Review

Radiation induced degradation of dyes—An overview

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A B S T R A C T

Synthetic dyes are a major part of our life. Products ranging from clothes to leather accessories to furniture all depend on extensive use of organic dyes. An unfortunate side effect of extensive use of these chemicals is that huge amounts of these potentially carcinogenic compounds enter our water supplies. Various advanced oxidation processes (AOPs) including the use of high-energy radiation have been developed to degrade these compounds. In this review, dye decoloration and degradation as a result of its exposure to high energy radiation such as gamma radiation and pulsed electron beam are discussed in detail. The role of various transient species such as $^\bullet H$, $^\bullet OH$ and e_{aq}^- are taken into account as reported by various researchers. Literature citations in this area show that e_{aq}^- is very effective in decolorization but is less active in the further degradation of the products formed. The degradation of the dyes is initiated exclusively by $^\bullet OH$ attack on electron-rich sites of the dye molecules. Additionally, various parameters that affect the efficiency of radiation induced degradation of dyes, such as effect of radiation dose, oxygen, pH, hydrogen peroxide, added ions and dye classes are also reviewed and summarized. Lastly, pilot plant application of radiation for wastewater treatment is briefly discussed.

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Contents

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1. Introduction

Dyes comprise an important part of waste water effluents, as they are discharged in abundance by many manufacturing industries. The environmental/health concern of these potentially carcinogenic pollutants in these contaminated waters has drawn the attention of many workers. In this regard various approaches have been forwarded to decontaminate these effluents. Typical techniques include the classical methods such as adsorption [1–3], coagulation [4,5], filtration [6] and sedimentation [7]. Although all these techniques are versatile and useful, they all end up in producing a secondary waste product which needs to be tackled further. A relatively newer, more powerful, and very promising approach called advanced oxidation processes (AOPs) has been developed and employed to treat dye-contaminated wastewater effluents [8]. AOPs are a set of techniques which normally utilize a strong oxidizing species such as $^\bullet$OH radicals produced *in situ*, which causes a sequence of reactions thereafter to break down the macromolecule into smaller and less harmful substances. In many cases the macromolecule is completely broken down to water and carbon dioxide. The AOP technique has drawn considerable attention from various quarters of scientific community as it is easy to handle and produces significantly less residuals as compared to the classical approaches. Amongst the many techniques employed in the AOP approach are the UV photolytic technique [9–12], Fenton process [13–18], photo-Fenton process [19–21], ozonation process [22], sonolysis [23–25], photocatalytic approach [26–30], biodegradation [31–33] and the radiation induced degradation of dyes [34–37]. Furthermore, many workers have coupled the various AOP techniques to obtain significant improvement in their results [38–43]. The present paper is a review of published studies on high energy radiation (α, β and γ) induced degradation/decoloration of dye solutions reported during the period of 2000–2008. As we will see, ionizing radiation is a promising tool for the treatment of textile dye waste effluents. This is primarily because the effect of radiation can be intensified in aqueous solutions by the primary products formed from the radiolysis of water. The main aim of this paper is to produce a condensed and coherent review on the subject of radiation induced dye degradation which can serve as a ready reference for future scientific endeavors in this area.

2. Experimental techniques used for studying dye degradation

Since most of the dyes are colored in nature, it is relatively easy to monitor their color change during the course of the experiment. In steady state radiolysis, the sample is normally irradiated for a given time period and the changes in solution property (such as color) is observed by using a spectrophotometer [37]. These experiments can be carried out in a lab setting using glass tubes or glass containers; however for large volumes of solutions, a scanning type of radioactive source is utilized. In some cases an encapsulated source of radioactive source such as Co-60 or Cs-137 is immersed in solution and the solution is continuously agitated for a given time period. Both these sources of irradiation are the major products of a fission process and thus are readily available as radiation sources. Besides this, they have a relatively long half life and give off high energy radiation. However, special precautions, shielding and monitoring are required to safeguard the personnel from getting the overdose of radiation while working with these sources. The radiated solution after irradiation is then transferred to a cuvette and subjected for absorption studies on a spectrophotometer. The degree of decoloration is then calculated from the decrease of absorbance of the dye solution at its maximum absorption wavelength as follows [44]:

$$\% \text{ decoloration} = \left[\frac{A_0 - A_i}{A_0}\right] \times 100 \qquad (1)$$

where A_0 and A_i are the absorbance values of the dye solution before and after irradiation respectively. The final degradation products of the irradiated dye solution can be further investigated using additional analytical tools such as HPLC [45], FTIR [46], GC/MS [47] and NMR [48], etc.

In the case of studying the formation and decay of reactive transients under radiolytic conditions, pulse radiolysis technique is generally employed [49]. In this technique, a short pulse of ionizing radiation is used to initiate the primary chemical reactions. The pulse length can be somewhere from a nanosecond to a microsecond. Most of the sources of pulse radiation are the Linear accelerators, Van de Graff generator and Febetrons. The pulse length and the energy delivered can be controlled to some extent in each case. The radiation introduced in the solution causes the formation of transient species such as radicals, ions and excited molecules which can then be monitored by using optical spectrum, electric spin resonance spectra, conductivity detection or some other suitable techniques. In many cases, fast kinetic absorption spectrophotometry is employed to study those reactive species which are capable of absorbing light and then decay in solution within a very short period of time [50]. This approach has been shown to be useful in studying the decay kinetics of solvated electron which is produced in the reaction and reacts very quickly with its environment in a very short period of time [51]. The decay kinetics data can then be used for calculating the rate coefficients of the intermediates and their role in the overall mechanism of radiolysis.

3. Radiolysis of aqueous solutions

The effect of radiation on a given compound depends on the composition of matter and the amount of energy that is transferred by the radiation. The radiolysis of water is very well documented and it been has known that it produces H_2, H_2O_2, H^+, OH^- and hydrated electron (e_{aq}^-), hydroxyl radical ($^\bullet$OH) and hydrogen atom ($^\bullet$H) as intermediate species in varying amounts depending upon the linear energy transfer value of the radiation. In dilute solutions the yield of these species are as follows: $G(e_{aq}^-) = G(^\bullet OH) = 0.28$, $G(^\bullet H) = 0.06$. These G values are the yields of primary intermediates in μmol/J. They can then take part in many different reactions with the solute molecule thereby causing a change in its composition [52]:

$$H_2O \rightsquigarrow {}^\bullet OH, {}^\bullet H, e_{aq}^- \qquad (2)$$

The hydrated electron (e_{aq}^-) and the hydrogen atom are the main reductive species produced in irradiated aqueous solution, whereas, the hydroxyl radicals ($^\bullet$OH) and perhydroxyl radicals ($^\bullet HO_2$ produced in subsequent reactions) are the main oxidizing species produced in water radiolysis. One of the consequences of radiolysis in aqueous solutions is that the charged species become hydrated within a very short interval of time (10^{-11} seconds). Furthermore, the excitational energy of these various species can be easily dissipated due to collisions and since diffusion is slower in liquids, one would expect both "track" and "cage" effects in such a system. This results in the non-homogeneous distribution of the primary species. In heavy particle irradiation of water, the ionization energy density is usually high which results in an enhanced cage effect and therefore resulting in molecular products such as hydrogen molecule and hydrogen peroxide. In the case of electron and gamma radiation, the lower ionization energy allows for greater diffusion of the primary species thereby resulting in other reactions. In very dilute aqueous solutions, practically all the radiation is absorbed by water molecule. Thus any change in solute composi-

tion would result from the secondary reactions of radiation induced species from water and solute molecule rather than the direct effect of radiation on the solute molecules. These secondary reactions arise from the reactions of solutes with the oxidizing and reducing species initially produced during water radiolysis. Thus the linear energy transfer (LET) value of radiation is the determining factor of the radiation effect besides the dose rate of the radiation. It is possible to reduce the types and amount of primary reacting radicals by selecting appropriate experimental conditions. One can therefore, obtain specific information about the mechanism of undergoing reactions and their possible reaction pathways.

