CHAPTER I
INTRODUCTION AND LITERATURE REVIEW

1.1. Radiolysis of aqueous systems:

Water and aqueous solutions of various solutes have attracted the attention of researchers since the foundation of radiation chemistry. This is due to the fact that it is a suitable way for investigating the key regularities of the interaction of ionizing radiation with condensed matter. Further studies of water radiolysis mechanism describe the formation of the products of water decomposition H_2, H_2O_2 and O_2 (*J*enks, 1965; Jenks et al.,1967)

The first experience in describing the data on the formation of stable products of water radiolysis, H_2O_2, O_2 and H_2, was reported in a number of publications (*Boyd et al.,1980; Burns et al.,1983*)

Ershov and Gordeev (2008) developed a kinetic model for the radiolysis of pure water describing the formation of H_2, H_2O_2 and O_2 and the radiation chemical transformations of aqueous solutions containing different compounds over a broad range of concentrations, pH, absorbed doses and dose rates are proposed and substantiated.

The majority of the radiation-chemical studies are carried out in dilute aqueous solutions. Hence, practically, all the radiation energy is absorbed in water and the radicals generated by the absorption of the ionizing radiations (reaction 1) interact with the solute. With the help of the pulse radiolysis technique the reaction rate constants of the water radicals with a large number of organic and inorganic substrates have been determined.

$$H_2O \rightsquigarrow e^{-}_{aq}\ ,\ {}^{\bullet}H\ ,\ {}^{\bullet}OH\ ,\ H^{+}\ ,\ H_2\ ,\ H_2O_2 \qquad [1]$$

G values 2.6 , 0.6 , 2.7 , 2.6 , 0.45 , 0.7 molecules/100eV

The measured G-values of e_{aq}^{-}, $^{\bullet}H$, $^{\bullet}OH$ and H_2 are found to continuously increase, while $G(H_2O_2)$ decreases with increasing temperature. The effect of temperature on the primary yields of e^{-}_{aq}, $^{\bullet}H$, $^{\bullet}OH$ and H_2O_2 is well understood within the generally accepted diffusion kinetic model of spurs and has been reproduced satisfactorily by deterministic calculations (*Swiatla and Buxton, 1998; Herve du Penhoat et al., 2000; Nogradi, 2003*)

Water radiolysis involves ionization and excitation of a water molecule. Direct ionization of water produces a radical ion and a free subexcitation electron (E < 7.4 eV).

$$H_2O \rightsquigarrow H_2O^{\bullet} + e^{-}$$

Energy transfer can produce a water molecule in an excited state.

$$H_2O \rightsquigarrow H_2O^{*}$$

The time scale for the creation of these species is of the order of 10^{-16} Sec. The three initial species begin to diffuse and react with each other or with other molecules in the medium. Some of these reactions produce radicals. By radicals we mean an atom or molecule that contains an unpaired electron. Radicals are highly reactive and can be neutral or charged.

The electron is captured by water molecules through dipolar interactions, becoming solvated, and referred to as an aqueous electron or a solvated electron:

$e^{-} + H_2O \rightarrow e^{-}_{aq}$ surrounded by a "cage" of water;

$e^{-} + H^{+} \rightarrow H^{\bullet}$ or it can react with H^+ to form a radical.

The positive ion of water can dissociate to produce a hydroxyl radical and a hydrogen ion.

$$H_2O^{+} \rightarrow H^{+} + HO^{\bullet}$$

The excited water molecule can dissipate excess energy by bond breakage to produce hydroxyl and hydrogen radicals.

$$H_2O^{*} \rightarrow HO^{\bullet} + H^{\bullet}$$

where * excited species.

It takes ~ 5 eV to break the O-H bond (*Introduction to Ionizing Radiation, 2003)*

The free radicals formed when water is irradiated (e_{aq}^{-}, H, OH, O_2^{-}) are generally referred to as the radical products; and the molecular species (H_2 and H_2O_2), as the molecular products. They may also be divided into reducing (e^{-}_{aq}, H) and oxidizing (OH, HO_2/O_2^{-}, H_2O_2) species;

$$H^{\bullet} + H^{\bullet} \rightarrow H_2$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$$

H_2 is relatively unreactive and in most cases escapes from the system without any further reaction. (HO_2/O_2^{-}) is not a major product with γ and electron irradiation.

