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Chapter 7

NON-CONVENTIONAL SORBENTS FOR THE DYE REMOVAL FROM WATERS: MECHANISMS AND SELECTED APPLICATIONS

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ABSTRACT

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.

Keywords: Synthetic dyes; Adsorption; Non-conventional sorbents; Wastewater treatment

1. INTRODUCTION

Great amounts of synthetic dyestuffs are emitted into wastewaters from various industrial branches, such as from dye manufacturing and textile finishing, causing a serious environmental problem because of their poor biodegradability in conventional wastewater treatment plants. The release of coloured effluents into the environment is undesirable not only from aesthetic reasons, but also because many dyes and their degradation products are toxic or mutagenic to life. Without adequate treatment these dyes are stable and can remain in the environment for tens of years (des Santos et al., 2007).

Synthetic dyes may be classified according to their application and chemical structure. They are composed of groups of atoms responsible for the dye colour, called chromophores, as well as an electron withdrawing or donating substituents that modify or intensify the colour of the chromophores, called auxochromes. The most important chromophores are azo (-N=N-), carbonyl (-C=O), methine (-CH=), nitro (-NO_2) and quinoid groups. The most important auxochromes are amine (-NH_2), carboxyl (-COOH), sulfonate (-SO_3H) and hydroxyl (-OH) (des Santos et al., 2007). It was estimated that the azodyes represent about 70% of the total dye production in the world (Zollinger, 1978). Because of the presence of various ionic or ionisable groups, the dyes exhibit (usually) a very good solubility in water. The ionisable groups bear either positive or negative charges. Thus the dyes behave like large organic cations (basic dyes) or anions (acid dyes) in aqueous solutions.

Traditional wastewater treatment technologies have proven to be markedly ineffective for handling the effluents containing synthetic dyes because of the chemical stability of these pollutants (Forgacs et al., 2004). Up to now, there is no single and economically attractive method for decolourisation of textile wastewaters, although notable achievements were made in the use of biotechnological approaches to this problem in recent years, as reviewed by dos Santos et al. (2007). In addition to the biological treatment, many physical and chemical methods have been employed for the dye removal from wastewaters, including coagulation, floculation, filtration, oxidation or reduction, complex-formation or neutralization (Slokar and Le Marechal, 1998; Forgacs et al., 2004). Advantages and drawbacks of some non-biological decolourisation processes are summarised briefly in Table 1. Very often, more sophisticated treatment strategies utilizing combined techniques (e.g. membrane microfiltration together with adsorption) are used to remove the dyes from complex industrial effluents (Jirankova et al., 2007). Novel adsorption/oxidation, adsorption/reduction and other combined processes were reviewed recently by Qu (2008), whereas Wojnarovits and Takacs (2008) reviewed the radiation-induced degradation processes for the removal of azodyes from waters.

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters. Currently, the most commonly used adsorption agent in industry is activated carbon that was successfully tested also for the removal of various kinds of synthetic dyes. However, relatively high operating costs and problems with regeneration of the spend activated carbon hamper its large-scale applications. Therefore, a number non-conventional sorbents have been tried for the treatment of wastewaters. Typically, various industrial wastes, agrowastes or natural materials available in great amounts at low prices are classified as alternative sorbents for the removal inorganic (e.g. heavy metals) as well as organic pollutants from wastewaters (Bailey et al., 1999; Babel and

Kurniawan, 2003; Kurniawan et al., 2006; Crini, 2006). Some of these materials will be overviewed briefly in the following chapter.

Table 1. Some non-biological methods for the removal of synthetic dyes from waters (adapted from dos Santos et al., 2007)

Method	Principle	Advantages	Disadvantages
Fenton reaction	Oxidation using mainly H_2O_2-Fe(II)	Effective decolourisation of soluble and insoluble dyes	Sludge generation
Ozonation	Oxidation with ozone gas	Application in gaseous state – no alteration of volume	Short half-life (20 min.)
Photochemical degradation	Oxidation using mainly H_2O_2-UV	No sludge production	Formation of by-products
Electrochemical destruction	Oxidation using electricity	Usually non-hazardous products	High cost of electricity
Membrane filtration	Removal of all dye types	Concentrated sludge production	
Ion exchange	Retention on ion exchange resins	Possible regeneration without a loss of efficiency	Not effective for all dyes
Electrokinetic coagulation	Coagulation with $FaSO_4$/ $FeCl_3$	Economically feasible	High sludge production

2. OVERVIEW OF NON-CONVENTIONAL SORBENTS

Since its first introduction in the 1940's, *activated carbon* has become the standard adsorbent frequently utilized for the removal of organic and inorganic pollutants in water industry (Pollard et al., 1992), (and as such, it may be hardly called a "non-conventional" sorbent). The term activated carbon is used to include a broad range of carbonaceous materials which exhibit a high degree of porosity and extended interparticulate surface area. Active carbons can be prepared from a huge variety of carbon-containing feedstocks. The production process involves usually carbonisation of the raw material below 800°C in the absence of oxygen typically followed by activation at elevated temperatures in the oxidising atmosphere (steam, carbon dioxide or air). Sometimes, chemical catalysts are used to modify the surface reactivity of the product.

The most common feedstocks for the commercial production of activated carbon are wood, anthracite or bituminous coal (Pollard et al., 1992). However, many alternative raw materials, such as various wastes from industry or agriculture, have been used to prepare activated carbon utilizable as a sorbent in wastewater treatment, as reviewed by Pollard et al.(1992), or more recently by Dias et al. (2007). The non-conventional activated carbons were prepared e.g. form peach stones by the H_3PO_4 treatment at 500°C and used for the removal of Methylene Blue from aqueous solution (Attia et al., 2008), or by the sulphuric acid treatment method from Parthenium biomass and used to remove another basic dye – Rhodamine B (Lata et al., 2008). Activated carbon prepared from oil palm shell was used for an adsorption of Methylene Blue (Tan et al., 2008), whereas jute fiber carbon was used for an adsorption of Eosin Yellow, Malachite Green and Crystal Violet (Porkodi and Kumar, 2007). Effective adsorbents with high adsorption capacity for large molecules including reactive dyes were prepared by the steam-activation method from several solid wastes, namely from waste PET, waste tires, refuse derived fuel and wastes generated during lactic acid fermentation from garbage (Nakagawa et al., 2004).

Among naturally occurring biosorbents, *chitin* is the second abundant biopolymer after cellulose. However, more important than chitin is *chitosan*, which has a molecular structure similar to cellulose and exhibits an excellent sorption ability for the dye retention (Crini, 2006). Chitosan can be prepared by alkaline deacetalation of chitin, which is widely found of the exoskeleton of shellfish and crustaceans. It is available in great amounts as a waste product from fishery industry. It was demonstrated that chitosan is especially suitable for the sorption of reactive and acid dyes – reported sorption capacities ranged from ca. 300 to 2500 mg/g (Crini, 2006). A certain limitation of chitosan as sorbent consists in its solubility in acidic media. To avoid this problem, chemically modified (mostly crosslinked) chitosan-based sorbents were developed and utilised e.g. for the sorption of Methyl Orange (Morais et al., 2007). Croslinked chitosan prepared by persulfate induced free radical polymerization was used as sorbent for basic dyes (Lazaridis et al., 2007). This modification improved considerably the rates of the dye sorption. An effect of the degree of deacetylation on the sorption ability of chitosan towards acid dyes was studied by Wong et al. (2008). It was shown that the highly deacetylated product exhibited reduced sorption ability, probably due to the changes in the internal structure of chitosan.

Attractive biosorbents with unique sorption properties can be prepared from *beta-cyclodextrin*, a torus-shaped cyclic oligosaccharide with an internal hydrophobic cavity. Thanks to this structure, cyclodextrins are capable to form inclusion complexes and thus retain various pollutants through host-guest interactions. The cyclodextrin-based sorbents are prepared by crosslinking, typically with epichlorhydrin (Crini, 2008). The cyclodextrin polymer exhibited good sorption capacities for basic dyes in the range of ca. 36 to 53 mg/g (Crini, 2008) and can be used also for the sorption of azodyes (Ozmen et al., 2008).

Zeolites are naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms. A negative charge on the three dimensional lattice is balanced by cations that are exchangeable with the cations in solution. Zeolites consist of a wide variety of species such as clinoptilotite and chabazite. During 1970's, natural zeolites gained a significant interest among scientists due to their ion-exchange capability that was frequently employed for the removal of metal ions from waters and industrial effluents (Babel and Kurniawan, 2003; Kurniawan et al., 2006). Numerous studies confirmed an ability of zeolites to retain various kinds of dyes from aqueous solutions (Armagan et al., 2004; Benkli et al., 2005; Meshko et al., 2001; Ozdemir et al., 2004; Wang et al., 2006), although the sorption capacities (especially for reactive dyes) were rather low (Armagan et al., 2004; Crini, 2006). More advantageous for the dye removal seem to be *clays* and *clay minerals*. There are several classes clays such as smectites (montmorillonite, sapionite), mica (illite) kaolinite, serpentine, pylophillite (talc), vermiculite and sepiolite (Shichi and Takagi, 2000). The adsorption capacities result from a net negative charge on the layered structure of minerals. Bentonite and other clay materials were used for the treatment of coloured wastewaters (Al-Bastaki and Banat, 2004; Al-Ghouti et al., 2003; Alkan et al., 2005; Atun et al., 2003; Ozcan et al., 2004; Li et al., 2007; Yue et al., 2007). The adsorption of ionic dyes onto the clay materials is governed by the ion-exchange mechanism and is strongly pH-dependent. Under common conditions, the sorption capacities for basic (cationic) dyes are higher than those for acid (anionic) ones. The retention of 300 mg/g (monolayer capacity) of Basic Blue 9 onto bentonite was reported by Bagane and Guiza (2000).

Inorganic materials such as zeolites or clays allow a relative simple physical or chemical regeneration. Wang et al. (2006) compared a chemical treatment based on the Fenton oxidation with high temperature combustion as methods for the regeneration of zeolite-based sorbents loaded with basic dye (Methylene Blue). The high-temperature treatment was more effective for the regeneration of synthetic zeolites. For natural zeolites, on the other hand, both regeneration methods gave comparable results, but the original adsorption capacity was not fully recovered – only 60% of the capacity of the fresh sample was achieved.

The surface properties of clays (and less often also other inorganic sorbents) and thus they sorption ability may be altered effectively by modification with surfactants. So called organo-clays are synthesised by exchanging the inorganic cations in the structure of the clay mineral with large organic cations, typically with quaternary ammonium compounds. In this way, Wibulswas (2004) modified the properties of montmorillonite with tetramethylammonium chloride, tetradecytrimethylammonium bromide, hexadecyltrimethylammonium bromide and benzyldimethylhexadecylammonium chloride, and tested the sorption ability of the prepared sorbents for Methylene Blue. The treatment with surfactants converts the clay surface from organophobic to organophilic in dependence on a number of carbon atoms in the chain of the surfactant molecule. Sepiolite modified with quaternary amines exhibited a high sorption capacity for reactive dyes (Everzol Black B, Everzol Red 3BS, Everzol Yellow 3RS), on contrary to unmodified sepiolite that was almost ineffective (Armagan et al., 2003). A mechanism involving electrostatic attraction of the anionic groups of dye molecules onto the oppositely charged amine-modified sepiolite surface was proposed to be responsible for the uptake of dyes. Cetyltrimethylammonium-bentonite was used for removing an industrial dye Supranol Yellow 4GL from wastewater (Khenifi et al., 2007). The same dye was retained also on pillared clays in the presence of non-ionic surfactants (Bouberka et al., 2005). Several textile dyes were removed successfully from water using hexydecyltrimethylammonium-bentonite as sorbent (Ceyhan and Baybas, 2001). A clay mineral hectorite was modified with cetyldimethylbenzylammonium chloride and cetylpyridinium chloride and used for an adsorption of an anionic dye Reactive Orange 122 (Baskaralingam et al., 2007). Dodecyltrimethylammonium cation was used to prepare organophilic clays capable to retain Rhodamine 6G (Salleres et al., 2008). A thiol-functionalized clay was prepared by the covalent grafting of 3-mercaptopropyltrimethoxysilane onto the surface of a natural smectite clay mineral. A significant enhancement of the adsorption capacity towards Methylene Blue was observed with the clay bearing thiol groups in comparison with the unmodified one (Tonle et al., 2008). A composite clay-based sorbent was prepared by polymerization of acrylamide with 2-acrylamido-2-methyl-1propanesulfonic acid and bentonite and tested for the sorption of basic dyes, such as Lauths Violet (Kundakci et al., 2008). An enhanced hydrophobicity of the surface of bentonite was achieved by intercalation of cationic polyelectrolyte polyepichlorhydrin-dimethylamine into the clay structure (Yue et al., 2007), causing better properties for the sorption of Reactive Blue K-GL (Li et al., 2007). Quaternary ammonium cations (tetraethylammonium-, hexadecyltrimethylammonium-, benzyldimethyltetradecylammonium-) were used also for the modification of the surface properties of fly ashes (Banerjee et al., 2006). The surface modification enhanced considerably the sorption of anionic dyes. Activated carbon modified with cationic surfactant (cetylpyridinium chloride) exhibited a higher sorption capacity for Reactive Black 5 in comparison with the untreated carbon (Choi et al., 2008). Somewhat different strategy was suggested by Eren and Afsin (2008), who employed bentonite pre-treated with divalent metal cations (Ni^{2+}, Co^{2+}, Zn^{2+}) for an adsorption of the basic dye Crystal Violet.

Various *industrial by-products* and *solid wastes* can be advantageously used as alternative sorbents because of their low-cost and local availability. For example, carbon slurry from fertilizer plants and blast furnace slag from steel plants were converted into low-cost sorbents by Gupta et al. (2003) and used for the removal of basic dyes (Basic Red 9) from wastewaters. Ramakrishna and Viraraghavan (1997) tested various low-cost materials available in Canada (peat, steel plant slag, bentonite clay, fly ash) for the removal of acid as well as basic dyes and found the capacities comparable with activated carbon. Waste newspaper was used for the removal of Methylene Blue in a special arrangement utilizing sono-sorption (Entezari and Al-Hoseini, 2007).

Fly ash is a waste material from thermal power plants and numerous other combustion processes that is found in abundance in the world and can be used as a low-cost sorbent for the dye adsorption and destruction from wastewaters (Wang and Wu, 2006), as well as in other technologies for the water pollution control (Viraraghavan and Dronamraju, 1992). The coal fly ash consists typically of silica (SiO_2), alumina (Al_2O_3) and iron oxides, with varying amounts of carbon, calcium, magnesium and sulphur. Two general classes of fly ash are recognised for coal combustion: Class F normally produced from anthracite, bituminous or sub-bituminous coals and containing less than 7 % CaO, and Class C normally produced from lignite coals, containing more lime (5-30%). Fly ash has a hydrophilic surface and porous structure. Unburned carbon plays a significant role in retaining less polar compounds, but also of ionic dyes (Wang and Li, 2007), on the fly ash surface. It was shown that both acid as well as basic dyes can be removed effectively from aqueous solution using coal fly ashes as adsorbents (Janoš et al., 2003). The high lime fly ash was used for an adsorption of Reactive Black 5 (Eren and Acar, 2007). Kumar et al. (2005) have found a relatively low capacity (5.7 mg/g) for the sorption of Methylene Blue onto coal fly ash. Recently, Lin et al. (2008) demonstrated that a treatment of the fly ash with sulphuric acid increased its specific surface area and the sorption capacity for basic dyes. The adsorption capacities in the range of 135-180 mg/g were reported for the reactive dye Remazol Brilliant Blue, but significantly lower values were obtained for Remazol Red or Rifacion Yellow (Dizge et al., 2008). Bottom ash was also used as a sorbent for the removal of dyes, e.g. basic fuchsin (Gupta et al., 2008).

Highly effective sorbents were prepared from *peat* and *low-rank coals* – materials containing *humic substances* as an active constituent. Peat is a complex material containing lignin, cellulose, fulvic acids and humic acids as its major constituents. These compounds carry polar functional groups such as alcohols, aldehydes, carboxylic and phenolic groups, which are responsible for binding chemical pollutans of ionic nature. Because of the presence of non-polar moieties in the structure of humic substances (aliphatic chains, condensed aromatic rings), these componds are capable to retain also less polar pollutants to some extent. As pointed out by Nandi and Walker (1971), mineral constituents always present in the coal- and peat-based sorbents play a significant role in binding chemical pollutants, including synthetic dyes. Peat was used for the removal of basic as well as acid dyes from aqueous solutions (Poots et al., 1976a; Allen et al., 1989; Ho and McKay, 1998a; Ho and McKay, 1998b; Ho and McKay, 2003). Poots and McKay (1979) deduced from kinetic measurements that the basic dye adsorption is predominantly a chemisorption process involving exchange sorption reaction with the hydroxylic groups in humic and fulvic acids, lignin and cellulose, whereas the acid dye adsorption is probably a physical process, in which coulombic forces are involved.