3.1. Properties of primary species

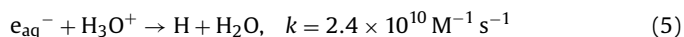#### 3.1.1. Solvated electron (e_{aq}^-)

The solvated electron is an excess electron localized in a cavity formed by solvent molecules [53]. It is a transient species found everywhere in various biological and chemical systems where a charge is transferred through a medium. It plays an important role in applications such as the radiation treatment of cancer and the neutralization of toxic wastes [54]. The structure of the solvated electron is analogous to an F-center (color center) found in alkali halide crystals with anion vacancy defects. Formation of the solvated electron is usually preceded by the injection of an electron from the parent molecule into the solvent. The injection of the electron occurs via direct or indirect ionization (for example, via charge transfer to solvent) of the parent molecule, depending on the conditions under which the electron is separated from its parent. The injected electron subsequently loses its initial kinetic energy while traveling through the solvent (known as thermalization), and eventually localizes in a solvent cavity to form an equilibrated solvated electron. After the solvated electron is formed, it undergoes reactions with electron-accepting species within the solution which ultimately sets a limit on its lifetime. Many of the solvated electron reactions (in case of water radiolysis, the term hydrated electron is also used), have very low activation energies so that almost all collisions between the reactants lead to reactions. The rate of reaction is governed by the species diffusing together thereby the reactions of solvated electron are diffusion controlled reactions and have a rate constant value of the order of $10^{10}\,M^{-1}\,s^{-1}$. Solvated electron reactions are generally single electron transfer reactions of the general form shown below [55]:

$$e_{aq}^- + S^n \rightarrow S^{n-1} \tag{3}$$

where n is the charge on the solute molecule. If the oxidation potential of solute cation is less than that of the solvated electron, the species is reduced:

$$e_{aq}^- + Cd^{2+} \rightarrow Cd^+, \quad k = 5.3 \times 10^{10}\,M^{-1}\,s^{-1} \tag{4}$$
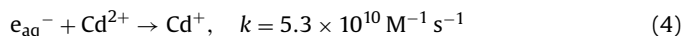
With proton donors, such as H_3O^+, solvated electron reacts very rapidly to produce H atom:

$$e_{aq}^- + H_3O^+ \rightarrow H + H_2O, \quad k = 2.4 \times 10^{10}\,M^{-1}\,s^{-1} \tag{5}$$
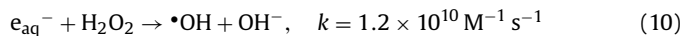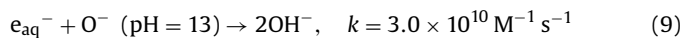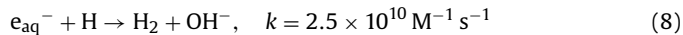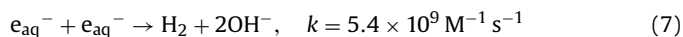
The H atoms can further react in the solution to produce either H_2 or some other species.

The reaction of solvated electron is pseudo order in nature in aqueous solutions and the half life of the species is estimated to be 2.1×10^{-4} seconds in neutral water and 7.8×10^{-4} seconds in basic solutions.

Solutes containing unpaired electrons generally react with e_{aq}^- to produce negative ions:

$$e_{aq}^- + {}^\bullet OH \rightarrow OH^-, \quad k = 3.0 \times 10^{10}\,M^{-1}\,s^{-1} \tag{6}$$
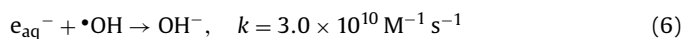
Some other important reactions of solvated electron in aqueous solutions are as follows:

$$e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2OH^-, \quad k = 5.4 \times 10^9\,M^{-1}\,s^{-1} \tag{7}$$

$$e_{aq}^- + H \rightarrow H_2 + OH^-, \quad k = 2.5 \times 10^{10}\,M^{-1}\,s^{-1} \tag{8}$$

$$e_{aq}^- + O^- \ (pH = 13) \rightarrow 2OH^-, \quad k = 3.0 \times 10^{10}\,M^{-1}\,s^{-1} \tag{9}$$

$$e_{aq}^- + H_2O_2 \rightarrow {}^\bullet OH + OH^-, \quad k = 1.2 \times 10^{10}\,M^{-1}\,s^{-1} \tag{10}$$

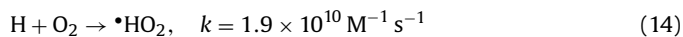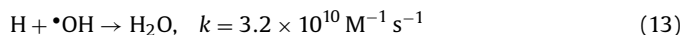$$e_{aq}^- + O_2 \rightarrow O_2^-, \quad k = 1.9 \times 10^{10}\,M^{-1}\,s^{-1} \tag{11}$$
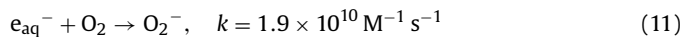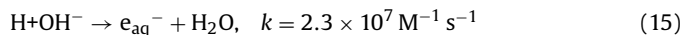
3.1.2. Hydrogen atom

The hydrogen atom has a slightly lower reducing power than the solvated electron, but can easily reduce cations with lower oxidation potentials [56]:
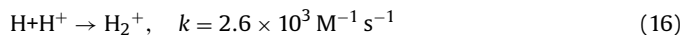
$$H + Cu^{2+} \rightarrow H^+ + Cu^+ \tag{12}$$

The hydrogen atom can also undergo addition reactions with species containing unpaired electrons:

$$H + {}^\bullet OH \rightarrow H_2O, \quad k = 3.2 \times 10^{10}\,M^{-1}\,s^{-1} \tag{13}$$

$$H + O_2 \rightarrow {}^\bullet HO_2, \quad k = 1.9 \times 10^{10}\,M^{-1}\,s^{-1} \tag{14}$$

In strong basic solutions, the hydrogen atom can react with OH^- to form a solvated electron:

$$H + OH^- \rightarrow e_{aq}^- + H_2O, \quad k = 2.3 \times 10^7\,M^{-1}\,s^{-1} \tag{15}$$

In acidic solutions, hydrogen atoms can react as follows:

$$H + H^+ \rightarrow H_2^+, \quad k = 2.6 \times 10^3\,M^{-1}\,s^{-1} \tag{16}$$

Its reaction with H_2O_2 produces ${}^\bullet OH$ radicals as follows:

$$H + H_2O_2 \rightarrow {}^\bullet OH + H_2O, \quad k = 9 \times 10^7\,M^{-1}\,s^{-1} \tag{17}$$
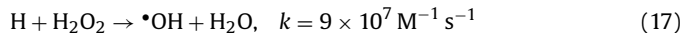
The fundamental difference between the reactions of the hydrogen atom and the hydrated electron being that the former can abstract hydrogen from the solute to produce molecular hydrogen, whereas the later can react with the solute to produce other products.