The peroxyl radical, which is a minor product when pure water is irradiated but may be formed in relatively large amounts when air or oxygen is present, dissociates at pH above 4 to give the superoxide ion, O_2^-, which is also generally an oxidizing radical (*Woods & Pikaev 1994*).

$$e^-_{aq} + O_2 \rightarrow O_2^- + H_2O$$

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

$$HO_2 \rightleftharpoons H^+ + O_2^-$$

1.1.1. Properties of $H^\bullet$, e_{aq}^-, $^\bullet OH$, $^\bullet O^-$:

1.1.1.1.The H atom:

Fragmentation of the water excited state is of special interest and one of the major products of this process is the H atom. H atom yields from initial water decomposition can be estimated in the vapor (*Armstrong, 1987; Johnson and Simic, 1967*) but the corresponding value for radiolysis of the liquid phase is not known accurate. A complete understanding of the initial radiolytic decomposition of liquid water requires an accurate and systematic investigation of the H atom yield.

The H atom is one of the minor radical species in the radiolysis of water except in very acidic media and its reducing reactions are generally overshadowed by the more abundant hydrated electron (*Buxton, 1987*). However, the development of fast time resolved radiolytic and photolytic techniques have led to a new emphasis on the initial decomposition of water (*Garrett et al., 2005*).

The production of H atoms is difficult to measure. They behave like hydrated electrons in some systems and like OH radicals in others, which makes it difficult to find selective scavengers (*Buxton, 1987).* Yields of H atoms are typically determined by difference measurements of H_2 yields (*Appleby and Schwarz, 1969; Draganic Z. and Draganic, I., 1972; Elliot et al., 1996*).

Radiolytically produced H atoms are allowed to abstract H atoms from selected solutes to give H_2, which is easily measured. Subtraction of the H_2 yield in water without the H atom scavenger is assumed to give a good measure of the H atom yield (*Parajon et al.,2008*).

1.1.1.2.The Hydrated Electron:

The hydrated electron may be visualized as an excess electron surrounded by a small number of oriented water molecules and behaving in some ways like a singly charged anion of about the same size as the iodide ion. Its intense absorption band in the visible region of the spectrum makes it a simple matter to measure its reaction rate constants using pulse radiolysis combined with kinetic spectrophotometry. As expected from its standard reduction potential of -2.9 V, the hydrated electron reacts rapidly with many species having more positive reduction potentials. Its mode of reaction can be generally represented as the one-electron transfer process.

$$e^{-}_{aq} + S^{n} \rightarrow S^{n-1}$$

Where n is the number of positive charges on the solute ions, although in some cases the electron adduct immediately dissociates.

The hydrated electron acts as a nucleophile in its reactions with organic molecules, and its reactivity is greatly enhanced by electron-withdrawing substituents adjacent to alkene double bonds or attached to aromatic rings. Increased reactivity is also observed when organic molecules contain substituent halogen atoms, in which case the negative ion formed rapidly eliminates the halide ion.

$$e^{-}_{aq} + RX \rightarrow RX^{-} \rightarrow R^{\bullet} + X^{-}$$

where X is the halide atom.

1.1.1.3.The Hydroxyl Radical:

The hydroxyl radical is a powerful oxidant, having a standard reduction potential of 2.7 V in acidic solution and 1.8V in neutral solution where the free energy of neutralization of OH^{-} by H^{+} is not available. The reaction of $^{\bullet}OH$ with positive ions is often represented as a simple electron transfer reaction,

$$^{\bullet}OH + S^{n} \rightarrow S^{n+1} + OH^{-}$$

where n is the number of charges on the positive ion.

In its reactions with organic molecules $^{\bullet}OH$ behaves as an electrophile which is most likely to attack a molecule at the point of highest electron density, whereas $^{\bullet}O^{-}$ is a nucleophile which is most likely to attack a molecule at the point of lowest electron density. Thus $^{\bullet}OH$ readily adds to unsaturated bonds but $^{\bullet}O^{-}$ does not. Both forms of the radical abstract H from C-H bonds, and this can result in the formation of different products when the pH is raised to where $^{\bullet}O^{-}$, rather than $^{\bullet}OH$, is the reactant. For example, if an aromatic molecule carries an aliphatic side chain, $^{\bullet}O^{-}$ attacks there by H abstraction while $^{\bullet}OH$ adds preferentially to the aromatic ring. Hydroxyl radicals and hydrogen atoms undergo similar types of reaction with organic molecules, but in abstraction from C-H bonds $^{\bullet}OH$ is more reactive and less selective than H because the formation of the H-OH bond is 57 kJ mol^{-1} more exothermic than the formation of the H-H bond (*Buxton et al., 1988*).