Naturally occurring kind of weathered and oxidised young brown coal called oxihumolite was used for an adsorptive removal of basic (Methylene Blue, Malachite Green) as well as acid (Egacid Orange, Midlon Black) dyes from waters. The maximum sorption capacities ranged from 0.070 mmol/g (for Midlon Black) to 0.278 mmol/g (for Malachite Green) and did not differ significantly for basic and acid dyes (Janoš et al., 2005). Karaca et al. (2005) studied the adsorption of Methylene Blue onto lignite–water interface and concluded that the adsorption is governed by physical interactions. Both basic as well as acid dyes were adsorbed also on chemically treated (sulfonated) coal (Mittal and Venkobachar, 1993). More complex composite sorbent in the form of humate/polyacrylamide/clay hydrogel was used for the removal of Methylene Blue from aqueous solutions (Yi and Zhang, 2008).

Sawdust and related waste materials from *timber industry* as relatively abundant, easily available and inexpensive sorbents have been used to remove unwanted chemical substances from waters, including dyes, oils, toxic salts and heavy metals – see a review of Shukla et al. (2002). Several authors tested various kinds of wood-based sorbents, e.g. sawdust from walnut and cherry tree, oak or pitch-pine (Ferrero, 2007), beech sawdust (Batzias and Sidiras, 2007a), cedar sawdust (Hamdaoui, 2006), pine sawdust (Özacar and Sengil, 2005) or spruce wood shavings (Poots et al., 1976b; Poots and McKay, 1979; McKay and Poots, 1980) for the removal of both basic as well as acid dyes from aqueous solutions. A composite sorbent (clay-wood mixture) was also effective in the basic dye retention (Yeddou and Bensmaili, 2005).

Diverse cellulose-based waste materials originate in great amounts from *agroindustry* and many of them can be used as sorbents for synthetic dyes, e.g. banana and orange peels (Annadurai et al., 2002), kohlrabi peel (Gong et al., 2007), olive pomace (Banat et al., 2007), deoiled soya (Gupta et al., 2008), yellow passion fruit waste (Pavan et al., 2008), rice husk (Vadivelan and Kumar, 2005; Kumar and Sivanesan, 2007), palm kernel fibre (Ofomaja, 2007), cotton fibre (Saleem et al., 2007), hazelnut shell (Ferrero, 2007) or silkworm pupa (Noroozi et al., 2008).

To improve a sorption ability of cellulose-based materials towards various kinds of chemical pollutants, some more or less sophisticated pre-treatment procedures have been developed. The sorption of basic dyes onto beech sawdust was enhanced after the sorbent pre-treatment with calcium chloride solution (Batzias and Sidiras, 2004); a similar effect exhibited also other inorganic salts, such as NaCl, $MgCl_2$ and $ZnCl_2$ (Batzias and Sidiras, 2007b). Other simple procedures utilized to modify the properties of biosorbents include the treatment with mineral acids and bases or their salts – HCl, NaOH, Na_2CO_3 (Kumar and Bandyopadhyay, 2006), Na_2HPO_4 (Ajmal et al., 1996) or H_2SO_4 (Taty-Costodes et al., 2003). More advanced modification procedures may introduce new active sites on the sorbent surface and enhance in this way its sorption capacity. For example, the ethylenediamine modified rice hull was applied successfully to remove basic and reactive dyes as well as metal cations from waters (Ong et al., 2007).

In recent time, *biosorption* become very popular as a promising technique for the removal and recovery of various chemical species from waters and effluents. It was defined as a property of certain molecules (or types of biomass) to bind and concentrate selected ions or molecules from aqueous solutions. Biosorption is a passive binding process utilizing dead biomass (or some molecules or their active groups) as biosorbent, on contrary to *bioaccumulation* that is a more complex process based on an active metabolic transport in(to) living organisms (Volesky, 2007). Biosorption has been established as an effective method especially for the recovery of metal ions from wastewaters, effluents and industrial solutions (Volesky and Holan, 1995). In numerous works, however, its ability to remove also various problematic organic pollutants (dyes, phenolic compounds, pesticides) was demonstrated, as reviewed by Aksu (2005). Diverse metabolism-independent processes may be effective in the binding of chemical pollutants to biosorbents, such as physical and chemical adsorption, electrostatic interaction, ion-exchange, complexation/chelation and microprecipitation or surface precipitation. As follows from a detailed discussion in the review of Aksu (2005), the biosorption ability depends strongly on the kind of dye and sorbent, as well as on operational conditions (pH, in the first place). Rather high sorption capacities above 100 mg/g were achieved with activated sludge for the removal of basic dyes from wastewaters (Chu and Chen, 2002). Various kinds of the inactivated fungal biomass were used for the removal of different industrial textile dyes (Prigione et al., 2008). Methylene Blue was retained successfully on a marine biomass *Posidonia oceanica* (Ncibi et al., 2007) or on an acid-treated weed *Parthenium hysterophorus* (Lata et al., 2007), whereas another basic dye – Basic Yellow – was retained on a green macroalga *Caulerpa scalpelliformis* (Aravindhan et al., 2007). A green macroalga *Caulerpa lentillifera* was used for the removal of different basic dyes (Astazon Blue, Astazon Red, Methylene Blue) from aqueous solutions and its sorption capacity was higher than the capacity of activated carbon for the same dyes (Marungrueng and Pavasant, 2007). Dried *Penicillium restrictum* biomass exhibited a sufficient sorption capacity close to 100 mg/g (at 20 °C) for the dye Reactive Black 5 (Iscen et al., 2007), which is comparable with the capacity of the NaOH pre-treated fungal biomass *Aspergillus foetidus* for the same dye (Patal and Suresh, 2008). The direct azodye Direct Brown was removed from aqueous solution by sorption onto the algal biosorbent *Spirogyra I02* (Mohan et al., 2008).

Mechanical, chemical and other pre-treatment procedures may improve sorption properties of various natural materials including biosorbents. Different procedures, such as milling and steam, ammonia or alkali steeping, were used to delignify the sorbent, or to increase its surface area (Robinson et al., 2002). The milling was identified as a cost effective procedure improving the dye removal efficiency. The brown seaweed *Laminaria* sp. biomass exhibited a considerably increased sorption capacity for Reactive Black 5 after an acid treatment with 0.1 M HCl (Vijayaraghavan and Yun, 2008). Nevertheless, the acid-treated sorbent (water hyacinth) was effective also in the removal of basic dye, namely Methylene Blue (El-Khaiary, 2007). A cationic sorbent was prepared by esterification of soybean hull by phosphoric acid with urea as catalyst, and used for the sorption of basic dyes Acridine Orange and Malachite Green (Gong et al., 2008). Methods for the preparation of adsorbents by the chemical modification of plant wastes were reviewed recently by Ngah and Hanafiah (2008).

During the past decade, a great attention has been paid to the development of new materials with unusual physical and chemical properties. *Nanosorbents* or *magnetic ion-exchangers* can serve as examples of advanced materials utilizable also in wastewater treatment for the recovery of both inorganic as well as organic pollutants (Türker, 2007). One of the most important properties on nanomaterials is that a majority of atoms are on the surface of the nanoparticle. The surface atoms are unsaturated, and therefore, they have a high chemical activity and adsorption ability. Magnetic or magnetizable (nano)sorbents allow to develop new and more advantageous separation strategies employing modern magnetic technologies and highly effective permanent magnet systems (Borai et al., 2007). The magnetic nanosorbents are based typically on Fe_3O_4 (magnetite) nanoparticles prepared by co-precipitation of Fe^{2+} and Fe^{3+} ions under controlled conditions (Liao and Chen, 2002). It was also shown that some low-cost waste effluents (e.g. acid mine drainage) can be used as starting materials for the preparation of magnetite nanoparticles (Wei and Viadero, 2007). A magnetic MnO-Fe_2O_3 composite was used as a novel material for an adsorptive removal of the azodye Acid Red B from water with an adsorption capacity of 105 mg/g (Wu et al., 2005). The iron oxide magnetic nanoparticles are often used in the form of composites – polyacrylic acid-bound magnetic nanparticles were used for an adsorption of Methylene Blue (Mak and Chen, 2004), similarly to the Fe_3O_4-activated carbon nanocomposite (Yang et al., 2008). Both basic (Methylene Blue) as well as acid (Methyl Orange) dyes were removed from waters with the aid of magnetic alginate beads; the nanosorbent combined the adsorption properties of activated carbon with magnetic properties of iron oxide nanoparticles (Rocher et al., 2008).

It should be noted that some traditional and naturally occurring materials may be classified as nanosorbents, too, e.g. clay minerals. Adsorption properties of the clay-based nanosorbents (raw clays, activated clays, organoclays) for the adsorption of dyes were reviewed by Liu and Zhang (2007). Chitosan in the form of nanoparticles with particle sizes of 180 nm was used as an adsorbent for the dye Acid Green 27 (Hu et al., 2006), whereas a chitosan/montmorillonite nanocomposite was used for an adsorption of Congo Red (Wang and Wang, 2007).

As can be seen from the above presented overview, there is a great amount of various non-conventional sorbents utilizable potentially for the removal of synthetic dyes from wastewaters. Because of an enormous diversity of the sorbents on one side, and a complex nature of the dye-containing effluents on the other side, it is very difficult to establish generally applicable criteria for the selection of the best sorbent for a given purpose. Naturally, the price of the sorbent will be always one of the main parameters that should be considered. Unfortunately, reliable and mutually comparable prices of the alternative sorbents mentioned in this article are mostly unavailable. Market prices of some non-conventional sorbents can be found in the review of Babel and Kurniawan (2003). In addition to the sorbent purchase costs, many other economical aspects should be considered, such as transportation costs, costs for the sorbent pretreatment, costs for its regeneration or costs for damping/disposal of the spent sorbent, etc. The technical aspects that should be taken into account include, among others: an availability of the sorbent in a sufficient amount and a stable quality, its physico-mechanical properties and homogeneity, chemical stability under desired conditions (working range), durability during the sorption process, possibility to regenerate the spent sorbent, selectivity and/or a resistance against the presence of substances accompanying the dyes, etc.

Table 2. Methylene Blue sorption capacities on various sorbents

Sorbent	Capacity (mg/g)	Experimental conditions	Reference
Steam activated bituminous coal	580		El Quada et al., 2006
Activated carbon from rattan sawdust	294		Hameed et al., 2007
Fly ash	6.4		Wang et al., 2005
Natural zeolite	16		Wang et al., 2005
Diatomaceous silica	127	30 °C	Al-Qodah et al., 2007
Spent activated clay	109	45 °C	Weng and Pan, 2007
Coal fly ash	6.05	22 °C	Janoš et al., 2003
Low-rank coal	21.3	22 °C	Janoš et al., 2005
Fe(III)/Cr(III) hydroxide	22.8		Namasivayam and Sumithra, 2005
Montmorillonite	323		Wibulswas, 2004
Palm kernef fibre	672	24 °C, pH 5	Ofomaja, 2007
Cedar sawdust	142	20 °C	Hamadaoui, 2006
Crushed brick	97	20 °C	Hamadaoui, 2006
Fallen tree’s leaves	81	22 °C, pH 4.5-10	Han et al., 2007
Mango seed kernel powder	143	30 °C	Kumar and Kumaran, 2005
Cereal chaff	20.3	25 °C	Han et al., 2006
Paper sludge	35.2		Hojamberdiev et al., 2008
Yellow passion fruit waste	44.7	25 °C	Pavan et al., 2008
Rice husk	44.6	32 °C	Vadivelan and Kumar, 2005
Pomelo peel(*Citrus grandis*)	345	30 °C	Hameed et al., 2008
Lemon peel	29		Kumar and Porkodi, 2006
Marine seaweed (*Caulerpa racemosa*)	5.23	18 °C	Cengiz and Cavas, 2008
Guava leaf powder(*Psidium guajava*)	295		Ponnusami et al., 2008
Pospalum notatum	31		Kumar and Porkodi, 2007
Green macroalga (*Caulerpa lentillifera*)	417		Marungrueng and Pavasant, 2007
Dead *Streptomyces rimosus*	34.3	20 °C	Nacera and Aicha, 2006
Immobilized *Corynebacterium glutamicum*	339	25 °C, pH 8	Vijayaraghavan et al., 2008

Probably the most important operational parameter for the selection of the sorbent is its capacity. Again, a direct comparison of the published values is somewhat questionable, as the measurements were often carried out under laboratory conditions (not always fully specified), and usually with pure (single-component) aqueous solutions of the examined dye. Moreover, only a limited number of data are typically available for any particular dye. Methylene Blue represents one of the exceptions, as it is probably the most frequently examined dye in adsorption studies and data on its adsorption behaviour on various sorbents are readily available. It may be considered a typical representative of basic dyes. In Table 2, the sorption capacities for the sorption of Methylene Blue on selected sorbents are listed. Acid Orange 7, on the other hand, was selected as representative of acid dyes; the sorption capacities are listed in Table 3.

Table 3. Acid Orange 7 sorption capacities on various sorbents

Sorbent	Capacity (mg/g)	Experimental conditions	Reference
Activated carbon	0.40	25 °C, pH 5.8	Aber et al., 2007
Cross-linked chitosan	1940	30 °C, pH 4	Chiou et al., 2004
Coal fly ash	83	22 °C	Janoš et al., 2003
Low-rank coal	49	22 °C	Janoš et al., 2005
Spent brewery grains	30.5	30 °C	Silva et al., 2004
Macro alga *Azolla filiculoides*	110	pH 3	Padmesh et al., 2005
Macro alga *Azolla rongpong*	72.5	30 °C, pH 3	Padmesh et al., 2006

For an effective design of the adsorption unit, data on adsorption kinetics are necessary. It is also desirable to estimate the equilibrium characteristics (parameters of adsorption isotherms) and to take into account the operational parameters that may affect potentially the dye sorption, such as pH, the presence of inorganic salts, surfactants, or other side equilibria in aqueous phase. These items will be discussed in the following paragraphs.

3. MECHANISMS AND KINETICS OF THE DYE REMOVAL

Adsorption of the dye molecules on the surface of non-conventional sorbents, typically highly heterogeneous by its nature, is a rather complicated process, in which various mechanisms may be effective. Because of an ionic nature of the dye species in aqueous solutions, electrostatic forces – attraction or repulsion between the dye species and ionised active groups on the sorbent surface – play an important role. Both chemisorption as well as ion-exchange and other physical phenomena will participate in the dyes sorption process, but their proportions and significance may differ for different dyes and different kinds of sorbents (Poots and McKay, 1979; Mohan et al., 2008). Carboxylic and hydroxylic functional groups are commonly present in the structure of most natural sorbents. These groups undergo dissociation at suitable pH values, forming negatively charged sites on the sorbent surface, which facilitates the retention of cationic (basic) dyes. On the other hand, some popular sorbents, e.g. chitosan, contain aminogroups that may be protonated in acidic medium, which increase their positive charge, and thus their ability to bind anionic (acid) dyes (Morais et al., 2007). A significance of various functional groups in the process of the dye sorption was demonstrated by Gong et al. (2005), who used various chemical treatments (methylation, esterification, acetylation) to modify the sorption ability of biosorbent (peanut hull). Synthetic dyes, as relatively large organic molecules containing usually several aromatic rings, may also exhibit a certain affinity towards less polar (organophilic) moieties that may be present in the structure of the non-conventional sorbents. Therefore, this kind of non-specific interactions should be also considered.

The dye sorption is usually a quite rapid process, in which most of the dye is retained in a time scale of a few hours or even (tens of) minutes, rather than days (McKay and Poots, 1980; Ho and McKay, 1998a,b; Eren and Acar, 2007; El-Khaiary, 2007; Marungrueng and Pavasant, 2007). To express the sorption kinetics in a mathematic form, two models are applied most often - a pseudo-first order model and a pseudo-second order model. These models are commonly used to describe the sorption of dyes as well as other pollutants (heavy metals) on solid sorbents, although, as pointed out by Ho and McKay (1998a), an application of a single kinetic model to the sorption on solid sorbents may be questionable because of a heterogeneity of the sorbent surfaces and diversity of sorption phenomena (transport, surface reactions). Recently, Azizian (2004) showed that the pseudo-first order kinetic model is more suitable for lower concentrations of solute, whereas the pseudo-second order model is more appropriate at high solute concentrations. A detailed discussion on applicability of these models for adsorption systems can be found in a review of Ho (2006).