3.1.3. Hydroxyl radical

The hydroxyl radicals are the main oxidizing species which are produced in the radiolysis of aqueous solution [57]. With high LET radiation, inter-radical reactions increase within the "tracks", thereby producing H_2O, H_2 and H_2O_2:

$${}^\bullet OH + H \rightarrow H_2O, \quad k = 2.0 \times 10^{10}\,M^{-1}\,s^{-1} \tag{18}$$

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2, \quad k = 5.3 \times 10^9\,M^{-1}\,s^{-1} \tag{19}$$
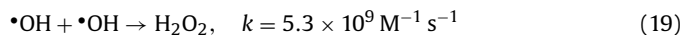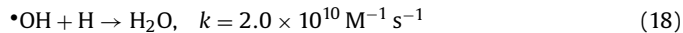
The ${}^\bullet OH$ can also react with H_2O_2 produced in solution and generate HO_2 species as follows:

$${}^\bullet OH + H_2O_2 \rightarrow H_2O + {}^\bullet HO_2, \quad k = 2.7 \times 10^7\,M^{-1}\,s^{-1} \tag{20}$$
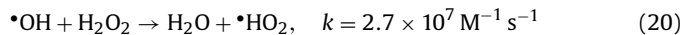
In strong basic solutions the hydroxyl radical can act as a weak acid to undergo the following reaction:

$${}^\bullet OH + OH^- \rightarrow O^- + H_2O, \quad k = 1.2 \times 10^{10}\,M^{-1}\,s^{-1} \tag{21}$$
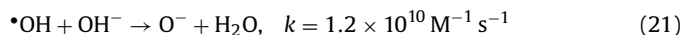
The ${}^\bullet OH$ radical usually abstracts H on reaction with saturated organic compounds, whereas it undergoes addition reaction with organic compounds containing double bonds or aromatic systems:

$${}^\bullet OH + CH_3COCH_3 \rightarrow H_2O + {}^\bullet CH_2COCH_3 \tag{22}$$

$${}^\bullet OH + CH_2 = CH_2 \rightarrow {}^\bullet HOCH_2 - CH_2 \tag{23}$$
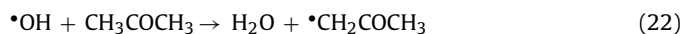
3.1.4. Perhydroxyl radical ($\bullet HO_2$)

The perhydroxyl radical may react as an oxidizing or reducing species depending upon the solute [58]:

$$\bullet HO_2 + Fe^{2+} \rightarrow Fe^{3+} + HO_2^- \tag{24}$$

$$\bullet HO_2 + Ce^{4+} \rightarrow Ce^{3+} + O_2 + H^+ \tag{25}$$

In the absence of other reactions, perhydroxyl radicals can also self-react to form hydrogen peroxide:

$$\bullet HO_2 + \bullet HO_2 \rightarrow H_2O_2 + O_2 \tag{26}$$

The radical can also cause hydrogen abstraction from organic compounds (RH) containing weakly bonded hydrogen atoms such as hydroquinones:

$$\bullet OH + RH \rightarrow H_2O + \bullet R \tag{27}$$

4. Irradiation of dye solutions

Dyes are mainly classified based on their structure, source, color and method of application in color index (C.I.), which has been continuously edited since 1924. Depending on the chromophores, dyes can be classified in various classes. These include the acridine dyes, azo dyes, arylmethane dyes, anthroqinone dyes, nitro dyes, xanthene dyes and the quinine-amine dyes etc. Table 1 summarizes the structures of various classes of dyes along with an example of each class. The investigation of radiation induced decomposition of dyes and their derivatives due to their environmental hazard is a rather popular subject and many papers have been published in this field. Radiation chemistry of dyes is one of the AOPs which takes into account the interaction of reactive species (such as $\bullet OH$ radicals) with a macromolecule and causes it to undergo a stepwise degradation or conversion to smaller species. The radiation induced changes in a given dye solution can be achieved either by steady state radiolysis or pulse radiolysis, as described earlier.

4.1. Steady state radiolysis

Steady state radiolysis is relatively simple in its use and has been used by many workers to investigate radiation induced dye degradation. For example, the radiolysis of two different reactive dyes (Reactive Blue 15 and Reactive Black 5) in aqueous solutions at different dose rates has been reported [37]. The change of absorption spectra and the degree of decoloration (percent reduction in optical density) were examined in the presence of air and H_2O_2. As expected, the absorption bands for both RB15 and RB5 decreased rapidly with increasing irradiation dose. The degree of decoloration of each dye solution with irradiation dose appeared to be 100% for the lower concentration (50 ppm) dye solutions. The authors reported complete decoloration of dyes using 1 and 15 kGy dose of radiation for RB5 and RB15, respectively. The degree of decoloration for both solutions increased with hydrogen peroxide concentration up to about 1.2 mM, suggesting that the decoloration reaction can be further promoted by the addition of hydrogen peroxide. Hydrogen peroxide reacts rapidly with hydrated electron formed in the radiolysis of water, leading to the formation of $\bullet OH$ radical. Therefore, the increase in the degree of decoloration by the addition of hydrogen peroxide would be mainly due to an increase in the $\bullet OH$ radical. This finding suggested that the $\bullet OH$ radical destroyed the dye chro-

Table 1
Structures of various dye classes.

Class	Structure	Representative dye	Structure
Acridine		Acridine O	
Azo		Amido B	
Diarylmethane		Auramine O	
Anthraquinone		Carmine	
Triarylmethane		Malachite green	
Nitro		Naphthol Y	
Xanthene		Rhodamine B	
Quinone-imine		Safranin O	

mophore more efficiently than the hydrated electron. Increasing the hydrogen peroxide concentration above 1.2 mM resulted in a decrease in the degree of degradation, probably due to the scavenging of •OH radicals by the excess hydrogen peroxide.

The radiation induced degradation and decoloration of three textile dyes namely, Janus Green B (JGB), Reactive Black 5 (RB5) and Apollofix Red (AR) have also been studied as a function of gamma irradiation dose and dose rate [46]. In all the three cases the *G* value strongly decreased with the decreasing dose. This may be interpreted in terms of reactions of the intermediates of the water radiolysis not only with the dye molecules but also with the decolorized products. Since the color is mainly due to the azo groups conjugated with the other parts of the molecules, the first act of radiation is most probably the destruction of the double bond of these groups. The main intermediates produced in air-saturated solution that react with the dye are the •OH radicals, H atoms and the superoxide radical anions (the latter species is formed in the hydrated electron/oxygen reaction). As opposed to air-saturated solutions, in N_2 saturated solution the intermediates are mainly hydrated electron, H and •OH radicals. While in the presence of N_2O, the •OH radical is the exclusive species. The results obtained in solution saturated with air, N_2 or N_2O also demonstrated that all the intermediates take part in the decoloration. In N_2O saturated solutions, highly effective radiation induced decoloration was observed, thus indicating the high reactivity of •OH radicals in solution.