1.2. Classification of some dye types:

All aromatic compounds absorb electromagnetic energy but only those that absorb light with wavelengths in the visible range (~350-700 nm) are colored. The color of a dye is provided by the presence of a chromophore group. A chromophore is radical configurations consisting of conjugated double bonds containing delocalized electrons, electron-withdrawing or electron-donating substituents that cause or intensify the color of the chromophore by altering the overall energy of the electron system. Some common chromophore groups include azo (─N═N─) or carbonyl (─C═O) groups. The chromogen, which is the aromatic structure normally containing benzene, naphthalene or anthracene rings, is part of a chromogen-chromophore structure along with an auxochrome. The presence of ionizing groups known as auxochromes results in a much stronger alteration of the maximum absorption of the compound and provides a bonding affinity. Some common auxochrome groups include $-NH_3$, $-COOH$, $-HSO_3$, $-OH$. Each different dye is given a color index

(C.I.) generic name determined by its application characteristics and its color.

There are various types of dyes belonging to different classes according to chemical structures and on the chromophore group. Thus, it is important to give some account on dyes and their general classification.

Dyes may be classified according to either their chemical structures or their application to fibers. For a systematic treatment of the chemistry of dyes a classification based primarily on characteristic structural units is more satisfactory.

Based on chemical structure or chromophore, 20-30 different groups of dyes can be discerned. Each different dye is given a C.I. (Color Index) generic name determined by its application characteristics and its color. The Color Index discerns different application classes which are as follows (*Abrahart, 1997*):

1. Acid dyes:

The largest class of dyes in the Color index is acid dyes. Acid dyes are anionic compounds that find their main application in dyeing nitrogen-containing fabrics like wool, polyamide, silk and modified acryl. They bind to the cationic NH_4^+ ions of those fibres. Most acid dyes are azo, anthraquinone or triarylmethane, azine, xanthene, nitro and nitroso compounds rather than the presence of acid groups (sulphonate, carboxyl) in the molecular structure of these dyes.

2. Reactive dyes:

Reactive dyes are dyes with reactive groups that are capable of forming a covalent bond between a carbon atom of dye molecule and OH-

, NH-, or SH- groups in fibres (cotton, wool, silk, nylon). The reactive group is often a heterocyclic aromatic ring substituted with a chloride or fluoride atom, e.g. dichlorotriazine. Another common reactive group is vinyl sulphone. Most (~80%) reactive dyes are azo or metal complex azo compounds but also anthraquinone and phthalocyanine reactive dyes are applied, especially for green and blue color. In the Color Index, the reactive dyes form the second largest dye class.

3. Metal complex dyes

Among acid and reactive dyes, many metal complex dyes can be found (not listed as a separate category in the Color Index). These are strong complexes of one metal atom (usually chromium, copper, cobalt or nickel) and one or two dye molecules, respectively i.e. 1:1 and 1:2 metal complex dyes. Metal complex dyes are usually azo compounds.

4. Direct dyes

Direct dyes are mostly azo dyes with more than one azo bond or phthalocyanine, stilbene or oxazine compounds. In the Color Index, the direct dyes form the second largest dye class with respect to the amount of different dyes.

5. Basic dyes

Basic dyes are cationic compounds that are used for dyeing acid-group containing fibres, usually synthetic fibres like modified polyacryl. They bind to the acid groups of the fibres. Most basic dyes are diarylmethane, triarylmethane, anthraquinone or azo compounds.

6. Mordant dyes

Mordant dyes are fixed to the fabric by the addition of a mordant, a chemical that combines with the dye and the fibre. Though mordant dyeing is probably one of the oldest ways of dyeing, the use of mordant dyes is gradually decreasing. They are used with wool, leather, silk, paper and modified cellulose fibres. Most mordant dyes are azo, oxazine or triarylmethane compounds. The mordants are usually dichromates or chromium complexes.

