutions. This treatment belongs to the class of Advanced Oxidation Processes (AOP): here also, as in most of AOP principally $^{\bullet}OH$ radicals induce the chemical transformations. The final result of the treatment depends on the absorbed radiation energy (dose); with sufficient dose mineralization can be achieved. Major benefits of EB treatment with respect to the conventional methods are: no usage of chemical additives, room temperature operation, penetration in the bulk of water even in case of turbidity, production of high concentrations of oxidizing radicals in a fraction of a second and simultaneous disinfection.

The book chapter summarizes the radiation sources and the experimental techniques used for studying the reactions of dyes in irradiated systems (e.g. pulse radiolysis, gamma radiolysis, UV-VIS spectroscopy), describes the decomposition of water under the effect of ionizing radiation, characterizes the reactive intermediates formed (hydroxyl radical, hydrogen atom, hydrated electron), and discusses their reactions with dye molecules. An essential part of the chapter is the description of the kinetics and mechanism of azo dye decomposition. At the beginning of the treatment the water radicals reacting with the dye cause destruction of the highly conjugated electronic system resulting in decoloration. The decoloration is followed by a step-by-step degradation, destruction of the aromatic rings, ring-opening, fragmentation to smaller molecular mass aldehydes, ketones, carboxylic acids, etc. When oxygen is present compounds with progressively higher oxygen-to-carbon ratio are involved in the conversion of an organic molecule to CO_2 and H_2O. The individual reactions are detailed on the examples of several dye molecules.

Pilot plant experiments on dye containing industrial wastewater have proven that combining conventional treatments with the EB based technology results in a considerable improvement of the treatment efficiency. Considerable reduction of chemical additive consumption, and also reduction in retention time were observed, with an increase in removal efficiencies as indicated by reduction in Total Organic Carbon content, TOC, Chemical Oxygen Demand, COD and Biological Oxygen Demand, BOD. Based on the pilot-plat experiments a full-scale plant for recycling EB-treated textile wastewater went into operation just at the end of 2005 in Daegu, Republic of Korea.

Chapter 9 - 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.

Chapter 10 - 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.

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?

Chapter 11 - 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 such as adsorption, coagulation, sedimentation, membrane-filtration processes (nano-filtration), reverse osmosis, electrodialysis, advanced oxidation processes etc. have been forwarded concerning the removal of these dyes from solution. Adsorption is a well known equilibrium separation process and is an effective method for water decontamination applications. It is well-known that natural materials, waste materials from industry and agriculture and biosorbents can be obtained and employed as inexpensive sorbents. Some of the reported sorbents include commercially activated carbon, clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite) and polymeric materials as low cost adsorbents for dye removal. This overview focuses on using adsorption method to remove dyes from solution and the literature findings of such studies on various types of clays are presented.

Chapter 12 - Dyes extracted from plants have been used for centuries for coloring materials. In this paper, typical behaviors of some naturally occurring colorants belonging to the class of flavonoids are presented. Their structures derive from that of flavone (2-phenylbenzopyrone), which is colorless, whereas hydroxy derivatives absorb UV and blue light, so appearing yellow colored. Current interest in flavonoids is mainly due to their varied biological activity in medicine, but also to their use as colored components in works of art (tapestries, carpets, miniatures).

The color of hydroxy-substituted flavonoids (flavonols) can be markedly modified by changing the pH or bonding with different metal ions, therefore, it critically depends on the acidity and the presence of metals in the environment. The absorption and emission spectra generally shift to the red by increasing the pH, due to stabilization of anionic forms. The number and sequence of acid-base dissociation steps depend on the number and position of the hydroxy-substituents. These aspects will be illustrated here with some significant examples concerning two naturally occurring colorants, old fustic and weld, and their main chemical components (morin, apigenin and luteolin). Absorption and fluorescence spectra recorded in solution provide the base for developing scientific investigations on the colorants spread on paper as watercolors or used in mordant dyeing of textiles.

Chapter 13 - Inorganic natural and synthetic pigments produced and marketed as fine powders are an integral part of many decorative and protective coatings and are used for the mass coloration of many ceramic materials, including glazes, ceramic bodies, and porcelain enamels. In all these applications, pigments are dispersed (they do not dissolve) in the media, forming a heterogeneous mixture. In conclusion, powders used for colouring ceramics must show thermal and chemical stability at high temperature and must be inert to the action of molten glass (frits or sintering aids). These requirements limit ceramic pigments to a very small number of refractory systems which are fully reacted and relatively inert to the matrix in which they are dispersed. This need for great chemical and thermal stability has dominated research and development in recent years. In this chapter the state of the art will be reported focusing in particular on the specific systems used in this industrial field. The advantages and the limitations of different colours will be underlined with particular emphasis on the current problems and on the possible way to solve them.

Chapter 14 - The twenty-four substituted metallophthalocyanines were synthesized, in two steps, from 4-nitrophthalonitrile or 3-nitrophthalonitrile, and characterized by MS, ^{1}H NMR, UV-vis, IR and element analysis. The results showed that they all were consistent with proposed structures. They behaved excellent solubility in some organic solvents, but the stability of them in solution was not good as in solid state. According to the scopes of red shift, the impact of metals, substituents and substitution positions on Q-bands could be displayed as follow: Mn > Zn ≈ Cu > Ni ≈ Co; 2-isopropyl-5-methylphenoxyl 4-tert-butylphenoxyl quinolin-8-yloxyl 2-methoxyethoxyl; non-periphery > periphery. The research displayed that the alternative ways to control the Q bands of Pc compounds to have a big change were to alter the chemical value of metal in the center of Pc ring, replace the atom banding directly with Pc ring or its chemical circumstance, and change the substitution position of substituent on Pc ring (periphery or non-periphery).