In the radiation induced degradation of Congo Red, the primary species generated from radiolysis of water were held responsible for the molecules degradation. Both the oxidative and reductive species yielded high degradation efficiency of Congo Red. It was suggested that the hydrated electron adds to the N=N double bond in very fast reaction thus causing the conjugated system of Congo Red to break down [35]. The UV absorption band near 200 nm was assigned to the absorption of fatty acids and its intensity was lower in the O_2 or N_2O saturated systems than other systems after irradiation. This suggests that Congo Red was oxidized by oxidative species, then converted into fatty acids and finally into CO_2. Among the oxidative species, •OH is the major oxidative transient, and is known to react with benzene and azo moieties with high rate coefficients. The •OH addition to the N=N bond also produces the hydrazyl radical, –N–N(OH). This reaction probably led to the destruction of the intensive color of the dye [59].

Gamma radiolysis with UV–vis spectroscopy and gradient ion pair HPLC separation has been used to follow the degradation of Apollofix-Red SF-28(AR-28) dye and subsequent measurement of the degradation products [36]. The absorbance in the visible range was found to gradually decrease with increasing dose of irradiation, while at the same time there was a shift of the band to longer wavelengths supporting the idea of incorporation of an •OH group into the chromophoric part of the molecule. It was suggested that •OH radicals may add to the azo group: this reaction probably immediately leads to the destruction of the intensive color in the visible range [60]. The radiolytic degradation of Acid Orange 7 (AO7) has also been reported in the literature [61]. The radiation induced decoloration was monitored by UV–vis and the end products were analyzed by different analytical methods. With theoretical analysis and degradation products identified, the mechanisms behind the radiolytic degradation of AO7 under both oxidative and reductive conditions were elucidated. Irradiated under reductive conditions AO7 was found to decompose through N–N cleavage with the formation of aniline, sodium sulfanilamide, 1-amino-2-naphthol, naphthalidine, 1,2,3,4-tetrahydro-2-naphthol, and 2-naphthol etc., whereas under oxidative conditions both N–N and C–N cleavages were suggested as the possible initial steps in the radiolytic degradation of AO7. The mechanism proposed involves the •OH radicals attacking the carbon atom bearing the azo linkage, leading to the cleavage of the C–N bond and the generation of benzene

with phenyldiazene as an intermediate. Moreover, the researchers showed that azo dyes with substituents on phenyl azo portions did not generate volatile products. Instead of C–N cleavage, N–N cleavage accompanying with the formation of nitroaromatics has also been proposed as the main process (60%) in the ultrasonic degradation of azo dyes initiated by the attack of •OH as well [62]. Based on quantum mechanical molecular orbital calculations using density functional theory, it has been proposed that oxidative degradation of amino-substituted azo dyes occurred through cleavage of N–N bond, following the •OH radical addition to the chromophore [63]. It was suggested that the presence of hydrazone tautomers might be responsible for the involvement of C–N cleavage in the degradation of azo dyes.

4.2. Usage of dyes as dosimeters

Quantitative study in radiation chemistry requires knowledge of the amount of energy absorbed from the ionizing radiation. Determination of this absorbed energy is carried out by using a dosimeter. These dosimeters are usually chemicals which respond linearly to radiation and other prevalent conditions. The use of many doped and undoped rare-earths, alkaline earth metal compounds that are conveniently used as dosimeter, is due to the change in their thermoluminescence and other optical properties upon reaction with ionizing radiation. On the other hand a chemical dosimeter generally works due to the change in the chemical composition or property upon irradiation.

Organic dyes which are usually colored compounds have been investigated and used as potential chemical dosimeters. They have been utilized as either in the solution form or embedded in various polymeric films. Various types of polymeric films have been widely used for measuring and mapping of the distribution of absorbed dose in materials treated by intense fields of ionizing photons and electron beams. These radiochromic thin film dosimeters have wide-spread application in radiation processing for installation and process qualification and routine dose control for both gamma and electron irradiation. The introduction of new types of films is due to the efforts of seeking for more reliable, more stable, simpler and cheaper systems as routine dosimeters and/or label dosimeters. In general, the most successful films for dosimetry have been either undyed polymer foils analyzed with UV spectrophotometry, e.g. cellulose triacetate.

Radiation effects on some dyes in non-aqueous solvents and in some polymeric films have also been reported in the literature [64]. The dyes investigated were Diazine red, Methyl Red, Methyl Orange, Janus Green, Dithizone, Congo Red, Phenol Red, Bromothymol Blue, Methyl Thymol Blue and Pyrocatecol Violet, etc. The results obtained showed good linear relationships in the percent color bleaching vs. irradiation dose plot in most of the systems. These findings also suggest the use of these dyes as possible chemical dosimeters in a given dose range.

Polymeric surfaces coated with few other dyes have also been investigated by some other researchers as a possible chemical dosimeter [65–68]. The ionizing radiation-induced bleaching of disazo (Direct) dyes dissolved in Cellophane was mainly attributed to a reduction involving reactive transient radiolytic species, mainly thermal electrons. This occurs when ionizing radiation provides transient reducing species, leading to the elimination of azo linkage and to colorless products in the form of mesomeric hydrazo intermediates and ultimately denitrogenation. The decoupling of disazo compounds occurs sequentially, and since they become strongly electrophilic with the formation of R–N$^+$≡N, they are especially susceptible to reduction by the electrons.

In another recent development, polyvinyl butyral films containing Leuco-Malachite Green (LMG) have been proposed as low-dose dosimeters [69]. The film shows significant color change in the vis-

ible range, and the sensitivity of the film to absorbed dose was enhanced by addition of chloride containing compounds, such as chloral hydrate. The film is suggested to be suitable as dosimeters for dose measurements, e.g. in food irradiation and environmental protection. The mechanism of the radiation induced color change of the LMG from colorless to green was attributed to the cleavage of $\equiv$C–H bond by irradiation which results in the structure rearrangement at one of the triarylmethane groups of the molecule leading to the formation of quinonoid chromophore structure which has a deep green color. Another example of a radiochromic dye film is the polyvinylalcohol based Tetrazolium Violet film [70]. This dosimeter film has been suggested to be used for process control in radiation sterilization. The radiation induced color at lower doses was pink, which turned to violet with increasing dose. Aqueous solution of Methyl Red dye has also been investigated as a potential chemical dosimeter [71]. Color bleaching was explained in terms of $^\bullet$H and $^\bullet$OH radical interaction with the dye in deaerated aqueous solutions and in terms of $^\bullet$HO$_2$/O^{2-} and $^\bullet$OH interactions in aerated aqueous solutions. $^\bullet$H is generally associated with the reversible reductive decolonization, and the radicals $^\bullet$OH and $^\bullet$HO$_2$/O^{2-} are considered to be the cause of the reversible oxidative decolonization.

