SCIENTIFIC RESEARCH OF THE SCO COUNTRIES: SYNERGY AND INTEGRATION

上合组织国家的科学研究：协同和一体化

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芳香族染料溶液的电子束处理
ELECTRON BEAM TREATMENT OF AROMATIC DYE SOLUTIONS

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1. Introduction

Aromatic dyes are among the stable compounds with high thermodynamic stability due to intramolecular conjugation of chemical bonds. Recently, more and more dyes are acquiring the status of "food additives", which creates an illusion in society about their harmlessness [1, 2]. The downside of persistence is the difficulty in degrading most dyes with traditional water treatment methods. As a result, getting into water bodies with sewage, dyes worsen their transparency and, thereby, weaken photosynthesis [2, 3]. Typical natural microorganisms living in water bodies are not always able to destroy aromatic dyes. Moreover, some dyes are converted into toxic products by the action of sunlight and dissolved impurities. For example, aqueous solutions of the azo dye E124 (Ponceau 4R) retain their mutagenicity even after prolonged photolysis by sunlight [4]. At the same time, electron beam radiolysis of these solutions reduces mutagenic activity to the level of spontaneous mutagenesis [5]. The reduction in color and mutagenicity induced by radiolysis occurs in parallel. Accordingly, the study of the unique mechanism of radiolytic decolorization and detoxification of food dyes is relevant for the development of promising methods for wastewater treatment. In this work, we studied the effect of accelerated electrons on solutions of dyes (quinophthalon E104; indigo E132; triphenylmethanes: E133 and E142; azo: E102, E122, E124, E129, E151, and E155), which differ both in the length of the conjugation system of intramolecular bonds and in the type of chromophore.

2. Experimental

Synthetic dyes from ABF (USA), Kerry Ingredients Flavors (Ireland) and Top Product (Russia) were used. The solutions contained 0.02 g dm^{-3} of the dye in distilled water. Tert-butanol (0.5 mol dm^{-3}) served as a selective scavenger for OH radicals. Perchloric acid ($HClO_4$; 1 mmol dm^{-3}) served as an electron scavenger. The radiation source was a linear accelerator LINS-03-350-EURF (USA) with 3 MeV electron beam energy of and 25 Hz pulse repetition rate (pulses: 4 µs; 0.88 Gy per pulse). Solutions were irradiated at 20 ± 2°C in glass test tubes with an outer diameter of 13 mm to a dose of 1–1.5 kGy. The dosimeter was a copolymer with phenazine dye SO PD(F)R-5/50 (GSO 7865-2000). The radiolysis of solutions was carried out with access to air (slow bubbling, 0.5 dm^3 min^{-1}). The optical absorption of solutions was measured on a Cary-100 UV-Vis spectrophotometer (Agilent) in quartz cuvettes. The initial radiation-chemical yield (G) of decolorization was determined from the dependence of the dye concentration on the absorbed dose in the range of low doses (up to 150 Gy).

3. Results and discussion

In azo dyes, the main chromophore functions are performed by one or several azo groups (–N=N–) connecting aromatic units. In triphenylmethane dyes, the function of a chromophore is performed by a quinoid unit formed by the introduction of an amino or hydroxy group in the para position to the central carbon of methane. The chromophore system of indigoid dyes consists of indole or benzothiophene derivatives and is characterized by the presence of an intraionized conjugation system with electron-donating and electron-withdrawing substituents at the ends. The conjugation system of the quinophthalone dye is formed by indandione and quinoline units. Regardless of the chemical structure of the studied dyes, radiolysis of both individual and mixed solutions leads to an irreversible decrease in their color with increasing dose.