The pseudo-first order (Lagergren) kinetic equation may be written in the form of

$$q_t = q_e \left(1 - e^{-k_1 t}\right) \tag{1}$$

whereas the pseudo-second order equation may be expressed as follows:

$$q_t = \frac{k_2\, q_e^2\, t}{1 + k_2\, q_e\, t} \tag{2}$$

q_e and q_t are amounts of the dye adsorbed per unit mass of the sorbent at equilibrium time and time t, respectively, k_1 and k_2 are the first- and second-order kinetic constants, respectively. Eqs. (1) and (2) are presented usually in their linearized forms (Ho, 2006).

The sorptive removal of dye from aqueous solution involves several mass transfer processes in liquid phase and at the solid-liquid interface. The sorption process consists of four consecutive steps (Vadivelan and Kumar, 2005; Ofomaja, 2007):

- Transport of the solute from the bulk solution.
- Diffusion across the liquid film surrounding the sorbent particle.
- Solute diffusion in the pores of the sorbent.
- Sorption of the solute onto the interior surface of the pores.

The overall rate of sorption is controlled by the slowest step. It is usually assumed that the last step (sorption on the internal surface) is rapid enough and may be neglected. The rate-limiting step will involve diffusion mechanisms – either film diffusion or particle diffusion. In diffusion studies, the rate can be expressed in terms of the square root time. The mathematical dependence of q_t vs. $t^{0.5}$ is obtained if the sorption process is considered to be influenced by diffusion in the spherical particles and convective diffusion in the solution (Allen et al., 1989; Ho and McKay, 1998). The root time dependence, known also as a Weber-Morris plot (Weber and Morris, 1963), may be expressed by the following equation:

$$q_t = k_{ID} t^{0.5} \tag{3}$$

where k_{ID} is a diffusion rate parameter. Eq. (3) is reported as an intraparticle diffusion model in literature (Vadivelan and Kumar, 2005; Janoš and Smidova, 2005; Ofomaja, 2007; Porkodi and Kumar, 2007) suggesting that the sorption process is considered to be controlled by the internal diffusion with a possible contribution of the external diffusion. The square-root plots for the dye sorption consist typically of two (or even more) separate linear parts with different slopes. This multilinearity is interpreted as a proof that the intraparticle diffusion is not solely the rate-limiting step and that the external mass transfer is also significant for the sorption process (Vadivelan and Kumar, 2005; Ofomaja, 2007). The intercept of the second part of the square-root plot is related to the boundary layer thickness – the contribution of the external surface sorption (Kumar et al., 2005). Marungrueng and Pavasant (2007), for example, deduced from the intraparticle diffusion plot that the sorption of basic dyes on the macroalga biosorbent and activated carbon is initially controlled by both film and pore diffusion, whereas only pore diffusion is the rate-limiting step at the later stage. The external mass transfer was identified as the rate limiting step at the beginning of the adsorption of Methylene Blue on the water hyacinth (El-Khaiary, 2007), and the intraparticle diffusion at the later stage. Both the external mass transfer and the intraparticle diffusion had rate-limiting effects during the sorption of reactive dyes onto fly ash (Dizge et al., 2008).

4. SORPTION EQUILIBRIA AND PARAMETERS AFFECTING THE DYE SORPTION

During the sorption process, solute is transferred from solution to the surface of the solid phase, where its concentration increases until a dynamic equilibrium is reached. At the equilibrium, there is a defined distribution of solute between the liquid and solid phases. The solute distribution function – adsorption isotherm – may be written in various forms. Probably the most commonly used equation is the Langmuir isotherm that can be easily derived from a "law of surface action" (similar to the "law of mass action") (Langmuir, 1916):

$$q_e = \frac{q_m K c_e}{1 + K c_e} \tag{4}$$

q_e is the adsorbed amount of the dye, c_e is the equilibrium concentration of the dye in the solution, K and q_m are parameters on the Langmuir isotherm. The Langmuir isotherm presupposes a homogeneous nature of the sorbent surface (equivalence of the binding sites) and a non-cooperative behaviour during the sorption (monolayer adsorption). As evident, the dye sorptions on non-conventional sorbents will seldom satisfy these conditions.

The empirical Freundlich isotherm is another popular equation utilized to describe the sorption equilibria:

$$q_e = K_F\, c_e^n \tag{5}$$

K_F and n are parameters of the Freundlich isotherm.

Although commonly used, the Langmuir and Freundlich isotherms do not express well the sorption behaviour of solutes in real systems, especially when non-conventional sorbents are used, highly heterogeneous by their nature. Many other isotherm equations were introduced – a general classification of the solute adsorption isotherms was given by Giles et al. (1974), a brief overview of the isotherm equations can be found in the paper of Kinniburgh (1986). The Langmuir-Freundlich isotherm is frequently used to describe the sorption processes in environmental chemistry:

$$q_e = \frac{q_m\, K\, c_e^m}{1 + K\, c_e^m} \tag{6}$$

q_m, K and m are parameters of the isotherm, again. q_m is a maximum sorption capacity under given conditions, m is called usually as a “heterogeneity parameter” (Kinniburgh, 1986) reflecting various kinds of a non-ideal behaviour that may occur during the sorption on heterogeneous surfaces (Koopal et al., 1994). The sorption equilibria on the heterogeneous surface can be treated also with the aid of generalized multi-site Langmuir (or Langmuir-Freundlich) isotherms; this approach taking into account several kinds of the active sites on the surface of the sorbent corresponds to the original Langmuir’s concept of “more than one kind of elementary space” (Langmuir, 1918). The multi-site Langmuir isotherm can be written in the form:

$$q_e = \sum_{i=1}^{n} \frac{q_{m,i}\, K_i\, c_e}{1 + K_i\, c_e} \tag{7}$$

In most cases, the two-site models gave a satisfactory fit to experimental data and no significant improvement was achieved when the three-site or even more complex models were used. It was shown that the two-site Langmuir equation can fit any convex sorption data that tend to a maximum asymptotically (Hinz, 2001).

The concentration of solute (dye) in the sorbent (q_e) depends not only on the solute concentration in solution (as predicted from the simple sorption isotherms presented above), but also on some parameters that may influence potentially the sorption equilibria. pH is probably the most important parameter affecting the sorption of ionic species. In general, both the dye molecules as well as the active sites on the sorbent surface may undergo dissociation/protonation in dependence on the pH value. With increasing pH, the acidic functional groups of the sorbent (e.g. carboxylic or hydroxylic) dissociate and the sorbent surface becomes negatively charged, which facilitate the sorption of cationic (basic) dyes. See, for example, the pH dependencies for the sorption of Methylene Blue on fly ash (Janoš et al., 2003), on dead macrofungi (Maurya et al., 2006), on palm kernel fibre (Ofomaja, 2007) or on fruit waste (Pavan et al., 2008). The opposite is true for the sorption of anionic (acid) dyes (Maurya et al., 2006; Wang and Li, 2007). A point of zero charge is an important parameter characterizing the surface properties of the sorbent (Ofomaja, 2007; Al-Degs et al., 2008). The dissociation of the dye molecules, on the other hand, plays probably less important role in affecting the sorption equilibria; note that the dye molecules contain often strongly acidic or basic groups (e.g. sulfonic), which degree of dissociation remains virtually unchanged over a wide pH range.

Apart from the dyes, wastewaters from dye-processing or textile finishing industries contain large amounts of dissolved substances, especially of inorganic salts that may potentially affect an effectiveness of the dye removal. An effect of the salt concentration on the dye sorption was studied in several works. Only a very slight decrease of the dye uptake with increasing concentration of NaCl was observed by Maurya et al. (2006) for the biosorption of Methylene Blue onto macro fungus-based sorbent. Possibly, the dye cation compete with inorganic cations for the binding sites on the sorbent surface. The sorption of both basic as well as acid dyes onto fly ash was not affected by the presence of inorganic salts (NaCl, $CaCl_2$) at concentrations exceeding several times the concentrations of the dyes (Janoš et al., 2003). Ozmen et al. (2008) observed a certain increase in the azodye sorption onto starch-based polymers in the presence of inorganic salts (NaCl) and explained this phenomenon as a result of the charge reduction on the sorbent surface. Similarly, the sorption of reactive (acid) dyes on activated carbon increased (but not dramatically) in the presence of NaCl (0.1 – 0.5 mol/l) (Al-Degs et al., 2008). It could be concluded that inorganic salts do not hamper in the sorption of either basic or acid dyes on the non-conventional sorbents even at high concentrations, which is important for potential practical applications.

Surfactants (especially anionic ones) are typically present in real wastewaters. Therefore, an effect of their presence on the dye sorption was also examined (Janoš et al., 2003; Janoš et al. 2005). It may be generalized that the sorption of ionic dyes is not affected significantly by the presence of the non-ionic surfactants. An increase in the sorption efficiency may occur in the presence of oppositely charged surfactants as a result of the formation of ion pairs or even more complex sub-micellar aggregates that cause an adsolubilization of the dye molecules on the sorbent surface. The surfactants bearing the same charge as the dye ion, on the other hand, exhibit usually a minor effect on the dye sorption, or they decrease the dye sorption to some extent as a result of a competition for the same binding sites on the sorbent. Similar trends were found by Talman and Atun (2006) for the sorption of Toluidine Blue (cationic dye) on fly ash or by Banerjee et al. (2006) for the sorption of anionic dyes in the presence of quaternary ammonium salts. More detailed discussion of the effects of surfactants on the dye sorption can be found in our previous works (Janoš, 2003; Janoš and Šmídová, 2005). It is important to note that surfactants exhibit usually only minor effects on the dye sorption on the non-conventional sorbents and thus do not impede their application in the wastewater treatment.

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Chapter 8

IRRADIATION TREATMENT OF AZO DYES IN AQUEOUS SOLUTION

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ABSTRACT

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.

Keywords: azo dyes, decoloration, mineralization, wastewater, EB irradiation treatment, dose requirement, decomposition, mechanism, pulse radiolysis, kinetics

1. INTRODUCTION

Advances to molecular design of azo dyes have improved their photostability and stability toward aerobic degradation or common oxidants, for these reasons the removal of azo dyes from wastewaters is extremely difficult. Effluents of textile dying and finishing industries are known to have considerable color, suspended solids, chlorinated organic molecules, surfactants, some heavy metals and to have variable pH, temperature and Chemical Oxygen Demand (COD). Especially reactive azo dyes cause special environmental concern: their precursors and their degradation products, such as aromatic amines, are considered highly carcinogenic. Consequently, dyes have to be removed from industrial wastewater before discharging. However, even with carefully selected microorganism and under favorable conditions their biodegradation is limited and takes long time. Moreover, conventional chemical methods are not efficient enough for the degradation of azo dyes. Due to these difficulties, the dye containing effluents coming from textile factories are treated by absorption onto activated carbon or by chemical coagulation. These conventional techniques mainly transfer the contaminants from wastewater to solid wastes. Therefore one of the major areas of interest in dye chemistry is to look for new efficient ways for disposal and treatment of azo dye containing wastewater by new oxidation/reduction processes [1-4]. Such processes can be initiated by highly oxidizing radicals (Advanced Oxidation Processes, AOP) that are produced for instance in photo Fenton reaction (UV light induced decomposition of H_2O_2 to produce $^{\bullet}OH$ radicals), photocatalytic reaction with suspended semiconductor such as TiO_2 (yielding also $^{\bullet}OH$ radicals) or in ionizing radiation induced decomposition of water. In the latter, in addition to the highly oxidizing $^{\bullet}OH$ radicals, highly reducing radicals, hydrated electrons (e_{aq}^{-}) and hydrogen atoms ($H^{\bullet}$) may also play role in dye degradation.

Radiation processing is often used in industry to produce a wide range of products [5-7]. Use of radiolysis in the environmental remediation of wastewater, contaminated soil and sediment is a promising treatment technology; the chemistry behind these technologies is under extensive investigation. Together with the removal of target chemical contaminant, one should also concern the elimination of a series of intermediates of progressively higher oxygen-to-carbon ratios that are involved in the conversion of an organic molecule to CO_2. Therefore, it is essential to improve substantially our basic understanding of the radiation chemistry of dye molecules (reactions, pathways, and rates) in various systems. The radiolytic reactions with respect to dye decomposition have been intensively studied during the last 10 years [8,9] and the research has lead to pilot-plant experiments, and finally also to full-scale realization.

In the present book chapter we summarize the results of scientific investigations, show the industrial realization and the advantages of the technique. Although we mainly refer to radiolysis results, the undergoing processes, the reaction mechanisms are also relevant to other AOP.

2. RADIOLYSIS OF WATER AND AQUEOUS SOLUTIONS

2.1. Primary Intermediate Formation in Oxygen-free System

In the radiolysis of water the transients and products are e_{aq}^{-}, H_3O^{+}, $H^{\bullet}$, ${}^{\bullet}OH$, H_2, and H_2O_2 (Reaction (1)). Since all the transients and products originate from water molecules, at any time the total number of H atoms in the transients and products should be twice the number of O atoms, and also, the total charge of the transients and products considered should be zero [5-7,10].

$$H_2O \rightsquigarrow e_{aq}^{-},\ H_3O^{+},\ H^{\bullet},\ {}^{\bullet}OH,\ H_2, \text{ and } H_2O_2. \tag{1}$$

The yields of species formed are as follows: 2.7, 2.7, 0.6, 2.7, 0.45, and 0.75 species/100 eV absorbed radiation energy (*G*-value). The traditional (so-called atomic) species/100 eV units can be transformed to SI units of $\mu mol\ J^{-1}$ by multiplying with factor of 0.1036.

The so-called water radicals, hydrated electron (synonymous with aqueous electron), hydrogen atom, and hydroxyl radical formed in water radiolysis are extremely reactive and in the absence of other reaction partners, in ultra pure water they disappear in very fast self-termination reactions. In the presence of proper solutes in the solution, e.g. dye molecules, they readily react with these compounds.

All the water radicals form simultaneously complicating the investigation of their individual reaction steps. By combining appropriately selected experimental conditions there are possibilities to reduce the kinds of primary reacting radicals, and therefore to obtain some information about the mechanism of undergoing reactions, or at least about the main possible reaction pathways [5-7,10].

The reactions of e_{aq}^{-} are generally studied in deoxygenated (N_2 or Ar bubbled) solutions above pH 3 and in the presence of 0.2 – 1 mol dm^{-3} *tert*-butanol. *Tert*-butanol converts the highly reactive ${}^{\bullet}OH$ radicals to less reactive ${}^{\bullet}CH_2(CH_3)_2COH$ radicals in Reaction (2). In such systems there is a small contribution from the $H^{\bullet}$ atom reactions.

Reactions of $H^{\bullet}$ atoms are usually investigated in N_2 or Ar saturated solutions containing 0.2 – 1 mol dm^{-3} *tert*-butanol below pH 2. In such solutions e_{aq}^{-} is converted to $H^{\bullet}$ atom in Reaction (3). The reaction between $H^{\bullet}$ and *tert*-butanol is slow: $H^{\bullet} + (CH_3)_3COH \rightarrow {}^{\bullet}CH_2(CH_3)_2COH + H_2$ ($k = 1\times10^{6}\ mol^{-1}\ dm^{3}\ s^{-1}$) [12]. In the systems used for studying e_{aq}^{-} and $H^{\bullet}$ reactions the relatively unreactive radicals formed from *tert*-butanol are also present, these radicals do not react with dye molecules.