Besides these few examples on the use of dyes as chemical dosimeters, there are many other citations available in the literature on this topic [72–78].

4.3. Electron beam irradiation of dyes

Radiation induced decomposition and decoloration of reactive dyes have also been investigated by using electron beam [79]. Two different reactive dye (Reactive Red, KE-3B and Reactive Blue, XBR) solutions were irradiated with electron beam at different doses in the absence and presence of H$_2$O$_2$. The characteristic peak value of KE-3B decreased rapidly with increasing absorbed dose from 0 to 5 kGy and then decreased slowly with increasing absorbed dose. The characteristic peak value of XBR decreased smoothly with increasing absorbed dose. The main reason of the difference of the absorption spectra changes after electron beam irradiation between the two dyes is the difference of the chromophores of the two dyes. The chromophore of XBR is –N=N– whereas the chromophore of KE-3B is O=C$_6$H$_5$=O. Therefore, XBR was found to decolorize more easily than KE-3B. The addition of H$_2$O$_2$ promoted the degradation of dye solutions in the same absorbed dose. The reason is that H$_2$O$_2$ can react with e$_{aq}^-$ and H (as shown in Eqs. (10) and (17)), which are produced when water is irradiated by electron beam. $^\bullet$OH is the main reactive species that degrade dyes in radiation treatment of these solutions. The produced amounts of $^\bullet$OH are much larger during the irradiation in the presence of H$_2$O$_2$ than in the absence of H$_2$O$_2$. The study also suggested that at the beginning of the irradiation, big dye molecules were decomposed into smaller organic compounds such as formic acid, acetic acid and other benzoid compounds. Continuation of irradiation by electron beam caused the intermediate compounds to react with active species as hydroxyl radicals to degrade them further to inorganic products.

4.4. Pulse radiolysis of dye solutions

Pulse radiolysis (PR) technique because of its capability to study the nature of transients in a given reaction has also been employed in the cases of dye solutions. The technique has developed to an extent that it is now used as an industrial plant for treating textile dyeing wastewater with electron beam [80]. The results in this case are very promising and have shown an increase in efficiency of removal of COD, and BOD up to 30–40%. A general problem of the PR experiments in connection with dye destruction is the very strong overlap of the absorption spectra of the intermediates and that of the starting compounds, which complicates the measurements. As a result of pulsed energy absorption in the sample, some of the dye molecules transform to intermediates (mainly to radicals) so due to the reaction of dye molecules there is bleaching. On the other hand, the transients usually have strong light absorption in the visible range; in PR one measures the sum of the two effects: bleaching and product formation. The practically obtained spectra are the resultant of the two effects showing decrease of absorption in the visible region. The absorbance of the final product formed in the process can be obtained after a few milliseconds because in this time period all the intermediates would have decayed or reacted in solution.

The pulse radiolysis studies has been used for the reduction of Congo Red and reported in the literature [35]. The study was done in nitrogen saturated dye solution and has the findings have shown that the solvated electron produced as a result of water irradiation reacted with the dye molecule to cause its reduction. The reaction rate constant of Congo Red with e$_{aq}^-$ was determined to be 3.6×10^9 M^{-1} s^{-1}. The transient absorption spectrum recorded after the pulse radiolysis of N$_2$O saturated Congo Red aqueous solution was also investigated and the bimolecular rate constant for the reaction between $^\bullet$OH and Congo Red was found to be 1.2×10^{10} M^{-1} s^{-1}. In this study it was proposed that e$_{aq}^-$ is transferred into $^\bullet$OH when the solution is saturated with N$_2$O. In the presence of O$_2$, both e$_{aq}^-$ and H are converted into oxidative species. The e$_{aq}^-$ adds to the –N=N– double bond of Congo Red in a very fast reaction and causes the molecule to break down. Besides this, the $^\bullet$OH adds to the –N=N– double bond and produces the hydrazyl radical, –N–N– (OH). This reaction probably led to the destruction of the intense color of the dye.

In another study on Apollofix-Red SF-28 (AR-28) the reactions of hydrated electron e$_{aq}^-$ and $^\bullet$OH radical were investigated separately and it was found that $^\bullet$OH radical preferentially reacted with the unsaturated bonds of the molecule [36]. Furthermore, the reactions of the $^\bullet$OH adduct radicals with the AR-28 molecules partly reformed the dye structure. The products formed in the reaction of $^\bullet$OH and AR-28 molecules were also found to be highly reactivity towards the $^\bullet$OH radicals. For these reasons the efficiency of $^\bullet$OH radicals in decoloration of the solution was relatively low. The efficiency was much higher, close to unity for e$_{aq}^-$. The reaction of e$_{aq}^-$ with AR-28 led to an immediate destruction of the color giving centre. The reaction of hydrated electron with the azo group is a fast reaction and the radical anion quickly protonates forming a hydrazyl radical as follows:

$$-N=N- + e_{aq}^- \rightarrow -N-N^- - \rightarrow (+H_2O) \rightarrow -N^\bullet-NH- + OH^-$$
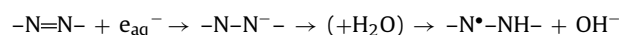
The effective fading of the dye solution was suggested due to the fast reaction of e$_{aq}^-$ with the unreacted AR-28 molecules and also to the low reactivity of the e$_{aq}^-$ with the transformed molecules.

The color changes accompanying one-electron reduction and oxidation of the azo dyes have also been reported in the literature [81]. Under cryogenic conditions, the radical anion of the dye 4-N,N-diethylaminoazobenzene, have been spectroscopically characterized by the electronic absorption spectra and color changes of the solution. The transient radical anion generated upon reduction of the 4-N,N-diethylaminoazobenzene was found to stabilize under cryogenic matrix conditions. Both the protic and aprotic solvents were used to show strong stabilization of the radical anion by a hydrogen bonding to solvent alcohol molecules. Thermal annealing of the matrix caused the radical anion to undergo fast protonation and form a hydrazyl radical. Azo dyes are known to form adducts with solvent or hydrazyl radicals. The results obtained in matrix experiments were found to complement the results obtained in solution at ambient temperatures. The products of a one-electron oxidation of the dye were also identified in this study which produces the radical cation, which further deprotonates to give the

aminoalkyl radical. It was observed that the yellow color of the dye solution changed to green upon one-electron reduction of the dye both in MTHF and in alcoholic matrices. Following protonation, the color changed to dark green. Finally, the formation of adduct of the azo dye with radical species caused the color change to dark orange indicating the presence of the radical cation.

The reactions of the C.I. Reactive Black 5 with short lived $e_{aq}{}^-$, $^\bullet$OH radical and H atom intermediates of water radiolysis in aqueous solution were investigated by pulse radiolysis with kinetic spectroscopic detection [49]. The $e_{aq}{}^-$ was found to add to the azo group, and adduct radical anion rapidly protonated forming hydrazil radical. Based on the transient spectra, similar intermediates were found to be in H atom and hydrated electron reaction. The $^\bullet$OH radical most probably adds to the azo group, however, it attacks also the aromatic rings. The strong absorbance found is attributed to the high conjugation of the radical site with the aromatic rings. The intermediates of water radiolysis, $e_{aq}{}^-$, H and $^\bullet$OH reacted with the dye molecules in very fast reactions with rate constant value in the 10^{10} M^{-1} s^{-1} range.