The correlations between color intensity and absorbed dose are similar for all dyes tested. In the range up to 60% decolorization, the dependences of the relative color on the dose are practically indistinguishable from each other. For all solutions, the curves are located in the region between the curves for E104 and E151 (Fig. 1). However, at higher degrees of decolorization, the differences become more noticeable, probably due to the competition of the original dyes and their colorless derivatives in reactions with water radicals, due to the lack of oxygen, due to the absorption of light by suspended substances, and due to some other effects [6- 8]. For most dyes tested, the observed decolorization yield is between 0.05 and 0.08 µmol J^{-1} (Fig. 2). However, in solutions of E133 and E155, the yields are about 0.03, and in solutions of E129, E132, and E142 they reach almost 0.1 µmol J^{-1}. The observed yields (G) generally correlate with half- decolorization dose values, $D_{1/2}$. The higher G, the smaller $D_{1/2}$ (Fig. 2).

The lower degradation yield of E155 is explained by the fact that, unlike other azo dyes, the intramolecular conjugation system in it contains 3 aromatic units linked by two azo groups, which makes it more resistant to radiolysis. Complete discoloration requires damage to the conjugation of both azo groups, which consumes twice as many radiolytic reagents as the degradation of one chromophore center, as, for example, in E122 or E124. The chromophore system of triphenylmethane dye E133 also consists of several parts, where the degradation of one of them does not lead to the decomposition of the entire chromophore system. Thus, E133 and E155 show a comparatively lower degree of discoloration. Dyes E129, E132 and E142, on the contrary, have the most compact chromophore system, including one chromophore center each, the damage of which breaks the conjugation between the parts of the molecule and, thereby, leads to discoloration.

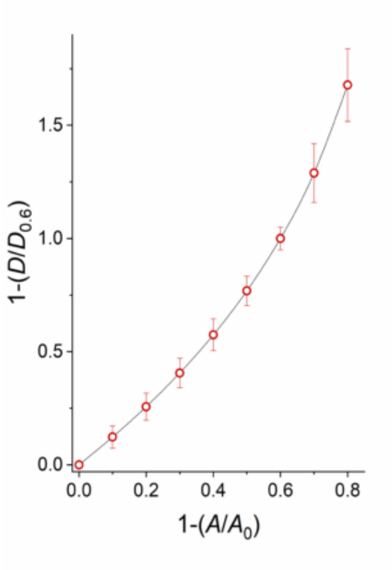

***Figure 1.** Correlation between the dose and the degree of decolorization of dyes (A_0 - optical absorption in a non-irradiated solution, $D_{0.6}$ - dose at a degree of decolorization of 0.6)*

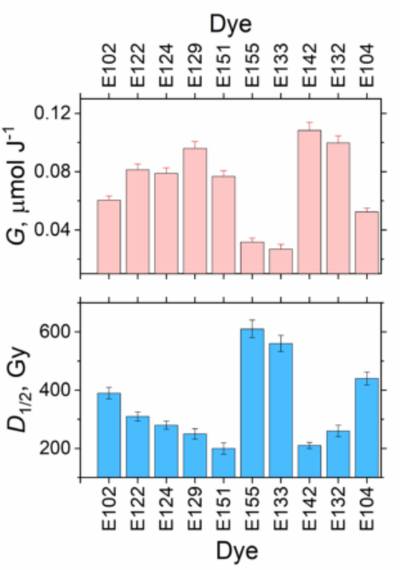

***Figure 2.** Decolorization yield G and half decolorization dose $D_{1/2}$*

Obviously, due to the low concentration of dyes in the studied solutions, their decolorization occurs by the mechanism of indirect action of radiation, i.e., as a result of reactions of the dye with radicals generated from water molecules [6]. In aerated solutions, decolorization is carried out mainly by OH radicals, since the reducing intermediates, a hydrated electron and an H atom (e_{aq} and H), are rapidly captured by oxygen to form low active radicals ($^{-}O_2$ and HO_2) [6, 7].