Reactions of ${}^{\bullet}OH$ radicals are investigated in N_2O saturated solution in the 3 – 11 pH range. In such solution e_{aq}^{-} is converted to ${}^{\bullet}OH$ in Reaction (4). (At saturation the N_2O concentration is 0.025 mol dm^{-3} at room temperature.) There is a small (~10%) contribution from the $H^\bullet$ atom reactions. In highly alkaline solutions $^\bullet OH$ transforms to O^- with an acid dissociation constant of 11.9 (Reaction (5)). O^- is generally less reactive than $^\bullet OH$.

$$^\bullet OH + (CH_3)_3COH \rightarrow {}^\bullet CH_2(CH_3)_2COH + H_2O \quad k = 6\times10^8\ mol^{-1}\ dm^3\ s^{-1} \tag{2}$$

$$e_{aq}^- + H_3O^+ \rightarrow H^\bullet + H_2O \quad k = 2.3\times10^{10}\ mol^{-1}\ dm^3\ s^{-1} \tag{3}$$

$$e_{aq}^- + N_2O + H_2O \rightarrow {}^\bullet OH + OH^- + N_2 \quad k = 7\times10^9\ mol^{-1}\ dm^3\ s^{-1} \tag{4}$$

$$^\bullet OH + OH^- \leftrightarrow H_2O + O^- \quad pK_a = 11.9. \tag{5}$$

2.2. Solutions with Dissolved Oxygen

In practical systems oxygen is always present with a molar concentration of 0.25 mmol dm^{-3} at room temperature. It reacts with e_{aq}^- and $^\bullet H$ rapidly to form superoxide radical anion ($O_2^{-\bullet}$) or perhydroxyl radical ($HO_2^\bullet$) in reactions (6) and (7):

$$e_{aq}^- + O_2 \longrightarrow O_2^{-\bullet} \quad k = 1.9\times10^{10}\ mol^{-1}\ dm^3\ s^{-1} \tag{6}$$

$$H^\bullet + O_2 \longrightarrow HO_2^\bullet \quad k = 2.1\times10^{10}\ mol^{-1}\ dm^3\ s^{-1} \tag{7}$$

$$O_2^{-\bullet} + H_3O^+ \leftrightarrow HO_2^\bullet + H_2O \quad pK_a = 4.8. \tag{8}$$

There is an acid/base equilibrium (8) between the two species with a pK_a of 4.8. The $O_2^{-\bullet}/HO_2^\bullet$ pair has rather low reactivity and in the absence of proper reaction partners the species decay in self-termination reactions [6,11]:

$$O_2^{-\bullet} + HO_2^\bullet \longrightarrow HO_2^- + O_2 \quad k = 9\times10^7\ mol^{-1}\ dm^3\ s^{-1} \tag{9}$$

$$HO_2^- + H_3O^+ \longrightarrow H_2O_2 + H_2O \tag{10}$$

$$HO_2^\bullet + HO_2^\bullet \longrightarrow H_2O_2 + O_2 \quad k = 8\times10^5\ mol^{-1}\ dm^3\ s^{-1}. \tag{11}$$

The reaction between two $O_2^{-\bullet}$ radicals is extremely slow, $k < 3\times10^{-1}\ mol^{-1}\ dm^3\ s^{-1}$.

The hydrogen peroxide formed in water decomposition (Reaction (1)) and also in the reaction of two superoxide radical anion/perhydroxyl radicals, as we will show later, under certain conditions may play an important role in the degradation of dye molecules.

2.3. Scavenging Capacity

The reactive intermediates formed in water radiolysis may react with several different molecules in the solution. E.g. $^\bullet OH$ radical reacts with intact dye molecules, with transformed dye molecules, or with other molecules in the solutions, such as cellulose fragments, carbonate, transition metal ions. The ratios of the different reactions are determined by the scavenging capacities of the individual molecule types: scavenging capacity is defined as the product of the rate coefficient and the concentration for a given molecule type [11]. Proportion (P) of the reaction of a given water radical with the intact dye molecules is calculated as follows:

$$P = \frac{k_{Dye}[Dye]}{k_{Dye}[Dye] + \sum_i k_i [X_i]}. \tag{12}$$

In the equation the i summation goes for all types of molecules being in the solution, k_{Dye} [Dye] is the scavenging capacity of the dye, and $\sum_i k_i [X_i]$ is the scavenging capacity of the other molecules together.

2.4. Methods for the Investigation of the Reaction Mechanisms

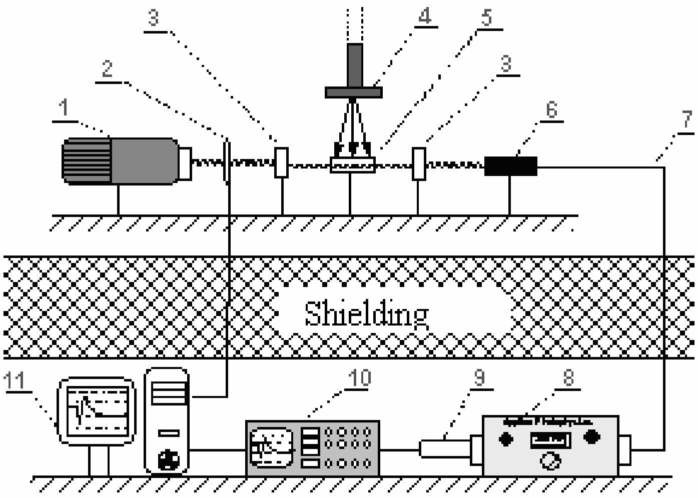
The degradation of high molecular mass dye compounds is rather complicated and for understanding the details of the processes highly sophisticated techniques are needed. By the application of fast intermediate observation techniques and new final product separation and identification techniques there was a great progress in understanding the degradation mechanism during the last decade [3].

2.4.1. Pulse Radiolysis

The *intermediates* of chemical changes in radiation chemistry are usually highly reactive and therefore their lifetimes are short: for their detection fast techniques are needed. In pulse radiolysis (Figure 1) an electron accelerator produces short pulses of electrons, accelerated to several MeV energy. The accelerated electrons are directed into a cell, which contains the sample to be irradiated. The chemical changes are induced by the energy absorbed when the short electron pulse hits the cell. In pulse radiolysis the time dependence of build-up and decay of intermediates and stable products are followed by their light absorption as illustrated by Figure 2, inset [13-15]. The method, also called kinetic spectrophotometry, or time resolved spectrophotometry, differs from the conventional spectrophotometric technique since it uses a single light path: the reference level is obtained as the light level passing the sample prior to irradiation. This is the basis for the high sensitivity of kinetic spectrophotometry: changes less than 1% in the transmitted light intensity are measured accurately. Averaging of a large number of traces is possible when using computerized data acquisition system. The second important difference as compared to the conventional spectrophotometry is the fast response time.

A schematic illustration of a pulse radiolysis setup is shown on Figure 1. In usual arrangements the measuring system is divided in two parts. The first part, including the light source for sample illumination, the lens system, the shutter preventing the heating and photolysis of the sample, light filters, and the measuring cell itself, is housed in the irradiation room. The measuring cell should be positioned in the beam so as to achieve an approximately homogeneous irradiation. The other parts of the setup are outside the radiation shielding concrete wall and the Faraday cage protecting against electromagnetic interference. These include monochromator, photodetector, oscilloscope/digitizer and computer system for data acquisition and processing. Light is usually transmitted from the irradiation room to the measuring room through a hole in the shielding by means of mirrors and lenses. Less frequently light guide cable is used.

By kinetic spectrophotometers the time-dependent absorbance (A) of the observed species is measured. According to the Lambert–Beer law:



1 – analyzing light source
2 – shutter
3 – lens
4 – electron beam
5 – cell
6 – light condenser
7 – light guide cable
8 – monochromator
9 – photodetector
10 – oscilloscope
11 – computer

Figure 1. Schematic representation of pulse radiolysis with kinetic spectroscopic detection.

$$A = \log\frac{I_0}{I} = \log\frac{100\%}{T} = \varepsilon_\lambda cd. \tag{13}$$

Where I_0 and I are the intensities of the incident and the transmitted light, respectively, T is the transmission in %, ε_λ is the linear molar absorption coefficient at wavelength λ, c is the concentration, and d is the optical path-length in the cell.

In dilute aqueous dye solutions basically the water absorbs most part of the energy and the intermediates formed in water radiolysis (e_{aq}^-, $^\bullet OH$ and $H^\bullet$) induce the chemical reactions. The reaction of these primary intermediates with dye molecules results in formation of secondary (dye) intermediates. The concentration of the intermediates is followed by detecting their light absorption. Kinetic curves taken at several wavelengths are used to compute the spectra of intermediates (Figure 2). The spectra are characteristic to the intermediates formed and any change either in the shape of the spectrum or in the wavelength of the maximum indicates modification in the chemical structure.

From the kinetic curves, usually taken at the maximum of the absorption spectrum on a short time scale (nanosecond or some microseconds), the rate coefficients of addition of the radiolysis intermediates of the solvent to solute molecules are obtained (decay of primary intermediates and formation of secondary (dye) intermediates). Based on long time scale measurements in the millisecond range, the rate coefficients of the disappearance of dye intermediates are calculated.

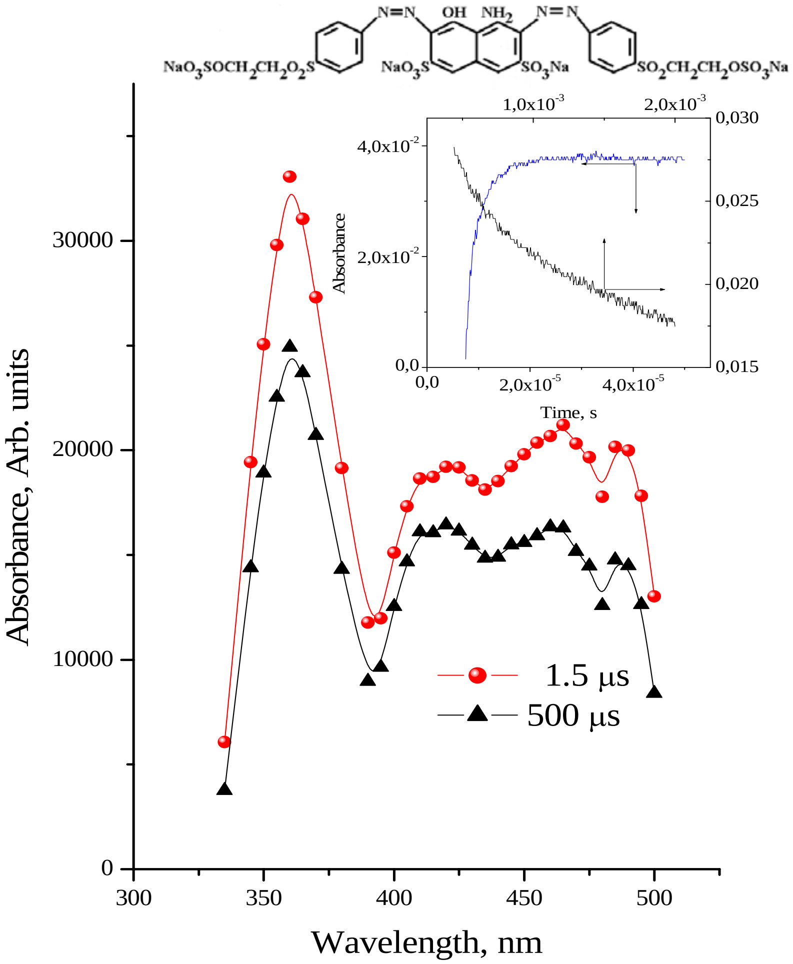


Figure 2. Typical absorption spectra of intermediates obtained in Reactive Black 5 (RB5) solution and typical absorbance build-up and decay profile (inset). (Both measured in the authors' laboratory.)

2.4.2. Steady State Techniques

In the field of environmental applications as irradiation sources mostly electron accelerators are used. These electron accelerators usually deliver 0.5-2 MeV electrons and have energy outputs up to several hundred kWs. However, experiments for research purposes are often carried out by gamma radiolysis, applying ^{60}Co radioactive sources emitting 1.19 and 1.33 MeV gamma photons.

The simplest method to follow the dye degradation caused by irradiation is UV-VIS spectroscopy (see e.g. Figure 3). In this case the degradation products are not separated from the starting compound [16-20]. When UV-VIS spectroscopy is used; the absorption spectrum of the starting dye and those of the products strongly overlap. Usually parallel several products form and their absorption spectra are not characteristic enough to allow identification.

For product separation gas chromatography (GC) or high performance liquid chromatography (HPLC) are used. The products are usually detected by standard techniques as flame ionization or absorbance [21-26]. Fourier-Transformed-Infrared spectroscopy (FTIR), Mass-Spectrometry (MS), and Nuclear-Magnetic-Resonance spectroscopy (NMR) are often useful in the identification of products.

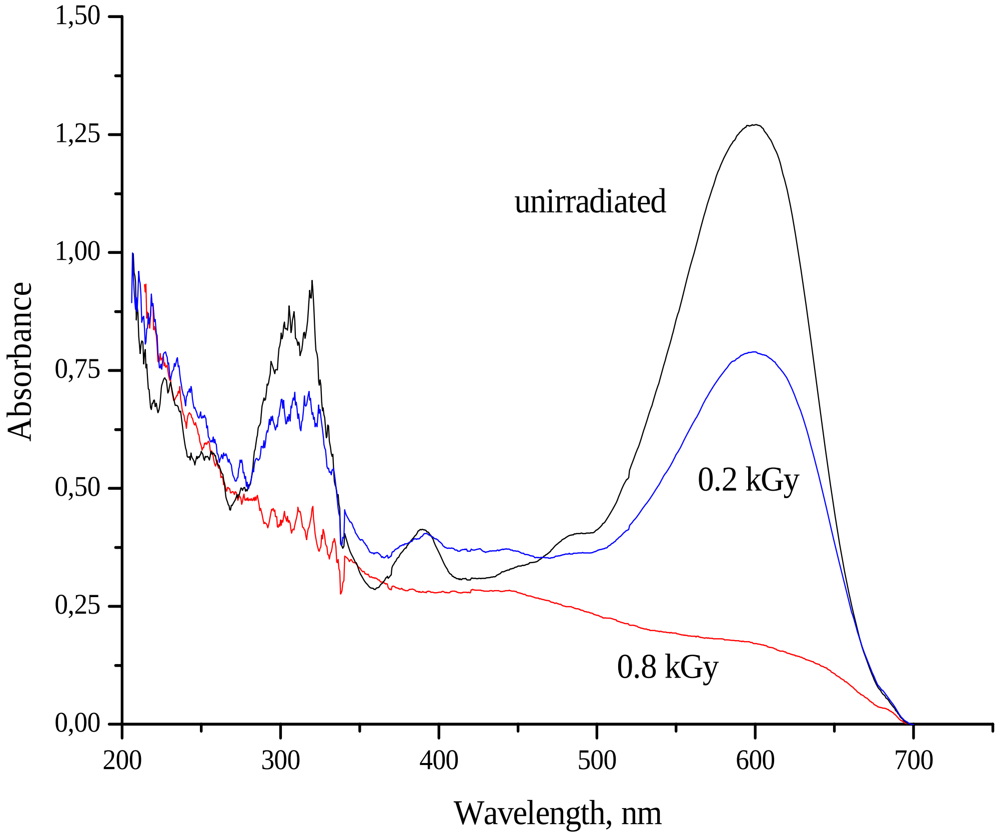


Figure 3. UV-VIS absorption spectrum of 5×10^{-5} mol dm^{-3} RB5 solution: unirradiated and irradiated with 0.2 and 0.8 kGy dose, air saturated. (Measured in the author’s laboratory.)

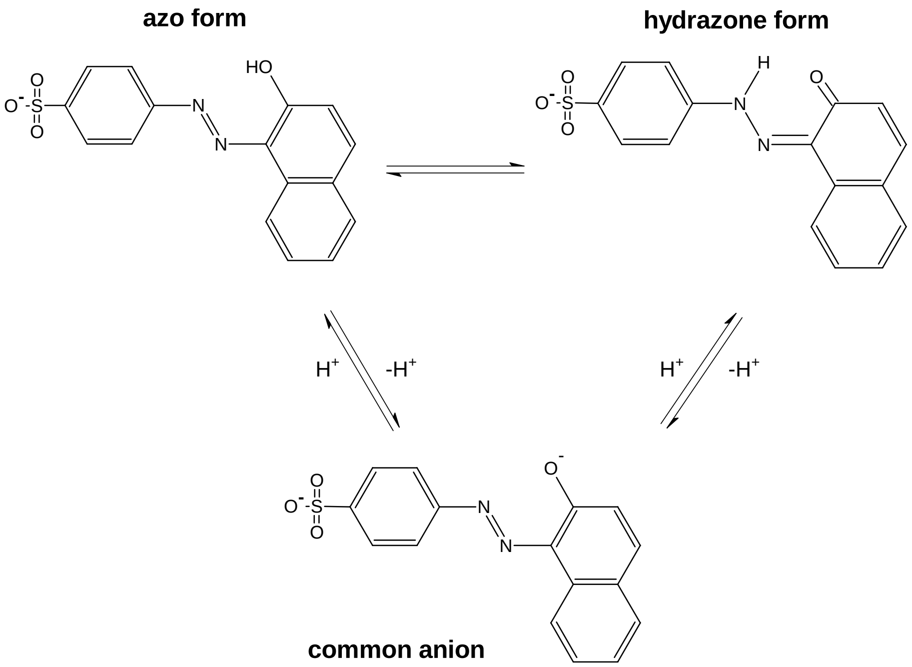


Figure 4. Azo-hydrazone tautomerism of AO7.