Kinetic and spectral properties of Rhodamine 6G free radicals produced in pulse radiolysis experiments have also been reported in the literature [82]. In the presence of Br$^\bullet{}^-$ (which are produced by a series of radiolytic reactions of bromide ions added to dye solution), it was found that these ions reacted at near diffusion-controlled rates with Rhodamine 6G to produce the cation radicals, RhH$^{\bullet 2+}$ and Rh$^{\bullet +}$ (the deprotonated form). Both forms of the cation radical showed characteristic difference absorption spectra, with maxima at around 470 nm, with the protonated form, RhH$^{\bullet 2+}$ absorbing more intensely than the deprotonated form. Both RhH$^{\bullet 2+}$ and Rh$^{\bullet +}$ were relatively long-lived species, the former was easily detected up to one second after the pulse. At the end of the decay of Rh$^{\bullet +}$, significant increases (relative to the dye ground state) in absorption in the typical rhodamine dye laser output wavelength range (555–620 nm) were observed. Oxygen did not react with either of the cation radicals. However, the peroxy radicals, $O_2{}^{\bullet -}$ (or its protonated form, $^\bullet HO_2$) were found to react with these dye radicals. It was suggested that the reaction regenerated the ground state of the dye, although the percentage regeneration was pH dependent, being in competition with the pH dependent dismutation of $O_2{}^{\bullet -}$/$^\bullet HO_2$.

Pulse radiolysis and chemical analysis of azo dyes in aqueous solution using p-Phenylazoaniline as a model dye has also been investigated [51]. The spectroscopic and kinetic characteristics of transients produced by electron reduction and oxidation of p-phenylaniline (PAA) at various pH values were studied. In the presence of air at pH 4–10 the transient spectra were found to be very similar to those observed by the $^\bullet$OH attack on PAA at pH 4. The main reaction path of the $^\bullet$OH radicals is expected to be on the –N=N– group, followed by that on the different positions of the aromatic rings, resulting in OH-adducts and on the NH$_2$ group. This indicated that in all cases the $^\bullet$OH radicals are the major reactive species towards PAA. Under the given experimental conditions, the very fast attack of $e_{aq}{}^-$ was found to take place predominantly on the azo-bond forming PAA$^{\bullet -}$ radical anion. The radical anion, in the presence of a scavenger, such as, 2-propanol, rapidly protonates to form hydrazyl radical (PAAH$^\bullet$).

Table 2 shows the rate constants of transient species with some dyes. Besides the above mentioned studies, there are some literature citations where a combination of laser and pulse radiolysis technique have been used to look at some of the dye related reactions in selective media [83–86]. The main aim of these studies was to produce transients by high energy radiation pulse followed by a laser pulse to excite the species. The properties of the transients such as their absorption characteristics like intensity, spectral broadening and contribution from the singlet or triplet state can then be evaluated by using the usual transient spectroscopic techniques.

Table 2
Rate constants of $^\bullet$OH, $e_{aq}{}^-$ and $^\bullet$H reactions with some dyes (Notre Dame Radiation Chemistry Data Center, www.rcdc.nd.edu).

| Compound	k (M^{-1} s^{-1})		
	$^\bullet$OH	$e_{aq}{}^-$	$^\bullet$H
Methyl Orange	1.1×10^{10}		
Calgamite	1.1×10^{10}		
Orange I	9×10^9		
Acid Orange 7	4.08×10^9		
Naphthol Blue Black			1.04×10^9
Acid Red 265	9.3×10^9		
Congo Red	1.2×10^{10}	1.6×10^9	
Arylazo-2-naphthol	1.1×10^{10}	2.5×10^{10}	

5. Effect of operational parameters
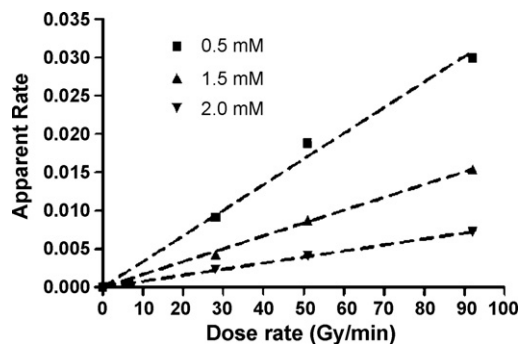
5.1. Effect of radiation dose

As would be expected, increasing the radiation dose dramatically increases the rate of dye degradation. This effect is seen by numerous groups on various dyes [34–38]. At a higher radiation dose, more reactive species are generated in solution, which in turn are available to react with and degrade dye molecules. A representative experiment is shown in Fig. 1, where Methyl Orange was exposed to different amount of radiation dose and its decoloration measured. Furthermore, increasing the radiation dose rate also caused a direct increase in the dye degradation rate at three different Methyl Orange concentrations (Fig. 2) [38].

5.2. Effect of oxygen and pH

In the presence of dissolved oxygen, the hydrogen atom would react rapidly with oxygen, leading to the formation of the highly
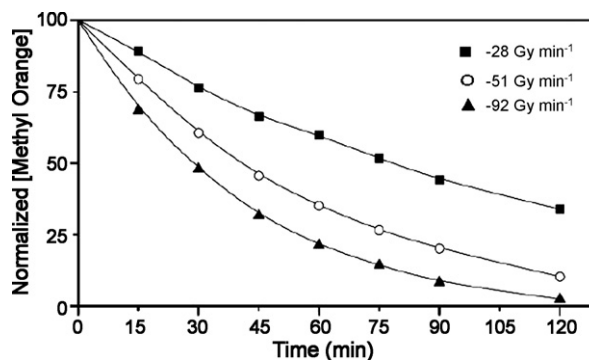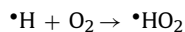

Fig. 1. Effect of increasing radiation dose on the degradation of Methyl Orange dye (0.5 mM) [38].


Fig. 2. Effect of increasing radiation dose on the apparent rate of Methyl Orange dye degradation at three different initial concentrations [38].

oxidizing hydroperoxy radicals ($^\bullet HO_2$), as shown below [89]:

$$^\bullet H + O_2 \rightarrow \ ^\bullet HO_2$$

Chemical oxidation of organic species, such as dyes, in the presence of oxygen is primarily due to the interaction of oxidizing $^\bullet OH$ and $^\bullet HO_2$ radicals with the dyes in the aqueous solution.

Literature review has shown limited findings on the effect of pH on the irradiation of dyes. One such study by Agustin et al. [89] on the degradation of dyes at different pH values was carried out by irradiating different aqueous dye solution to a dose of 0, 2, 4, 6, 8 and 10 kGy. Surprisingly, the authors found the effect of pH to be very structure and radiation dose dependent. However, in general, the degradation process showed reduced sensitivity at high pH values, probably due to the acid–base properties of the $^\bullet OH$ radicals. In strong basic solution, the $^\bullet OH$ radicals dissociate to the less reactive $O^{\bullet -}$ radicals:

$$^\bullet OH \leftrightarrow H^+ + \ ^\bullet O^- \ (pH \ 11.9)$$
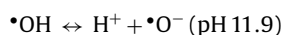
In the above-mentioned study, only two of the three different azo dyes tested namely, Cibacron Violet and Cibacron Golden Yellow, degraded in the pH range from 3 to 9 with a reduced sensitivity at high pH.