7. Disperse dyes

Disperse dyes are scarcely soluble dyes that penetrate synthetic fibres (cellulose acetate, polyester, polyamide, acryl, etc.). Disperse dyes form the third largest group of dyes in the Color Index. They are usually small azo or nitro compounds (yellow to red), anthraquinones (blue and green) or metal complex azo compounds (all colors).

8. Pigment dyes

Pigment dyes (i.e. organic pigments) represent a small fraction of widely applied group of colorants. These insoluble, non-ionic compounds or insoluble salts retain their crystalline or particulate structure throughout their application. Pigment dyeing is achieved from a dispersed aqueous solution and therefore requires the use of dispersing agents. Pigments are usually used together with thickeners in print pastes for printing diverse fabrics. Most pigment dyes are azo compounds(yellow, orange, and red) or metal complex phthalocyanines (blue and green). Also anthraquinone and quinacridone pigment dyes are applied.

9. Vat dyes

Vat dyes are water-insoluble dyes that are particularly and widely used for dyeing cellulose fibres. The dyeing method is based on the solubility of vat dyes in their reduced (leuco) form. Reduced with sodium dithionite, the soluble leuco vat dyes impregnate the fabric. Next, oxidation is applied to bring back the dye in its insoluble form. Almost all vat dyes are anthraquinones or indigoids.

10. Anionic dyes and ingrain dyes

Anionic dyes *and* Ingrain dyes (naphthol dyes) are the insoluble products of a reaction between a coupling component usually naphthols, phenols or acetoacetylamides and a diazotized aromatic amine. This reaction is carried out on the fibre. All naphthol dyes are azo compounds.

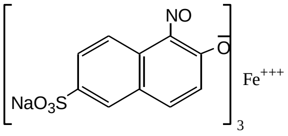
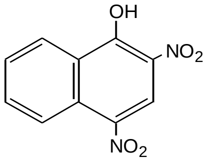
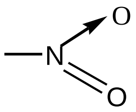
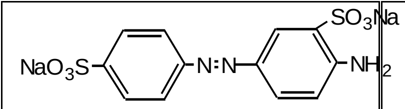
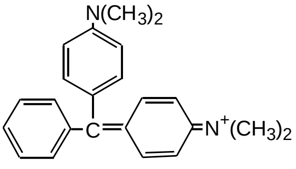
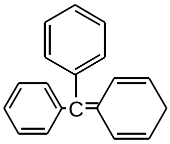
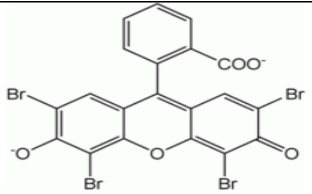
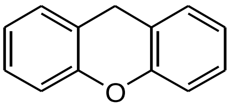
11. Sulphur dyes

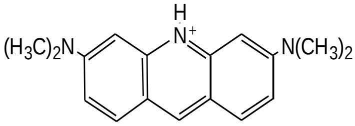
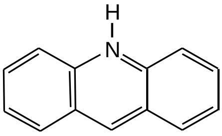
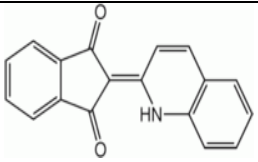
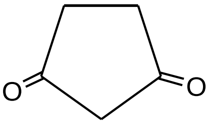
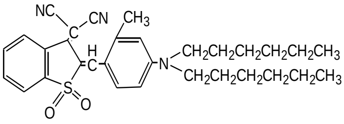
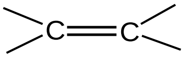
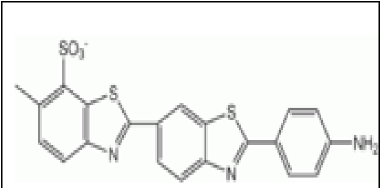
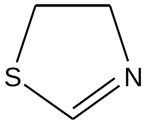
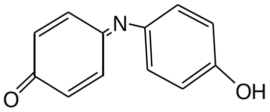
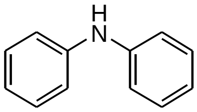
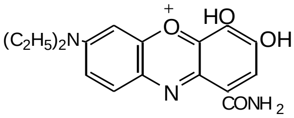
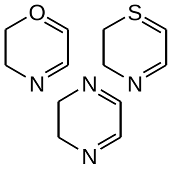
Sulphur dyes are complex polymeric aromatics with heterocyclic S-containing rings. Though representing about 15% of the global dye production, sulphur dyes are not so much used in Western Europe. Dyeing with sulphur dyes involves reduction and oxidation, comparable to vat dyeing. They are mainly used for dyeing cellulose fibres.