The key role of OH radicals in decolorization is revealed by experiments with the addition of tert-butanol (a selective scavenger of OH radicals) and perchloric acid (a selective scavenger of e_{aq}, which converts e_{aq} into less reactive H radicals). As can be seen from Fig. 3, when tert-butyl alcohol is added, the optical absorption of the solution decreases insignificantly during irradiation. In turn, the presence of $HClO_4$ provides the greatest decrease in optical density: the combined action of OH and H radicals leads to deep discoloration already at a dose of about 0.5 kGy. However, H radicals have less bleaching effect, as evidenced by the combined action of acid and tert-butanol. It is also noticeable in Fig. 3 that, with increasing dose, the absorption maximum shifts to the short-wavelength region, which indicates a decrease in the conjugation length in the chromophore system of the dye.

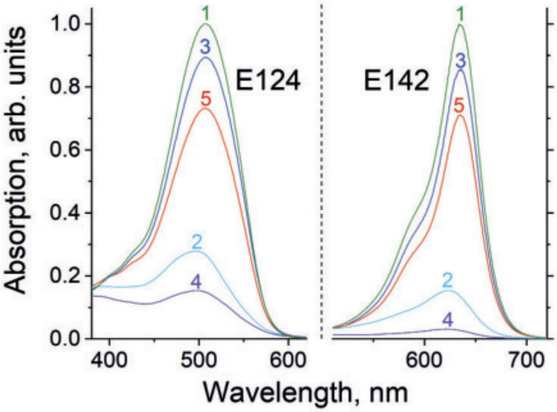

Figure 3. *Optical absorption of solutions of 0.02 g dm^{-3} E124 and E142 without additives (1; 2), with the addition of tert-butanol (3), with the addition of acid (4), and with the addition of alcohol and acid (5). 1 - 0 kGy; 2-5 - 0.5 kGy.*

Figure 4 shows the effect of the absorbed dose on the optical density of a solution containing a mixture of E104, E122, E132, and E142 (0.005 g dm^{-3} each), representing all four classes of the studied dyes. The initial difference between the observed spectrum (a) and the calculated spectrum (b), which is the sum of the spectra of individual solutions, indicates the presence in the unirradiated mixed solution (dose 0) of interaction and mutual screening of molecules/ions of different dyes compared to individual solutions. Nevertheless, almost independent discoloration of each of the components of the mixture is observed in the dose range up to 1 kGy, while spectra (a) and (b) demonstrate a similar proportionality of the change in optical absorption with dose. The observed effect of parallel degradation is important from the point of view of the possibility of discoloration of dye mixtures in real multicomponent wastewater [6].

The elimination of color and mutagenicity of solutions is associated with a number of effects (Fig. 5). First, there is a decrease in the stability of the molecule due to damage caused by radicals to the intramolecular system of conjugated bonds. This is evidenced by the discoloration of the solution. Secondly, the molecule loses side sulfo groups, which reduces its solubility and, consequently, mobility in reactions with microbial DNA. Thirdly, there is a splitting of the connecting bridge -N=N- between the naphthalene units. Moreover, this cleavage occurs without the formation of amines or amides.

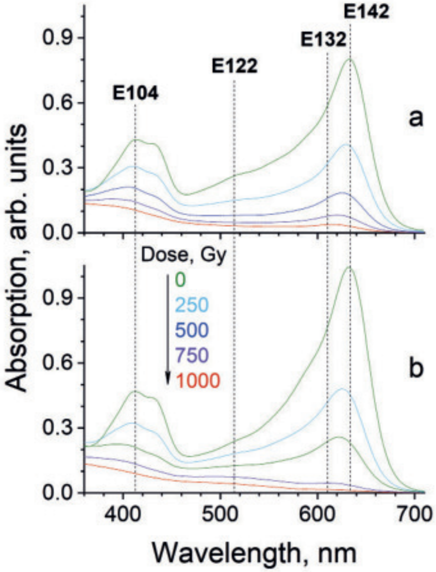

Figure 4. *Effect of dose on the optical absorption spectrum of a mixed solution of E104, E122, E132, and E142 (0.005 g/dm3 each): a – experimental results for the mixture, b – sum of the spectra for individual dyes. The values of the absorption maxima are shown by the dotted line*