In fact the degradation scheme depends on the relative reactivity of the various species, availability of oxygen, dose, pH of the solution and temperature:

$$\text{in acidic solution}: \quad e_{aq}^- + H^+ \rightarrow H^\bullet, \quad k = 2.3 \times 10^{10} \ M^{-1} \ s^{-1}$$
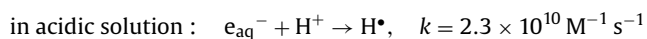
The reducing H atoms are scavenged by oxygen leading to a formation of $^\bullet HO_2$ which can be involved in the degradation process. The $O_2^{\bullet -}$ species are not very reactive but at pH >7 the $^\bullet OH$ radicals are the major primary attacking transients. The sharp decrease in the degradation at pH >9 may be a result of the low reactivity of $O^{\bullet -}$ and $O_2^{\bullet -}$ species to the attack of the dyes.

5.3. Effect of hydrogen peroxide

Hydrogen peroxide reacts rapidly with hydrated electron formed in the radiolysis of water, leading to the formation of $^\bullet OH$ radical Therefore, the increase in the degree of decoloration by the addition of hydrogen peroxide would be mainly attributable to an increase in the $^\bullet OH$ radical. The degree of decoloration for 50 ppm Reactive Blue 15 (RB 15) and 50 ppm Reactive Black 5 (RB 5) solutions containing hydrogen peroxide as a function of hydrogen peroxide concentration showed that the degree of decoloration for both solutions increased with hydrogen peroxide concentration up to about 1.2 mM. This suggests that the decoloration reaction is promoted by addition of hydrogen peroxide [88]. This finding suggested that the $^\bullet OH$ radical destroyed the dye chromophore more efficiently than the hydrated electron does. Increasing the hydrogen peroxide beyond concentration above 1.2 mM resulted in a decrease in the degree of degradation. As the hydrogen peroxide concentration increases, a part of the $^\bullet OH$ radicals are scavenged by the excess hydrogen peroxide. The same trend was observed when conventional AOPs were used for dye degradation, Fig. 4 [93].
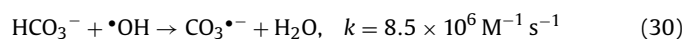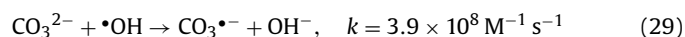
5.4. Effect of ions

The degradation of dyes by convential AOPs has shown that the dye degradation is also effected by the presence of additives in solution matrix [44]. These additives are generally present as ions which are initially added to the dye solution as ionic compounds in order to improve the industrial process. However on release of wastewater, the ions become an integral part of the effluent. Many common ions present in dye wastewater are Fe^{2+}, Zn^{2+}, Ag^+, Na^+, Cl^-, PO_4^{3-}, SO_4^{2-}, BrO_3^-, CO_3^{2-}, HCO_3^- and persulphate ions. Each of these added ions causes a certain decrease in percentage degradation of the dye solution. The change in dye degradation in the presence of some selective ions is explained below on the basis of their chemical reactions in solution. For example, Fe^{2+} ions most likely undergoes the following chemical reaction in solution with $HO^\bullet$ radicals already produced in solution:

$$^\bullet OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \tag{28}$$

The above reaction has an appreciably high rate constant value of $3.5 \times 10^8 \ M^{-1} \ s^{-1}$ [90]. Thus in the presence of Fe^{2+}, $^\bullet OH$ radicals are easily converted into OH^-, thereby decreasing their concentration and thus less degradation of dye solution is observed.

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

$$CO_3^{2-} + \ ^\bullet OH \rightarrow CO_3^{\bullet -} + OH^-, \quad k = 3.9 \times 10^8 \ M^{-1} \ s^{-1} \tag{29}$$

$$HCO_3^- + \ ^\bullet OH \rightarrow CO_3^{\bullet -} + H_2O, \quad k = 8.5 \times 10^6 \ M^{-1} \ s^{-1} \tag{30}$$

Similarly, a decrease in degradation value in the presence of Cl^- is due to the following reaction:

$$^\bullet OH + Cl^- \rightarrow HOCl^{\bullet -} \tag{31}$$

$$HOCl^{\bullet -} + H^+ \rightarrow Cl^\bullet + H_2O \tag{32}$$

The presence of sulphate ions in solution also causes a decrease in percentage degradation because these ions can react with $HO^\bullet$ radicals in solution and result in their depletion as follows [91]:

$$SO_4^{2-} + \ ^\bullet OH \rightarrow SO_4^{\bullet -} + OH^- \tag{33}$$

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

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\bullet -} + SO_4^{2-} \tag{34}$$

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

$$SO_4^{\bullet -} + H_2O \rightarrow \ ^\bullet OH + SO_4^{2-} + H^+ \tag{35}$$
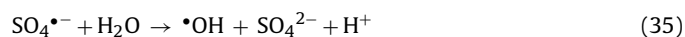
Since $SO_4^{\bullet -}$ is less reactive than $^\bullet OH$ radicals, therefore SO_4^{2-} concentration increases in solution which leads to less dye degradation.

The addition of bromate ion (BrO_3^-) can also decrease percentage degradation. This can be explained on the basis that this species is an efficient electron scavenger and can react in the solution as follows [44]:

$$BrO_3^- + 6e^- + 6H^+ \rightarrow Br^- + 3H_2O \tag{36}$$
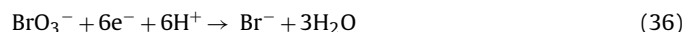
The bromide ions produced in the reaction can react with $^\bullet OH$ radicals in solution (rate constant value $= 1.1 \times 10^9 \ M^{-1} \ s^{-1}$) thus decreasing their concentration which result in less degradation:

$$Br^- + \ ^\bullet OH \rightarrow \ ^\bullet Br + OH^- \tag{37}$$

The above reaction schemes should also be valid in the case of irradiation of dye solutions as the fundamental species produced in this process is also $^\bullet OH$ radical which causes further reactions to degrade the dye.

Dyes can also sometimes act as sensitizers and can enhance degradation of other compounds present in solution. Due to synergistic effect, when dyes are degraded by radiation due to oxidation process, some metal ions may be reduced simultaneously to a lower oxidation state. This phenomenon has been reported in the literature with photolytic illumination of dyes [92], but is not reported
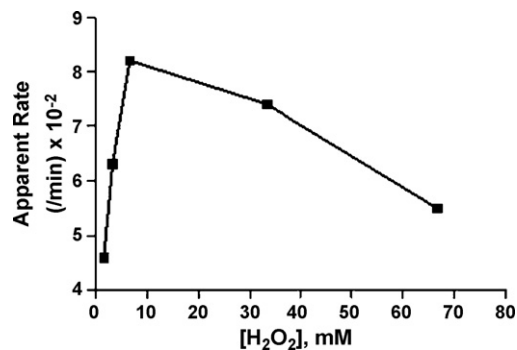
Table 3
Effect of various ions on Safranin O (SO) degradation (after 30 min), [SO] = 20 μM and [H_2O_2] = 1.67 mM [12].