3. PREFERED SITES OF RADICAL ATTACK

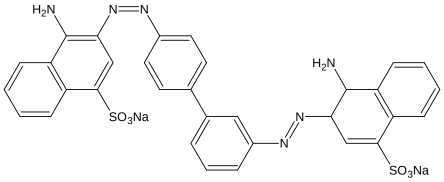
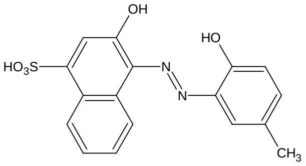
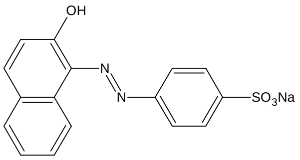
Since most of the azo dyes are high molecular mass structured molecules with several functional groups, it is usually difficult to determine the primary place of radical attack and the reaction mechanism. In this respect experiments with smaller molecular mass model compounds, like phenols, anilines, azobenzenes, H-acid or simpler dye molecules are of great help. Many experiments were carried out in order to identify the intermediates by pulse radiolysis technique. In order to observe the final products chemical separations were applied with simpler model compounds or simpler dye molecules. The authors of these works based on the transient absorption spectra and the final products formed tried to identify the preferential sites of radical attack. Theoretical calculations were also of great help during the identification [3].

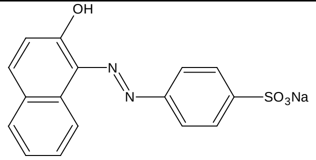
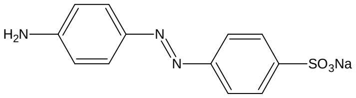
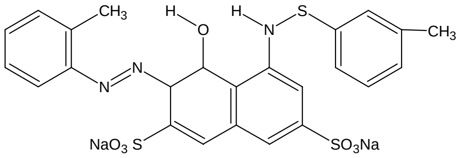
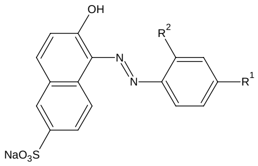
According to the frontier orbital theory, chemical reactions preferentially occur at the position of the molecule where their frontier orbital strongly overlap. Nucleophilic reactions (e_{aq}^-, $H^\bullet$) may occur at the atom where the electron density of the lowest unoccupied molecular orbital (LUMO) is the largest, whereas electrophilic reactions ($^\bullet OH$) may occur at the position where the density of the highest occupied molecular orbital (HOMO) is the largest [2].

3.1. Hydroxyl Radical

Hydroxyl radical ($^{\bullet}$OH) is a powerful oxidant that adds to unsaturated bonds with practically diffusion-controlled rate coefficient ($k \approx 10^{10}$ mol^{-1} dm^{3} s^{-1}, Table 1) and abstracts H atom from C-H bonds. The latter reaction is generally 1-3 orders of magnitude slower than the addition reaction; therefore abstraction reaction is unimportant from the point of view of primary radical attack. (However, abstraction reactions are more important in the mineralization process, when all of the aromatic rings have already degraded.) It is considered to be a strong electrophilic radical, therefore, it reacts preferably with molecule sites with higher electron density. Due to the high reactivity, the hydroxyl radical exhibits relatively little selectivity in radical addition reactions.

Table 1. Rate coefficients of $^{\bullet}$OH radical reactions with selected organic molecules and dyes

Molecule	Rate coefficient, k mol^{-1} dm^{3} s^{-1}
Benzene [10]	7.9×10^{9}
Toluene [10]	5.1×10^{9}
Phenol [28]	1.4×10^{10}
Aniline, pH basic [10]	8.6×10^{9}
N,*N'*-Dimethylaniline [10]	1.4×10^{10}
Azobenzene [10]	2.0×10^{10}
Naphthalene [10]	9.4×10^{9}
1-Aminonaphthalene-4-sulphonate ion [10]	7.9×10^{9}
p-phenylazoaniline (*p*-PPA) [30]	1.1×10^{10}
Congo Red (C.I. Direct Red 28) [31]  	1.2×10^{10}
Calgamite [32]  	1.1×10^{10}
Orange I [1]  	pH 4, 7×10^{9} pH 6.6, 9×10^{9} pH 10.5 1.1×10^{10}
Acid Orange 7 (AO7) [33]	4.08×10^{9}

	
Methyl Orange [32] 	$(2\pm0.3)\times10^{10}$
Acid Red 265 [34] 	$(9.3\pm1.4)\times10^9$
Arylazo-2-naphthol [35] $R^1=R^2=H$ $R^1=H, R^2=OCH_3$ $R^1=OCH_3, R^2=H$ $R^1=Cl, R^2=H$ $R^1=CH_3, R^2=H$ 	1.1×10^{10} 1.0×10^{10} 1.1×10^{10} 1.0×10^{10} 1.2×10^{10}

As probable site of $^\bullet$OH radical attack on dye molecules the following possibilities are considered: attack on the azo bridge or on the azo-linkage bearing carbon atom, attack on the rings, and in case of dyes with amino group, direct oxidation here.

Azobenzene reacts with a rate coefficient of $k = 2.0\times10^{10}$ dm^3 mol^{-1} s^{-1} with $^\bullet$OH radicals. About 40% of $^\bullet$OH add to the benzene ring producing a transient with absorption maximum at 330 nm (cyclohexadienyl type radical), and ~60% add to –N=N– double bond forming transient with maximum absorbance at 420 nm (hydrazyl type radical) [27].

Acid Orange 7 (AO7, synonymous with Orange) may be considered a simple, but typical dye in textile wastewaters. It is a phenylazonaphtol with azo and hydrazone forms. In aqueous solution the hydrazone form predominates (Figure 4). Being one of the simplest azo dyes, the radiolytic reactions of Acid Orange 7 were very often studied in dilute solutions by pulse and gamma radiolysis, spectrophotometry and HPLC separation techniques, and also by theoretical calculations. So there is ample possibility to compare analytical results with the results of theoretical calculations.

According to the electron densities of HOMO and LUMO calculated by Hihara et al. [36], the electrophilic attack by $^\bullet$OH radical should occur at the N atom bound to the benzene ring and at the C atom where the naphthalene ring and the azo group of AO7 link up. The electron densities of HOMO at the two positions are similar. The quantum chemical molecular orbital calculations of Özen et al. [37] using density functional theory are more or less in agreement with that of Hihara et al. [36,38]. The oxidative degradation is proposed to occur through cleavage of N=N bond, following the $^\bullet$OH radical addition to the chromophore. The presence of hydrazone tautomers might be responsible for the involvement of C–N cleavage in the degradation of azo dyes.

Spadaro and co-workers [39] used Fenton's $^\bullet$OH radicals to investigate the decomposition of simple azo dye model compounds. They presented evidence for the generation of benzene and substituted benzenes from $^\bullet$OH radicals induced decomposition of azo dyes with phenylazo substitution. They suggested a mechanism in which $^\bullet$OH adds to the azo linkage-bearing carbon atom (C-4) of hydroxyl or amine substituted ring (Figure 5). The resulting $^\bullet$OH adduct breaks down to produce phenyldiazene (Ph–N=NH) or substituted phenyldiazene and phenoxyl radical (PhO$^\bullet$). Phenyldiazene is extremely unstable, $^\bullet$OH, or O_2 can readily transform it by one electron oxidation to yield phenyldiazene radical. The latter intermediate is also unstable and cleaves homolytically to generate phenyl radical and N_2. Phenyl radical transform to benzene by H atom abstraction, e.g. from $HO_2^\bullet$. The phenoxyl radical may stabilize in bimolecular self-termination reactions (Figure 5).

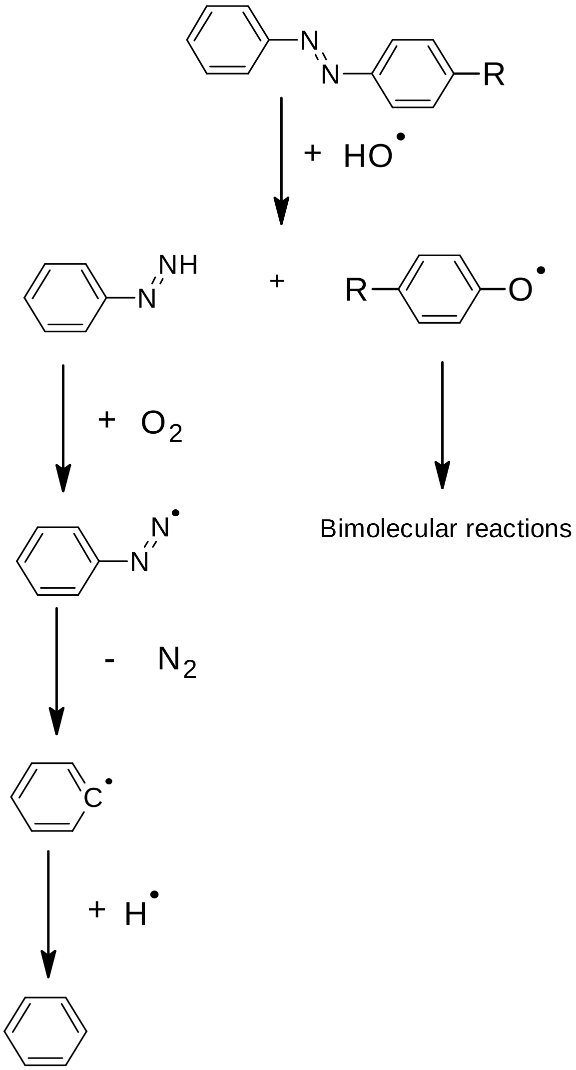


Figure 5. Mechanism of benzene formation in dye decomposition: R = NH_2, or OH.

No Ph–N=NH formation is reported in experiments using sonochemical initiation [40,41]. In the this case the extreme conditions (high pressure, gas-liquid interface) may facilitate immediate decomposition of labile products. By oxidizing azobenzenes and related azo dyes with combined sonochemical and Fenton reactions Joseph et al. [40] reported the oxidation of nitrogen to NO_x yielding nitroaromatic compounds. A portion of these products is able to partition within the gas phase inside the bubbles of cavitations and undergo fast decomposition forming NO_2.

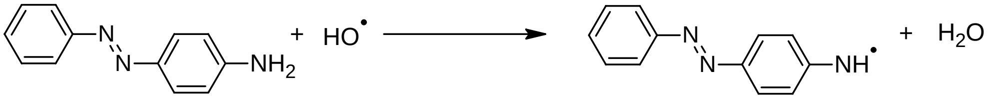
Concerning phenyldiazene product Coen and co-workers suggested a formation route through phenoxyl type radical and then carbenium ion intermediate (Figure 6) [42].

We know very little about the preferred site of electrophilic radical attack on the aromatic ring (except the azo bridge bearing carbon atom). Some experimental findings suggest $^{\bullet}OH$ radical addition on the carbon atom bearing the sulfonate group, this reaction may be followed by subsequent elimination of SO_3 [29]. The electron withdrawing character of the sulfonate group and steric hindrances do not support this reaction. However, the reaction was observed during the degradation of several dyes e.g. AO7 and AO52.

The H-acid based azo dyes and several other dye molecules contain OH groups on aromatic ring. When $^{\bullet}OH$ radical addition takes place on the OH substituent bearing aromatic ring the cyclohexadienyl type radical thus formed may stabilize in an acid-base catalyzed water elimination reaction. This reaction is slow in neutral solutions. Phenoxyl type radical forms in the elimination. We show the addition/elimination mechanism on the example of phenol [28,43]:

$$C_6H_5OH + {}^{\bullet}OH \longrightarrow [C_6H_5OHOH^{\bullet}] \longrightarrow C_6H_5O^{\bullet} + H_2O \quad k = 1.3\times10^{10}\ mol^{-1}\ dm^3\ s^{-1}. \quad (14)$$

As we mentioned before hydroxyl radicals as electrophilic oxidants may react with the electron-rich site on the amino group [29,30]. Krapfenbauer et al. [30] for the reaction with *p*-phenylazoaniline suggested a simple H atom abstraction:



$k = 1.1\times10^{10}\ mol^{-1}\ dm^3\ s^{-1}$. (15)

Galindo for the $^{\bullet}OH$ radical reaction with AO52 which contains dimethylamino group (aminoazobenzene derivative) suggested a more complicated mechanism (Figure 7) [29]. The reaction can be initiated by one-electron extraction from the amino substituent by hydroxyl radical. The resulting radical cation undergoes oxidation to give iminium ion, from which secondary amine can be formed by solvolysis. The eliminated methyl groups are expected to convert to formaldehyde and consequently to formic acid.

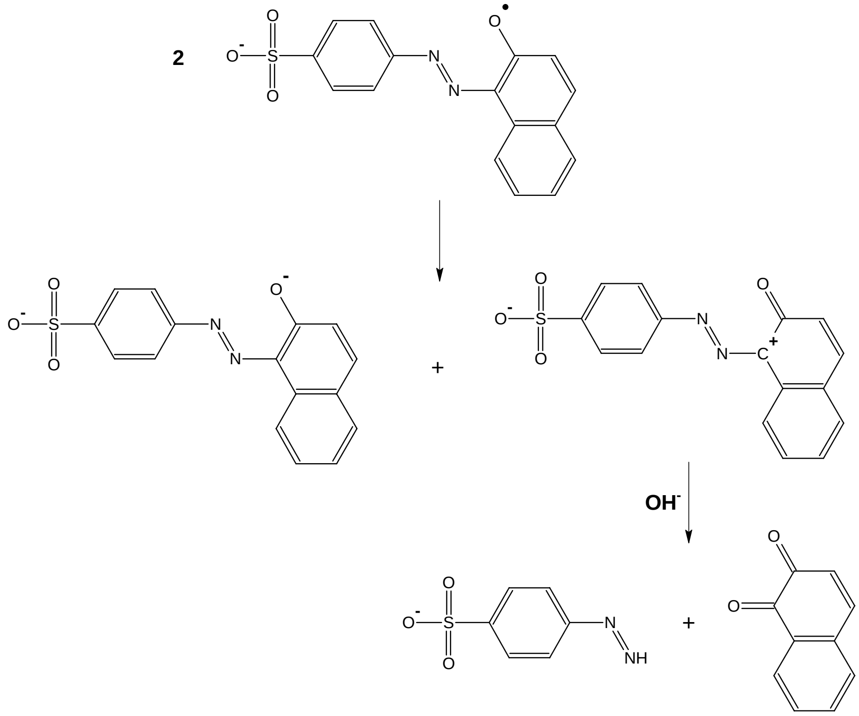


Figure 6. *p*-Sulfonate phenyldiazene formation through disproportionation of two phenoxyl radicals.

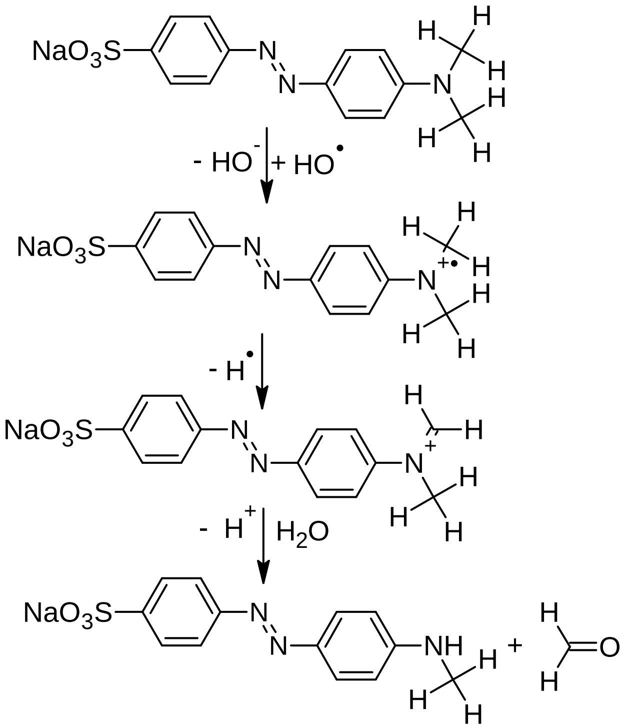
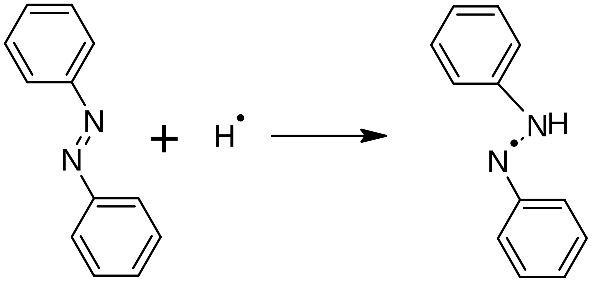


Figure 7. •OH radical attack on the amino group of AO52.