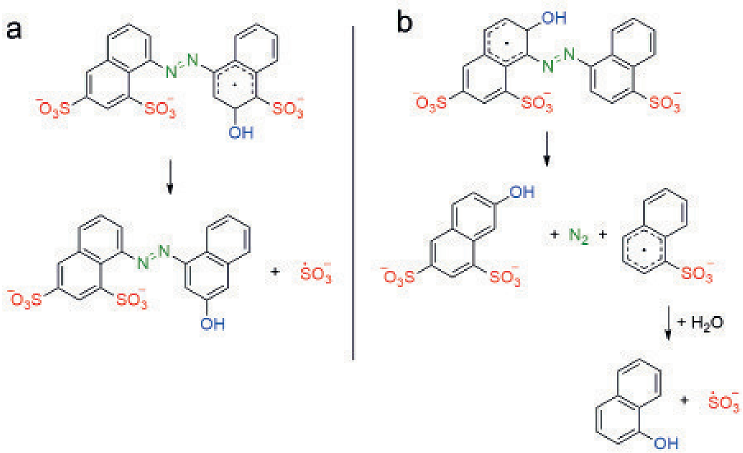

Figure 5. *Degradation of the E124 OH adduct (options a and b)*

The probability of degradation of OH adducts by a bimolecular reaction is low due to the low concentration of the dye, its low diffusion coefficient, and steric hindrance. Accordingly, most of the rapid transformations of the OH adduct proceed via the mechanism of monomolecular decomposition or pseudo-first order reactions with water molecules. The introduction of a new substituent (OH) into the naphthalene unit changes the electron density distribution that existed before the formation of the OH adduct. The unpaired electron of the OH adduct is delocalized over the remainder of the conjugation system, which includes aromatic rings, azo and sulfo groups. At the same time, the energy of the new C-OH bond is much higher than the energy of splitting of existing C-N and C-S bonds [9]. Thus, the relaxation of the OH adduct occurs due to the elimination of a substituent with a weaker bond (Fig. 5). In this case, the unpaired electron ends up on the split-off fragment. Similar dissociative processes could also occur in the absence of air due to the capture of a hydrated electron or H radical [6, 10].

At 1.5 kGy dose, each dissolved E124 molecule can interact with several OH radicals and, thus, lose all side groups without the formation of mutagenic products and intermediates. The degradation of the chromophore system occurs with the elimination of the connecting bridge and side substituents due to the radical addition of a new OH functional group, the binding energy of which is higher than that of the sulfo groups and the diazo bridge. Initially, the E124 dye in 0.02% aqueous solution is a nonspecific mutagen [5]. Without metabolic activation, it induces G→A transitions as well as +1 and -1 frameshift mutations. In turn, in the presence of liver enzymes, it causes mutations of the first two types. Electron beam-induced decolorization and detoxification occur in parallel and are due to the same radical processes. The above-described neutralization of dyes does not require special preparation of the solution, which is attractive from the point of view of the use of electron beam processing in large-scale wastewater treatment [11].

4. Conclusion

The example of radiolysis of food coloring solutions shows the possibility of effective irreversible degradation of systems of conjugated bonds. In dye solutions, the effect of radiolysis on bond conjugation can be conveniently observed from changes in the color of the solutions. At 20 mg dm-3 dye concentration, complete discoloration is observed at 1–1.5 kGy dose. The effect is achieved under conditions of deficiency of dissolved oxygen. It is these conditions that are most attractive for large-scale electron-beam treatment of colored wastewater using powerful electron accelerators [11–13]. Radiolytic decolorization of representatives of the 4 considered classes of dyes with limited air access has an undoubted similarity, since it consists in the degradation of the intramolecular system of conjugated bonds. The main transformations consist in the addition of OH radicals to conjugated bonds and the subsequent interaction of organic radicals with dissolved oxygen or with each other. Damage to chromophore systems consists in the same type of interaction of radicals with double bonds responsible for the conjugation of atoms into a combined chromophore system.

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