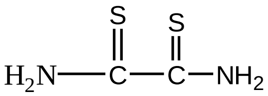
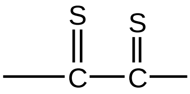
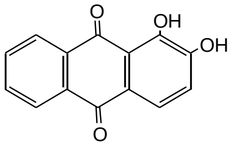
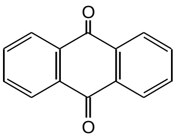
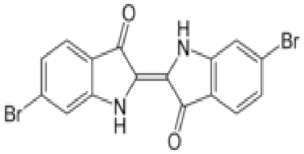
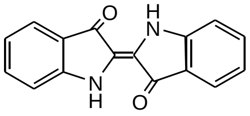
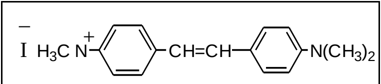
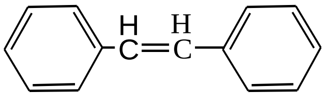
12. Solvent dyes

Solvent dyes are non-ionic dyes that are used for dyeing substrates in which they can dissolve, e.g. plastics, varnish, ink, waxes and fats. They are not often used for textile-processing but their use is increasing. Most solvent dyes are diazo compounds that underwent some molecular rearrangement. Also triarylmethane, anthraquinone and phthalocyanine solvent dyes are applied.

1.2.1.Classification of dyes according to chemical structures

Class of dyes	Formula	Chromophore group
Nitroso	 Acid Green 1	$-N=O$
Nitro	 Naphthol Yellow	
Azo (monoazo, diazo,……, polyazo dyes).	 Acid Yellow 9	$-N=N-$
Arylmethane Triphenylmethane, Diphenylmethane	 Basic Green 4	
Xanthene	 Acid Red 87	

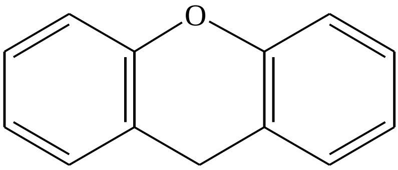
Acridine	 Acridine orange	
Quinoline	 Solvent yellow 33	
Methine	 Disperse Blue 354	
Thiazole	 Direct yellow 7	
Indamine and Indophenol	 Indophenol Blue	
Azine (Azines, Oxazines, Thiazines).	 Mordant Blue 14	

Sulfur	 $H_2N-\overset{\overset{S}{\|}}{C}-\overset{\overset{S}{\|}}{C}-NH_2$ Dithioxamide	 $-\overset{\overset{S}{\|}}{C}-\overset{\overset{S}{\|}}{C}-$
Anthraquinone	 Mordant Red 11	
Indigoid	 Tyrian Purple	
Stilbene	 Styrylcyanine	

The dye types chosen to be used in the present work are described in the following:

1- Xanthene dyes

Xanthen is an organic heterocyclic compound. The parent substance of this group of dyes is xanthen (dibenzo-1,4-pyran) and its chemical formula is $C_{13}H_{10}O$.



Xanthenes are an important class of organic compounds that find use as dyes, fluorescent materials for visualization of biomolecules and in laser technologies, due to their useful spectroscopic properties (*Banerjee and Mukherjee, 1981; Menchen et al., 2003*). Oxidation of these compounds can be converted to the corresponding xanthylium salts, which are also effective as dyes and fluorescent materials (*Kamel and Shoeb, 1964; Nogradi, 2003).* Xanthenes have also received considerable attention from many pharmaceuticals and organic chemists, actually because of the broad spectrum of their biological and pharmaceutical properties such as agricultural bactericide effects (*Hideo, 1981*). Rhodamine B is a member of the xanthene class of dyes.