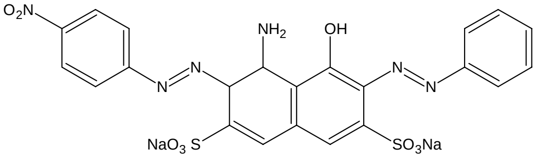
3.2. Hydrogen Atom

Hydrogen atom ($H^\bullet$), similarly to hydroxyl radical, reacts with double bonded compounds in radical addition reactions, however the rate coefficients of radical additions are often smaller by an order of magnitude then the diffusion controlled limit ($k_{\mathrm{diff}} \approx 3\times10^{10}$ mol^{-1} dm^3 s^{-1}, Table 2) [44]. Therefore the reactions show higher selectivity. As the experiments of Flamigni and Monti with azobenzene have shown [45] $H^\bullet$ adds to the azo bond:



(16)

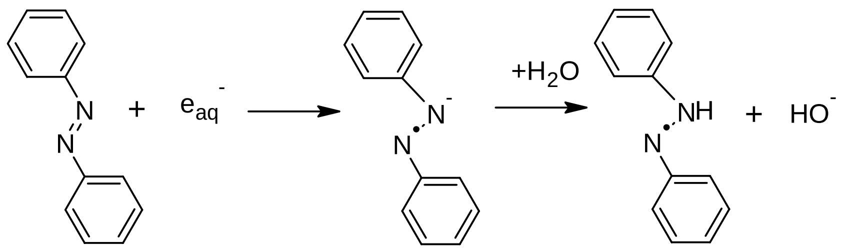
Table 2. Rate coefficients of $H^\bullet$ atom reactions with selected organic molecules [10]

Molecule	Rate coefficient, k mol^{-1} dm^3 s^{-1}
Benzene	1.1×10^9
Phenol	1.7×10^9
Aniline, pH basic	2×10^9
Azobenzene	3.3×10^{10}
Naphthalene	3.4×10^9
2-Naphthol	1×10^9
Naphthol Blue Black (Acid Black I) [46] 	1.04×10^9

3.3. Hydrated Electron

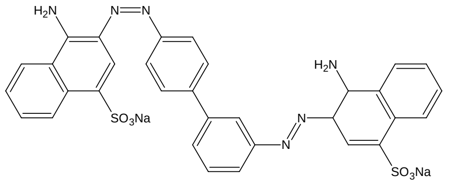
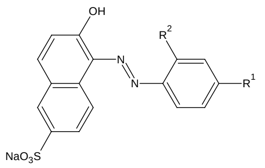
The hydrated electron (e_{aq}^-) in its chemical reactions shows very strong nucleophilic character. According to the frontier orbital theory, nucleophilic reactions (e_{aq}^-, $H^\bullet$) may occur at the atom where the electron density of the lowest unoccupied molecular orbital (LUMO) is the largest. Hydrated electron reacts with azo compounds usually with very high rate coefficients of ~10^{10} dm^3 mol^{-1} s^{-1} (Table 3). As Flamigni and Monti have shown [45] on the example of *trans*-azobenzene e_{aq}^- attacks the –N=N– double bond: hydrazyl radicals (the same as produced in $H^\bullet$ reaction (16)) are the primary species resulting from the rapid protonation of the corresponding anions (Reaction (17)). Hydrazyl radicals react with the parent compound to give dimer radicals in competition with other second order processes. Subsequently the dimer radicals undergo disproportionation with a low rate coefficient (10^6–10^7 mol^{-1} dm^3 s^{-1}).

According to the electron densities of HOMO and LUMO calculated by Hihara et al. [36], the nucleophilic reaction of AO7 may occur primarily at the N atom bound to the naphthalene ring. End-product measurements are in agreement with this suggestion: hydrated electrons (and also $H^\bullet$ atoms) induce decoloration with close to 100% efficiency, which is expected if e_{aq}^- has low reactivity with other parts of the molecules and if Reaction (17) finally leads to destruction of the extensive conjugation through the –N=N– double bond.



(17)

Table 3. Rate coefficients of e_{aq}^- reactions with selected organic molecules and dyes [10]

Molecule	Rate coefficient, k mol^{-1} dm^3 s^{-1}
Benzene	9.0×10^6
Phenol	3.0×10^7
Aniline, pH basic	3.0×10^7
Azobenzene	3.3×10^{10}
Naphthalene	5.0×10^9
1-Aminonaphthalene-4-sulphonate ion	6.7×10^9
p-phenylazoaniline (*p*-PPA) [30]	3.5×10^{10}
Congo Red (C.I. Direct Red 28) [31] 	1.6×10^9 3.6×10^9
Arylazo-2-naphthol [35] $R^1=R^2=H$ $R^1=H$, $R^2=OCH_3$ $R^1=OCH_3$, $R^2=H$ $R^1=Cl$, $R^2=H$ $R^1=CH_3$, $R^2=H$ 	2.5×10^{10} 1.5×10^{10} 8×10^9 1.9×10^{10} 1.6×10^{10}

The reductive attack of AO7 leads to the formation of amino substituted compounds as it is shown on Figure 8. The e_{aq}^{-} adds to the sp^2- hybridized N atom attached to the naphthol moiety of the dye forming dye radical anion, which is protonated in very fast reaction by water leading to the formation of hydrazyl radical [2,35]. Further second order reactions lead to the formation of 1-aminonaphthalen-2-ol and 4-aminobenzenesulfonate stable products.

3.4. Superoxide Radical Anion/perhydroxyl Radical Pair ($O_2^{-\bullet}/HO_2^{\bullet}$)

As the rate coefficient of e_{aq}^{-} and $H^{\bullet}$ with O_2 are around 2×10^{10} mol^{-1} dm^3 s^{-1} (Reactions (6) and (7)) and the concentration of dissolved oxygen in water at room temperature is c.a. 0.25 mmol dm^{-3}, the scavenging capacities for both species are around 5×10^6 s^{-1}. The rate coefficients of e_{aq}^{-} reactions with dye molecules are in the range of 10^{10} mol^{-1} dm^3 s^{-1}. In the absence of other competing reactions practically the concentrations determine whether e_{aq}^{-} predominantly reacts with the dye inducing reduction or e_{aq}^{-} is captured by the oxygen molecule transforming to the $O_2^{-\bullet}/HO_2^{\bullet}$ pair. In the case of $H^{\bullet}$, due to its lower reactivity with double bonded molecules, high dye concentrations are needed for effective scavenging.

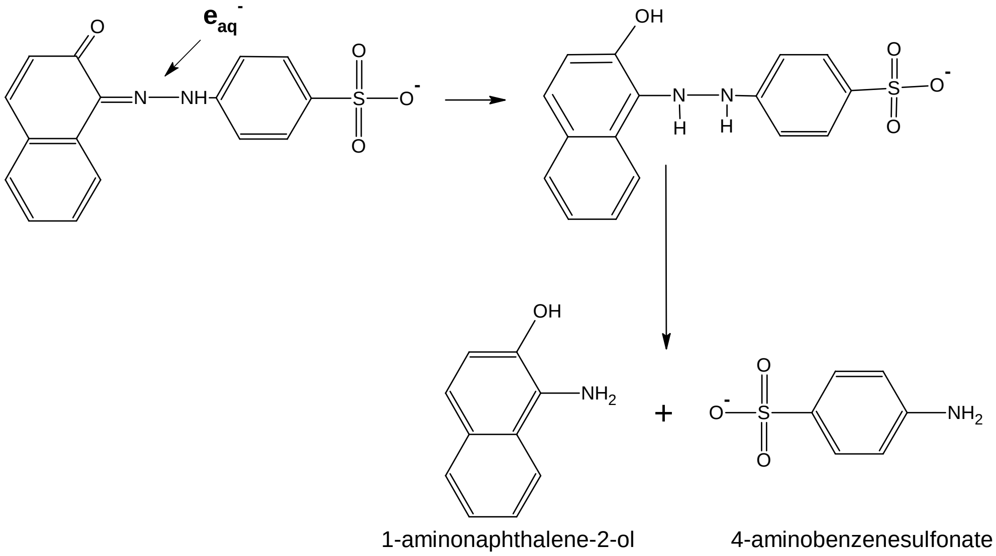


Figure 8. Reductive degradation of AO7.

In connection with the degradation of pesticides and chlorinated aromatic compounds there is an intensive research in order to apply combined irradiation and ozone technique. Ozone addition was found to increase the efficiency of organic molecule decomposition in combined treatment. $O_2^{-\bullet}/HO_2^{\bullet}$ pair also forms in ozone decomposition in alkaline media:

$$O_3 + OH^{-} \longrightarrow HO_2^{\bullet} + O_2^{-\bullet} \tag{18}$$

$$\longrightarrow {}^{\bullet}OH + O_3^{-\bullet} \tag{19}$$

$$O_3 + H_2O \longrightarrow HO_3^+ + OH^- \leftrightarrow 2HO_2^\bullet. \qquad (20)$$

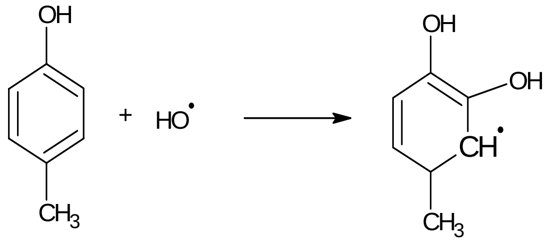
Since the $O_2^{-\bullet}/HO_2^\bullet$ pair can easily be produced in radiolysis of aqueous oxygen containing solutions, pulse radiolysis is a convenient method to study their reactions. According to the general experiences $HO_2^\bullet$ and $O_2^{-\bullet}$ are rather unreactive with the intact dye molecules (in general with aromatic molecules) [23,24,30,47].

Due to the low pK_a of $O_2^{-\bullet}/HO_2^\bullet$ pair (4.8) in neutral and basic solutions the $O_2^{-\bullet}$ form is present. $O_2^{-\bullet}$ is a reducing species with a standard reduction potential of $E(O_2/O_2^{-\bullet}) = -0.33$ V *versus* Normal Hydrogen Electrode (NHE) [7]. Hydrated electron (a strongly reducing species ($E(aq/e_{aq}^-) = -2.9$ V *vs.* NHE), as it was discussed before, reduces the dye molecules (see Figure 8 and Equ. (17)). Similar reduction is also observed with the 2-hydroxy-2-propyl radical ($E(CH_3COCH_3,H^+/CH_3{}^\bullet C(OH)CH_3) = -1.9$ V *vs.* NHE). Hydrogen atom which is also strongly reducing species ($E(H_{aq}^+/H^\bullet) = -2.4$ V *vs.* NHE) causes reduction in radical addition reaction. It seems that the reduction potential of $O_2^{-\bullet}$ is not negative enough to carry out reduction. The reduction potential of methyl orange dye was determined to be $E(Dye/Dye^{-\bullet}) = -0.66 \pm 0.02$ V, after correction for the ionic strength of the solution [1].

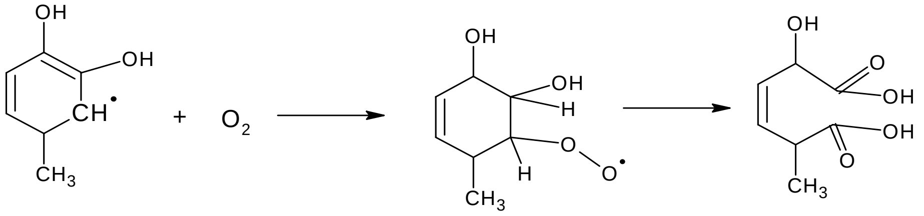
The $O_2^{-\bullet}/HO_2^\bullet$ pair is known to react with quinone type molecules [48]. Therefore they may react with some of the intermediate products in the mineralization process [49].

3.5. Reaction of Dye Radical with Dissolved Oxygen

Molecular oxygen reacts with most of the carbon centered radicals with rate coefficients close to the diffusion controlled limit. So when dissolved O_2 is present in the liquid there is a competition between the reactions of dye radicals with each-other (self-termination), with other molecules present, and with oxygen molecules. The peroxy radicals formed in O_2 radical scavenging reaction are involved in a large number of relatively slow bimolecular and unimolecular processes. As Getoff and co-workers have shown [30,47,50] such processes may lead to opening of the aromatic rings forming aliphatic carboxylic or dicarboxylic acids. There is a step-by-step fragmentation to smaller molecular mass aldehydes, ketones, carboxylic acids, etc. In the presence of oxygen compounds with progressively higher oxygen-to carbon ratio are involved in the conversion of an organic molecule to CO_2 and H_2O. We show the ring-opening reaction on the example of *p*-cresol:



(21)



(22)

4. DYE DEGRADATION

4.1. Decoloration

In most of the works on radiation induced dye degradation decoloration experiments were carried out utilizing UV-VIS spectrophotometry. This is usually done by preparing appropriate solutions, treating them by stepwise increasing doses and after each treatment taking the absorption spectra. In radiolysis investigations this treatment is often done in a glass container, which has attached quartz cuvette for taking the absorption spectra in a spectrophotometer. The cuvette should be made of good quality Suprasil quartz, which does not change its transparency during irradiation.

Azo dyes have wide absorption bands in the visible region [51]. In the absorption spectrum of AO7 (Figure 9) there is a strong peak at 484 nm and a shoulder at 430 nm. The peaks in the UV region at 228, 254 and 310 nm originate from the aromatic rings, the peak in the visible range at 484 nm with a shoulder at the lower wavelength side reflect the conjugated structure. The 484 nm peak suggests the presence of hydrazone form (Figure 4), whereas the shoulder may belong to the azo form [2,52].

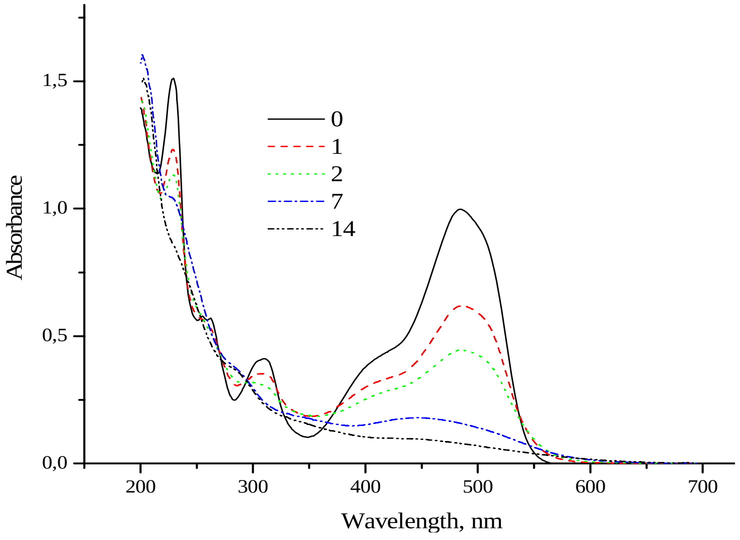


Figure 9. Absorption spectra of aerated AO7 solution prior to irradiation and irradiated with absorbed doses indicated (in kGy). Initial concentration 0.5 mmol dm^3, all solutions were 10 times diluted before spectrophotometric measurements taken in the authors' laboratory.

In Figure 10 we show the absorption spectrum of Apollofix-Red (Ar-28, also called as CI. Reactive Red or CI. 18215). AR-28 is a triazine and H-acid containing azo dye with intensive red color, λ_{max} = 514, 532 nm, ε_{max} =31400 mol^{-1} dm^{3} cm^{-1}. The dye undergoes an acid dissociation at the OH group with pK = 11.74. It also exists in azo-hydrazone tautomer pair. (Below the pK_a value of H-acid containing azo dyes either of the two isomers may dominate, depending on the chemical structure of the dyestuff. In the case of *p*-substituted dyes the azo configuration very strongly prevails. When a phenyl group is attached to the –N=N– azo group with a substituent in *o*-position, like for AR-28 the hydrazone tautomer dominates.) In the case of H-acid containing dyes with secondary amino group (i.e. there is an H atom attached to the amino N atom), for instance AR-28, the H atom on N may also be involved in the tautomerizm.