Chapter 15 - A review of the basic ecological problems related to the application of dyes and pigments for textile, foods and polymers is presented. A modern approach for solving the problems is shown. Along with a review of the synthesis and application of functional dyes and pigments already reported, in this paper we present a synthesis of 20 new bifunctional azo- and anthraquinone dyes-triazine derivatives. Six of them are metallized (Cu, Cr^{III} and Co^{III}) dyes and two of them contain a tetramethylpiperidine (TMP) stabilizer fragment in their molecule. In a color assessment of the new dyes, the percentage of exhaustion and fixation to cotton was found to be with 10-15 % higher compared to those of the model ones.

The photo degradation of 10 fluorescent naphthalimide dyes, synthesized before, was investigated and the structure-stability dependence was determined.

The copolymers of acryl amide and five fluorescent 9-phenylxanthene dyes derivatives, allylic ether-esters were obtained. The percentage of the chemical bound in the polymer dye was found to be 45-80, providing an intensive, stable to wet treatment and solvent's color and fluorescence, thus making the dyes suitable for ecologically tolerant application in food and cosmetics.

The photo stability of the triazine azodyes with a TMP fragment in the molecule was 25-30 % higher than those of the similar bifunctional azodyes without TMP. Their polymers of acrylonitrile were obtained and it was found that they have a good stabilizing effect on the photo degradation of the copolymer thus making these dyes suitable for "one-step" coloration and stabilization of materials with more tolerant ecological behavior.

Chapter 16 - Synthetic and natural analogues of 9,10-anthracenedione are well-known and widely used substances in the food and dye industries. Beyond their dyeing ability some anthraquinones are used as medicines as they exhibit beneficial effects in mammals and humans; moreover, anthracyline antibiotics have been applied therapeutically in the case of several malignant diseases. Total synthesis of anthraquinone derivatives using organic chemical methods is common; however, sophisticated biotechnological techniques provide alternatives for synthesis and overcome some environmental and economical concerns. The most frequently studied plant cell culture systems originate from members of the *Rubiaceae* family because these cell cultures are capable of producing high amounts of anthraquinone derivatives. Several methods to enhance the dye yield in order to obtain the best results have been and are still being used on a small-scale prior to applying them in large-scale industrial production. Numerous factors regulate the biosynthesis of anthraquinones in cell cultures like compartmentation, environmental stimuli (e.g. light, precursors) and endogenous (metabolic and developmental) factors. Since major points of the anthraquinone biosynthesis regulation are known in the *Rubiaceae* family, various possibilities have been raised to exploit these findings. Formation of hairy root and other transgenic cell cultures have proved to be useful tools to increase the anthraquinone production capacity; moreover, newer approaches (DNA and protein microarrays, proteomics) are promising techniques to define biosynthetic pathways to elucidate the unknown and rate limiting steps. Another effective approach to dye production enhancement in plant cell cultures is elicitation: exogenous stimuli induced gene activation. Various elicitors have been introduced during the past two decades affecting anthraquinone yields of measured cell cultures; however, the background of the influence on physiological events caused by elicitors is not fully understood. Elicitors are recognized by plant receptor(s) localized in the plasma membrane or cytoplasm. After elicitor signal perception, plant receptors activate effectors and signal transduction leads to the modulation of genes via second messengers. Altered gene expression might manifest itself in heightened production of antraquinone derivatives. An increasing knowledge of plant signal transduction enables us to choose a suitable elicitor, which activates/modulates the desired pathways for anthraquinone production leading to a more selective production of the needed compounds. This commentary summarizes results of the latest studies on elicitor induced signal transduction leading to anthraquinone production in plant cell cultures and discusses other relevant techniques on a comparative basis. Furthermore, major problems and a future outlook are also debated.

Short Commentary - Dyes are normally difficult to eliminate from effluents by conventional biological wastewater treatments. There are many references in which it is proven a poor removal by activated sludge or other systems in wastewater treatment plants. Their xenobiotic nature and their low concentration in residual streams (20 – 200 mg/l) make them to be difficult substrates for bacterial growth. Actually it is not clear the role they play in biological systems. Under anaerobic environment, it seems they act as electron acceptors in organic matter biodegradation. Under aerobic environment, it seems that a few number of microorganisms are able to use them as electron donors, in the presence of oxygen. Combined anaerobic-aerobic processes have efficiency on dye removal due to the first step in dye degradation, the breakdown of the azo bond, is assumed to be done under anaerobic conditions.

The use of solid supports for bacteria which utilize azo dyes is an attractive alternative for remove them from residual streams. These supports need to have two characteristics: an

adequate texture for bacterial growth (particle and porous size) and affinity for dye. Under this situation, dye is adsorb and concentrated on solid surface and bacteria can grow and degrade it on the surface of the solid. The surface of the solid seems to be a good environment for dye degradation, because oxygen concentration can be low inside the porous structure and microaerophilic conditions can be established, therefore cleavage of the azo bond can be performed easily. Several solids can be used on this purpose: activated carbon, bentonite and kaolin, for example. The solid used has to be investigated in terms of texture of the surface, growth of microorganisms and dye degradation.