Ions	k (×10^{-2} min^{-1})	%Degradation
–	5.9	84
Anions		
NO_3^-	4.35	72
SO_4^{2-}	3.96	69
CO_3^{2-}	3.7	68
Cl^-	2.84	57
Br^-	2.7	56
CH_3COO^-	1.15	30
SO_3^{2-}	0.52	14
Cations		
Fe^{3+}	38.85	98 (10 min)
K^+	6.19	85
NH_4^+	5.88	83
Ni^{2+}	5.63	82
Co^{2+}	5.12	79
Ca^{2+}	4.84	77
Mg^{2+}	4.99	77
Pb^{2+}	4.09	72
Cd^{2+}	3.9	72
Cu^{2+}	1.89	44
Ag^+	0.17	3

for high energy radiation degradation of dyes. However, the same effect of ions as reported for other AOPs would be expected for radiation induced dye degradation. Table 3 summarizes the results of our own study on photolytic degradation of Safranin O [12].

5.5. Correlation of dye degradation with its type

Although literature survey has revealed many examples of dye degradation studies, however, there is no example of any correlation which might exist between % degradation and structure or class of dyes. For example, a comparative study of Reactive Blue 15 (RB 15) and Reactive Black 5 (RB 5) has shown that the decoloration of RB5 by irradiation was much more than that of RB15. This was attributed to the difference in the structure of both dyes (Fig. 3). The (–N=N–) groups are very sensitive to radiation and the ruptured immediately when exposed to low doses of gamma irradiation [87,88]. However, it is expected that dye degradation rates for different dyes will not

Fig. 4. Effect of increasing hydrogen peroxide on the photolytic decoloration of Acridine O (dye concentration = 2 μM) [Rauf et al., unpublished data].

Table 4
Comparative % degradation of various classes of dyes [93].

Dye	%Degradation	Dye class
Auramine O	81	Diarylmethane
Safranin O	77	Quinone-imine
Malachite green	76	Triarylmethane
Amido Black	68	Azo
Rhodamine B	50	Xanthene
Carmine	49	Anthraquinone
Auramine O	81	Diarylmethane
Safranin O	77	Quinone-imine
Malachite green	76	Triarylmethane
Amido Black	68	Azo
Rhodamine B	50	Xanthene
Carmine	49	Anthraquinone

be too different (within one order of magnitude). This is based on the data showing that reaction rates of hydroxyl radicals with various dyes are all within an order of magnitude, as shown in Table 2 (Fig. 4).

Our own studies on different classes of dyes have helped us establish a relative rank order of ease of dye degradation as follows (Table 4): Auramine O > Safranin O > Malachite Green > Amido Black > Rhodamine B > Carmine [93]. Although, this rank order was established using the UV/H_2O_2 photolytic AOP, it is most probable that the same rank order will be observed in the case of irradia-
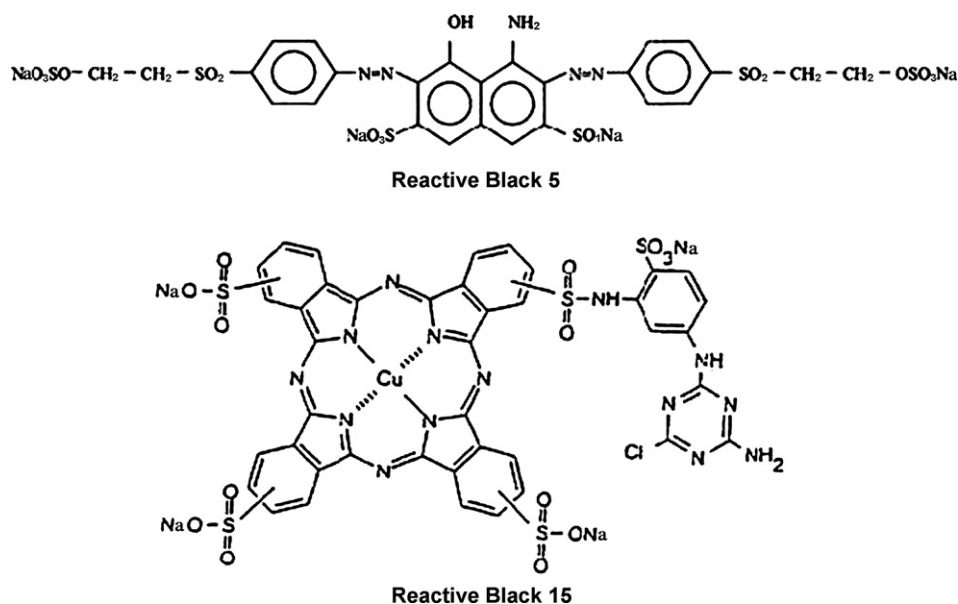
Fig. 3. Chemical structures of Reactive Black 5 and Reactive Black 15 dyes.

tion of dyes (another type of AOP) as hydroxyl radicals (which are responsible for dye degradation) are generated in all the AOPs. In general, our findings have revealed that diarylmethane class dyes are most effectively degraded, whereas anthraquinone class dyes are least degraded. At this stage it might not be possible to elaborate more on this aspect as more detailed studies are needed in this direction.

6. Pilot plant application

Pilot plant application and industrial scale experiments have demonstrated the effectiveness of high-energy irradiation pretreatment of wastewater when combined with conventional methods. In most cases these plants were constructed to treat municipal wastewater [94]. A pilot plant (output $1000 \, m^3$/day) with ELV electron accelerator (energy 1 MeV, beam power 40 kW) for combined electron-beam and biological treatment of industrial textile dyeing wastewater is operating in Taegu Dyeing Industrial Complex (Daegu, Korea) since 1998 [82]. This plant has shown considerable reduction of chemical additive consumption, and also an increase in removal efficiencies of chemical oxygen demand and biological oxygen demand. On the basis of data obtained from pilot plant operation, construction of an industrial scale plant was started in 2004, and finished in December 2005. 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 biotreatment facility. The continuous operation of this facility provides additional data on reliability for a detailed evaluation.

7. Conclusion

During the radiolysis of aqueous dye solutions, and saturated with air, most of the e_{aq}^- and $^\bullet H$ atoms are converted to $O_2^{\bullet-}$ and $^\bullet HO_2$, respectively. The $O_2^{\bullet-}$ and $^\bullet HO_2$ are rather unreactive towards aromatics. However, they may react readily with some of the intermediate products in the mineralization process. On the other hand, e_{aq}^- is very effective in decolorization but is less active in the further degradation of the products formed. The degradation of the dyes is initiated exclusively by $^\bullet OH$ attack. Besides this, the hydroxyl radicals produced upon water radiolysis are electrophilic oxidants and they attack the electron-rich sites of the molecules such as the aromatic rings and the $–NH_2$ group which are generally present in many dye molecules.

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