When a dye containing solution is irradiated, the visible absorbance generally strongly decreases, and the intensity of some of the peaks in the UV region increases, however no clear isosbestic point is detected (Figs. 3, 9, 10). This suggests that there is no direct conversion of the dye into a specific product: the degradation occurs through a number of parallel reactions and through a number of stages [2,23,24,29,31,34,53-59].

It follows from the identification of the absorption peaks discussed before, that decoloration simply means destruction of the extended conjugation through the azo bond. The peaks in the UV region (mostly substituted aromatic molecules) show much less alterations due to irradiation than the visible absorbances.

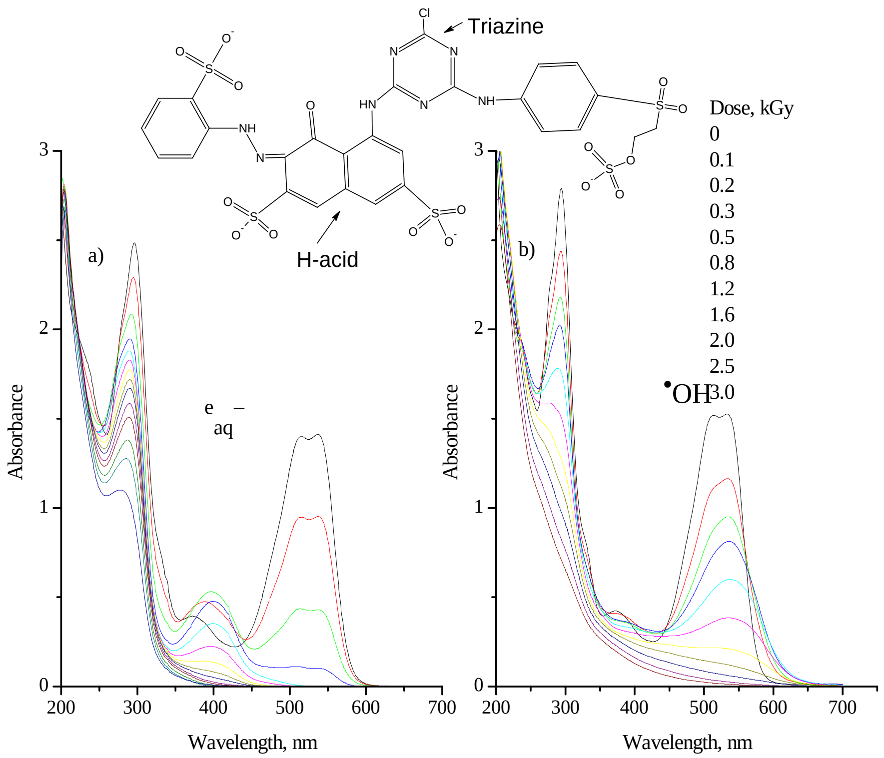


Figure 10. Decoloration of 8.5×10^{-5} mol dm^{-3} concentration aqueous AR-28 solutions in the reaction of hydrated electron (b) and in the reaction of hydroxyl radical (a) taken in the authors' laboratory.

The degree of decoloration is usually calculated from the decrease of absorbance at a selected wavelength, most conveniently at the maximum absorbance by using the equation:

$$\text{Decoloration}(\%) = \frac{A_0 - A}{A_0} \times 100\%. \tag{23}$$

where A_0 and A_i are the absorbances before and after the treatment, respectively.

When irradiating dye containing solutions the absorbance in the 400 – 600 nm region decreases. In some of the cases together with this decrease the shape of the spectrum also changes [3,23,24,53,54].

In those cases when the absorption spectrum in the visible range *does not change during the treatment* it is also observed that the absorbance at the wavelength of maximum decreases nearly linearly with the absorbed dose (or – at constant dose rate – with the time of treatment). A detailed kinetic analysis was carried out on this system and published in [3,54,60]. Here we show only the developed equation describing the change in dye concentration (proportional to absorbance) with time:

$$[A_1] = [A_1]_{t=0} - rt = [A_1]_{t=0}\left(1 - \frac{r}{[A_1]_{t=0}}t\right) = [A_1]_{t=0}(1 - k_{obs}t). \tag{24}$$

In the equation $[A_1]_{t=0}$ and $[A_1]$ are the concentration of intact dye molecules (in mol dm^{-3}) at the beginning and at time t, r is the formation rate of attacking radicals (in mol dm^{-3} s^{-1}), and $k_{obs} = r/[A_1]_{t=0}$ is the observed first-order rate coefficient.

At longer irradiation times (higher doses) the depletion of the starting dye molecules can be so high that the intermediate reacts to considerable extent with the transformed molecules [3,30], for that reason the kinetics deviates considerably from linearity (Figure 11).

In the case of linear dose dependence it was also observed that the effectiveness of decoloration is close to unity: *G*(decoloration) ≈ *G*(primary intermediate). Such behavior is observed when the intermediate reacts with the color giving chromoforic part (e.g. –C–N=N–C– bridge connecting the aromatic groups) of the dye molecule resulting in irreversible reaction here. This reaction leads to the destruction of extensive electron conjugation giving the color. The products formed do not have considerable light absorption in the visible range (and may have low reactivity with reducing species). The linearity of the dose dependence persists until the main reaction of the given primary intermediate is the reaction that induces the chromophore decomposition. Formerly we mentioned that the $H^{\bullet}$ atoms and e_{aq}^{-} react with the azo part of the molecules leading to saturation of the –N=N– bridge or to its complete destruction.

We have to mention also, that although $H^{\bullet}$ atoms and e_{aq}^{-} are very effective in the decoloration, these intermediates are much less effective in the mineralization following decoloration: for complete destruction of the organic subparts of molecules (fragments) oxidizing radicals and oxidizing conditions are needed to transfer organic carbon atoms to CO_2 and hydrogen atoms to H_2O.

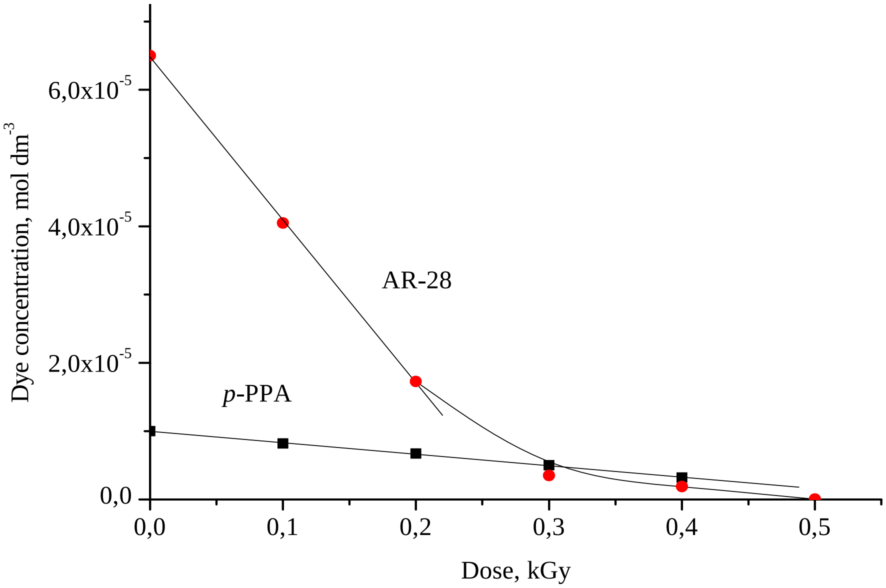


Figure 11. Linear decrease of dye concentration as a function of absorbed dose when Ar-28 or *p*-PPA reacted with e_{aq}^{-} in N_2 or Ar saturated solutions.

When the decoloration is due to the reaction of $^{\bullet}$OH radicals with the dye molecules *the absorption spectrum changes in the visible range during the treatment* [34,49,56-59]: the visible band gradually shifts to longer wavelengths as it is shown for AO7 and AR-28 on Figs 9 and 10b. When the visible spectrum changes during the treatment the kinetics of dye disappearance follows logarithmic time (dose) dependence. This dependence is described by the equation [3,54,60]:

$$[A_1]=[A_1]_{t=0}\exp\left(-\frac{r}{[A_1]_{t=0}}\right)=[A_1]_{t=0}\exp(-k_{obs}t). \tag{25}$$

In the equation $[A_1]_{t=0}$, $[A_1]$, t, r and k_{obs} have the same meaning as in the case of Equ. (24).

It should be mentioned that due to the changing absorption spectrum the spectrophotometric measurement does not supply the correct intact dye molecule concentration. For correct concentration measurement GC or HPLC separation and quantitative determination is needed [54].

The non-linear dye concentration-time (dose) dependence and also the changing absorption spectrum are due to the very high reactivity of $^{\bullet}$OH radicals with double bonds. After the color giving extensive conjugation is destroyed the transformed molecules (products) have still several double bonds to react with $^{\bullet}$OH radicals. Therefore the reactivity of $^{\bullet}$OH radicals with the primary products, and also with the secondary, tertiary etc. products is practically the same as with the intact molecules. As we described it in [3,54,60], such behavior leads to logarithmic time dependence. Logarithmic dependencies are shown in Figure 12.

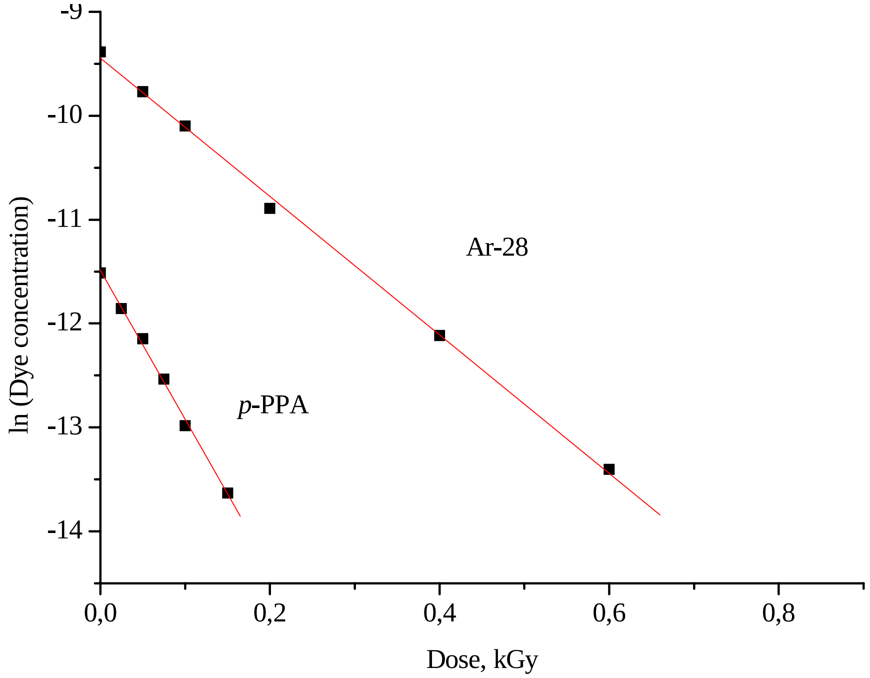
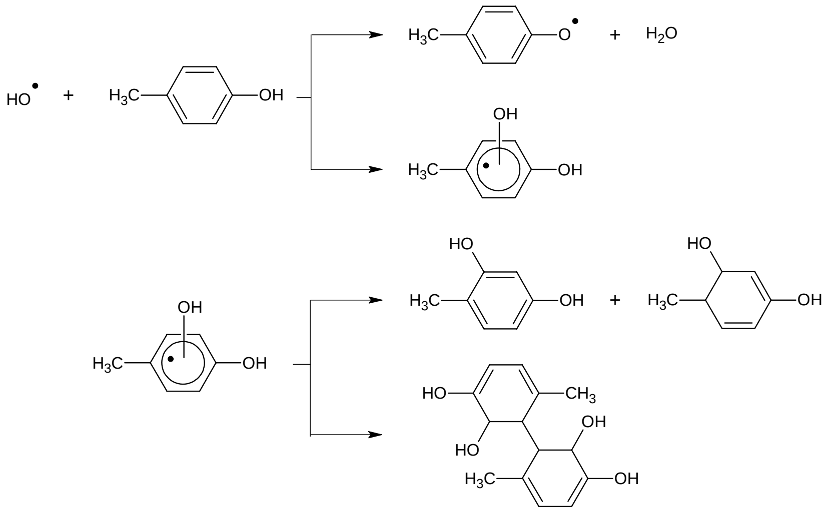


Figure 12. Logarithmic decrease of dye concentration as a function of absorbed dose when Ar-28 or *p*-PPA reacts with $^{\bullet}OH$ radicals in N_2O saturated solutions.

The change of the absorption spectra and also the relatively small efficiency of decoloration also observed are due to $^{\bullet}OH$ radical addition to the aromatic rings. As a result of radical addition to any of the aromatic rings cyclohexadienyl type radicals form. In order to illustrate the probable reactions when $^{\bullet}OH$ radical adds to an aromatic ring (not to the azo bearing carbon atom) we show the example of *p*-cresol:



(26)

(27)

(28)

(29)

The cyclohexadienyl type radicals may transform to stable end-products in self-termination (disproportionation or combination) reactions. The combination leads to dimerized molecules in which the connecting rings lost the aromatic character. In disproportionation in one of the reacting molecules one ring looses the aromacity, in the other molecule the aromatic character and by that the extensive conjugation is regenerated. However, the regenerated dye molecules have extra OH group attached to one of the aromatic rings. If this extra OH-group is on the part of the dye molecule that is involved in the extensive conjugation, the spectrum in the visible range shifts to the red.

When the dye molecules react with $^{\bullet}OH$ radical with the progress of reaction the number of color giving intact and transformed molecules decreases and those of the transformed decolored molecules increases. The competition between the $^{\bullet}OH$ radical reaction with the decolored and colored molecules can explain the logarithmic-like decoloration curves described by Equ. (25) (Figure 12) often observed under circumstances when $^{\bullet}OH$ radical is the main reacting species.

4.2. Products of Chemical Transformations

In the previous sections of this chapter we have already touched the question of product formation. In general one can say that due to the attack of $H^{\bullet}$ atoms and e_{aq}^{-} transformed molecules with destroyed –N=N– bond form: saturation of this bond may occur, N_2 elimination or scission forming C-NH_2 groups in complex processes may take place. In $^{\bullet}OH$ radical reactions destruction of the conjugation through the –N=N– bond happens when the radical attack occurs on the azo bond, or on the carbon atom bearing the azo group. When the addition occurs on the other parts of aromatic rings OH substituted products form with or without color giving extensive conjugation.

The chemical identification of the individual products formed is extremely complicated because large number of compounds forms parallel and also because some of the products are labile and easily decompose during separation (e.g. in gas-chromatography). For these reasons the products of the primary transformations are known only in very few cases. The secondary, tertiary, etc. transformation products are even less known. In the case of smaller “model” compounds, like AO7 GC or GC coupled with MS can be applied for separation and identification. In case of larger molecular mass “real” dyes HPLC, eventually HPLC-MS is the proper tool [25,26].

Due to the large number of products (large number of parallel reactions) the process of mineralization is generally followed by such standardized methods as the determination of chemical oxygen demand (COD), biological oxygen demand (BOD), and total organic carbon content (TOC) [61,62]. As the degradation products can be toxic, toxicity measurements are also of essential importance [55].

The values of chemical oxygen demand, COD(Cr), biological oxygen demand BOD, and content of suspended solids (SS) are measured in accordance with standard methods, utilizing dichromate method at closed reflux (for COD(Cr)), Wincler’s azide modification method (for BOD), and weighting the total filterable residue dried at 105°C (for SS). Permanganate method in acid medium via standard procedure is utilized for measuring COD(Mn). Total organic carbon content (TOC) values are determined as the difference between total carbon and inorganic carbon contents, both measured by registering CO_2 evolved due to catalytic incineration of dry residue and due to acidifying the solution by phosphoric acid, respectively [63].

When TOC measurement is used to follow the destruction of organic molecules, the degree of mineralization is calculated by the relation [3]:

$$\mathrm{Mineralization\%} = \frac{\mathrm{TOC}_{\mathrm{initial}} - \mathrm{TOC}}{\mathrm{TOC}_{\mathrm{initial}}} \times 100\%. \tag{30}$$

The mineralization curves substantially differ from the decoloration curves (Figure 13) [59,64,65]. Although generally TOC reduction (i.e. mineralization) starts in the early stages of the treatment, during the decoloration period the TOC or COD reduction is very small. The TOC- and COD-values decrease substantially after the color disappeared. Generally COD and TOC measurements indicate a nearly linear decrease of the organic content with the time of treatment. At very high conversions the trends change and COD and TOC removals slow down. This is suggested to be due to formation of some aliphatic by-products which have low reactivity with the oxidizing $^{\bullet}OH$ radicals [29]:

In mineralization the dissolved oxygen concentration plays a very important role. Experiments carried out with air saturation, oxygen saturation and also with pressurized oxygen applied, have shown that under identical irradiation conditions the degree of TOC reduction increases with the oxygen concentration and the highest values were measured with pressurized O_2 applied [49,56,66-69].

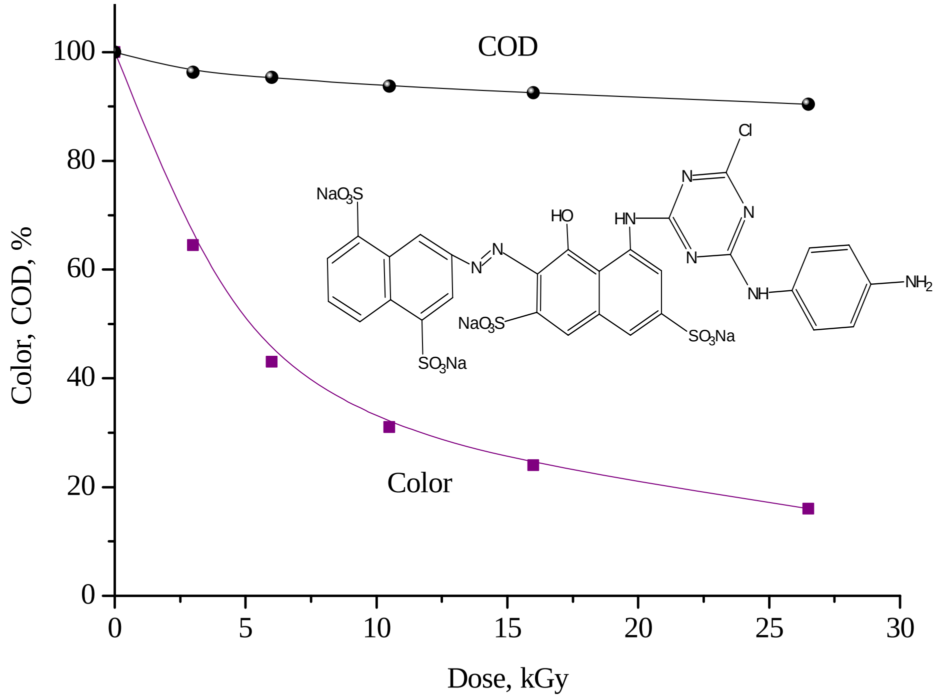


Figure 13. Color and COD removal during EB irradiation of reactive red (KA-3B) in air. Initial concentration 9×10^{-4} mol dm^{-3}.

During dye degradation there is also a change in the pH of the solution, the pH gets more and more acidic with the degradation. In laboratory experiments in neutral solutions with initial dye concentration of 10^{-4} - 10^{-3} mol dm^{-3} the pH decreases by about 2 pH units during the degradation [17,59]. Due to the decreasing pH value it is assumed that the solution contains the oxidized organic fragments in anion forms of their corresponding acids. Among the transformation products of several dye molecules terephthalic-, oxalic- and formic acids and in small quantities malonic-, acetic- and succinic acids were determined together with traces of phenol [62].

4.3. Influence of Contaminants other than Dye Molecules in Wastewater

Dye-bath effluents generally contain a complex mixture of dyes, dispersing, leveling and wetting agents, fragments of the dyed textile (cellulose, polyester, etc.) and trace metals, especially copper and chromium salts. These additives modify the dye degradation rate by competing for the reactive radicals produced in water radiolysis [34]. The effects of such common anions as HCO_3^-, $CH_3CO_2^-$ and SO_4^{2-} at concentrations frequently present in industrial wastewaters was investigated in $^{\bullet}OH$ radical induced decomposition of AO52 [29] (HCO_3^- and SO_4^{2-} form also during dye degradation). It was shown that sulfate ion practically does not influence the dye degradation rate since this ion is rather inactive in the reaction with $^{\bullet}OH$ radicals. On the contrary, bicarbonates or acetates inhibited the dye degradation [29,32]. The decomposition rate decreased by 20-50% as compared to the reactions in distilled water, and longer irradiation times were necessary to obtain complete decoloration. The radical ions that form in $^{\bullet}OH$ radical reactions with HCO_3^- and $CH_3CO_2^-$ have much smaller oxidation potential as hydroxyl radical:

$$HCO_3^- + {}^{\bullet}OH \longrightarrow CO_3^{-\bullet} + H_2O \quad k = 1.5\times10^{7}\ mol^{-1}\ dm^{3}\ s^{-1} \tag{30}$$

$$CH_3\text{-}CO_2^- + {}^{\bullet}OH \longrightarrow {}^{\bullet}CH_2\text{-}CO_2^- + H_2O \quad k = 4.3\times10^{7}\ mol^{-1}\ dm^{3}\ s^{-1}. \tag{31}$$

Dissolved transition metals may influence the dye degradation by complexation of organic molecules involving nitrogen atoms of the azo linkage or the amino groups. However, it should be mentioned that adding copper or chromium cations to AO52 solutions did not alter the UV-VIS absorption spectra of the dye reflecting the absence of complexation.

The iron ions present in aqueous solutions during irradiation may induce Fenton reactions since in the direct decomposition of water (Equ. (1)) and in the presence of dissolved oxygen in the self-termination reactions of the $O_2^{-\bullet}/HO_2^{\bullet}$ radicals (Reactions (9)-(11)) hydrogen peroxide constantly forms in the system. Fe^{2+}/Fe^{3+} ions react with H_2O_2 and $HO_2^{\bullet}$; in catalytic process $^{\bullet}OH$ radicals also form. $^{\bullet}OH$ radicals accelerate the decomposition.

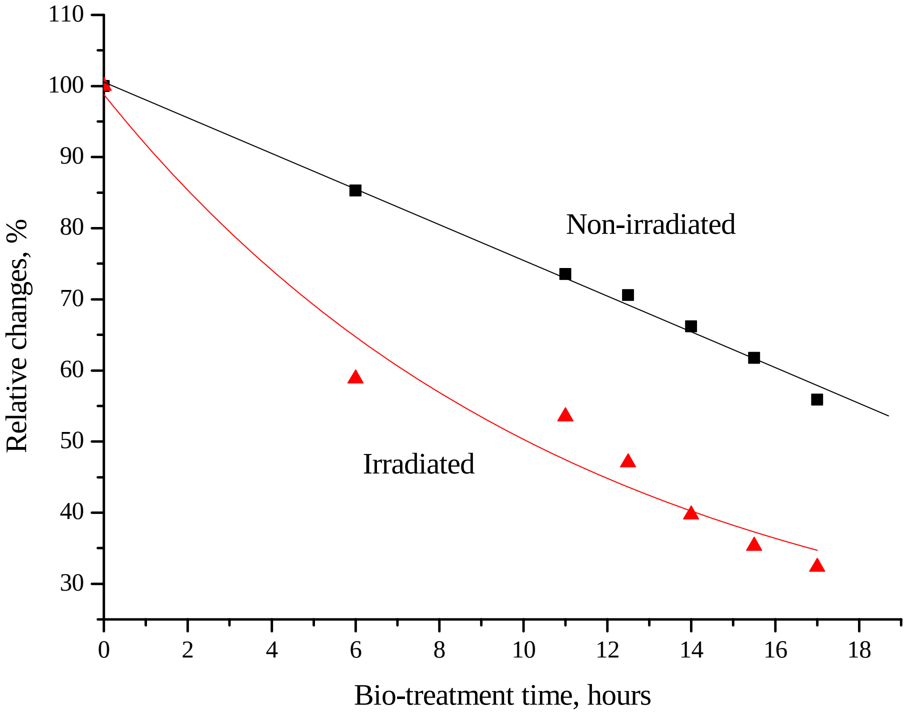


Figure 14. Effect of bio-treatment time on the COD value in electron beam irradiated (2 kGy) and non-irradiated dying complex wastewater in the area of Taegu Industrial Complex, Taegu, Republic of Korea. (Courtesy of Bumsoo Han [77])

$$Fe^{2+} + HO_2^{\bullet} + H_3O^+ \longrightarrow Fe^{3+} + H_2O_2 + H_2O \quad k = 1.2\times10^6\ mol^{-1}\ dm^3\ s^{-1} \tag{33}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad k = 5\times10^1\ mol^{-1}\ dm^3\ s^{-1} \tag{34}$$

$$Fe^{3+} + H_2O_2 + H_2O \longrightarrow Fe^{2+} + HO_2^{\bullet} + H_3O^+ \tag{35}$$

$$Fe^{3+} + HO_2^{\bullet} + H_2O \longrightarrow Fe^{2+} + O_2 + H_3O^+. \tag{36}$$

Many other transition metal ions, e.g. Cu^{2+} or Cr^{3+} can take part in similar, so-called Fenton-like reaction [29]. These ions, similarly to the iron ions are not able to induce the dye decomposition, but through H_2O_2 decomposition may enhance the degradation.

The Fenton-like reactions induced by copper ions are listed as follows:

$$Cu^{2+} + HO_2^{\bullet} + H_2O \longrightarrow Cu^+ + H_3O^+ + O_2 \tag{37}$$

$$Cu^+ + H_2O_2 \longrightarrow Cu^{2+} + OH^- + {}^{\bullet}OH \tag{38}$$

$$Cu^+ + HO_2^{\bullet} \longrightarrow Cu^{2+} + HO_2^-. \tag{39}$$

In the UV/H_2O_2 photocatalytic process copper ions were found to be much more effective in enhancing dye decomposition than chromium ions.

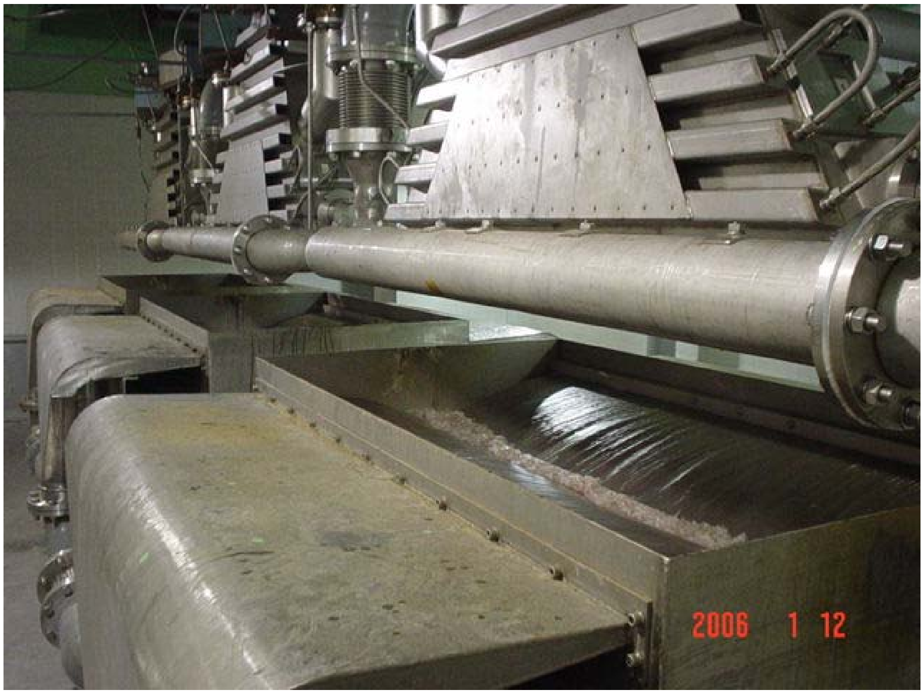


Figure 15. Irradiation of industrial dying complex wastewater in the area of Taegu Industrial Complex, Taegu, Republic of Korea (Courtesy of Bumsoo Han [77]).

5. PRACTICAL APPLICATIONS OF EB FOR DYEING WASTEWATER TREATMENT

Pilot plant and industrial scale experiments demonstrated the effectiveness of high-energy irradiation pre-treatment of wastewater when combined with conventional (mechanical screening, biological and chemical) methods [70]. In most cases these plants were constructed to treat municipal wastewater [71], or industrial wastewater containing some organic pollutants [8,70-76]. E.g. a synthetic rubber plant in Voronezh (Russia) had applied electron accelerator to convert the non-biodegradable emulsifier Nekal (isobutyl naftonate) in plant waste to biodegradable form. The dose requirement at 10^{-3} mol dm^{-3} concentration was 300 kGy. The plant had two production lines and could treat up to 2000 m^3 effluent per day.

In order to treat industrial wastewater of dying factories first a pilot plant (output 1000 m^3 day^{-1}) was established in the area of Taegu Industrial Complex, Taegu, Republic of Korea. The Complex includes about 100 factories with some 13,000 employees. The pilot plant is operating since 1998 with ELV electron accelerator (energy 1 MeV, beam power 40 kW) for large-scale test of combined electron-beam and biological treatment of industrial textile dyeing wastewater [62,76]. This plant has shown considerable reduction of chemical additive consumption, and also reduction in retention time, with an increase in removal efficiencies of

COD and BOD (Figure 14). According to the pilot-plant investigations of the dying complex wastewater equal purification degree corresponds to 17 h of bio-treatment without preliminary irradiation and about 8 h of bio-treatment with preliminary electron-beam treatment at absorbed dose 1-2 kGy [62].

On the basis of data obtained from pilot plant operation, in the area of the Complex construction of an industrial scale plant was started in 2004, and finished in December 2005 [77,78]. The industrial plant is located on the area of an existing wastewater treatment facility and its capacity is 10,000 m^3 of wastewater per day. The facility is operating with 1 MeV, 400 kW accelerator and the radiation pre-treatment is combined with the existing bio-treatment facility. The continuous operation of this facility will provide additional data on reliability and for a detailed economic evaluation (Figure 15). With 10 000 m^3/day capacity the price for treating dying wastewater for recycling by 2 kGy dose is about 1 \$/m^3 [77].

CONCLUSION

1. The reactive intermediates formed in water radiolysis (e_{aq}^-, $H^\bullet$ and $^\bullet OH$) react with the dye molecules with high rate coefficient forming dye radicals. Radiation chemical techniques, especially pulse radiolysis with the time resolved observation of intermediates can help to clarify the undergoing chemical reactions. Although in the book chapter the radiolysis results were reviewed, the undergoing processes, the reaction mechanisms are also relevant to other AOP.
2. The water radiolysis intermediates effectively destroy toxic dye molecules causing first decoloration, but with sufficiently high doses mineralization to CO_2, H_2O, N_2, NO_x, SO_4^{2-} and to other inorganic ions can be achieved.
3. At the beginning of decoloration the dye concentration decreases linearly with time (dose) when $H^\bullet$ or e_{aq}^- are the main attacking species. In such cases the absorption spectrum in the visible range dose not changes during the treatment.
4. Logarithmic time dependence is observed in the reaction of $^\bullet OH$ radicals. There is also a gradual shift in the visible absorption maxima to longer wavelengths. This shift is attributed to formation of hydroxylated dye molecules.
5. $O_2^{-\bullet}/HO_2^\bullet$ species formed in e_{aq}^- and $H^\bullet$ reaction with O_2 molecules have very low effectiveness in decoloration and their contribution to the mineralization process is probably also small. However, there are suggestions that some inorganic ions, e.g. Fe(II)/Fe(III) or Cu(I)/Cu(II) in catalytic reactions transforming the peroxides (formed during radiolysis) to $^\bullet OH$ radicals, enhance the efficiency of $O_2^{-\bullet}/HO_2^\bullet$ contribution in dye destruction.
6. Large number of parallel and consecutive reactions are involved in decoloration and mineralization. The products were individually identified in very few cases. As intermediate products compounds with destroyed –N=N– bond, hydroxylated dye molecules, dimers, molecules with opened rings, aldehydes, ketones, carboxylic acids form. The process of mineralization is usually followed by such techniques as chemical or biological oxygen demand, total carbon content measurement, etc.

7. Oxygen is not necessary for the decoloration, but it is essential for the destruction of the skeleton of the dye molecule and for mineralization. As the degradation products can be toxic, toxicity measurements are also of essential importance.
8. The biodegradation of the slightly irradiated solutions needs shorter time than that of the starting wastewater. The efficiency of dye destruction is enhanced when irradiation/ozone or irradiation/hydrogen peroxide combined treatments are applied.
9. Pilot-plant experiments and an industrially established technology show that irradiation treatment is a cost-effective technology that can compete with other dye containing wastewater purification technologies.

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