

Luminescence of dye after exposure to electron beam radiation

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Abstract. The article presents the results of measuring the luminescence of ambient air and a solution of an organic compound, when they are irradiated with a high-current pulsed electron beam with an average energy of $E_e = 170$ keV and a duration of 2 ns, formed by the RADAN-303 accelerator. It has been shown that under the action of UV radiation, the transformation of the Crystal Violet dye is only 2%. The addition of hydrogen peroxide leads to an increase in the phototransformation of the dye. The action of an electron beam on an aqueous dye solution is accompanied by a decrease in the intensity of air luminescence bands with an increase in the number of irradiation pulses. The results showed the degradation of both the dye itself and its transformation products under the action of an electron beam.

Keywords: electron beam, UV irradiation, phototransformation, absorption, luminescence, Crystal Violet.

1. Introduction

Currently, one of the priority scientific tasks of the Russian Federation is the development of fundamental research into the behavior of matter under extreme parameters. In the world, there is an intensive use of a low-energy electron beam in various areas of technological production: processing in the synthesis of bisphenol-A-polycarbonate for the production of organic electronic devices; study of photoconductivity during electron bombardment; production of sensitive and inexpensive capacitive sensors; micro-/nanofluidics devices and others [1–6]. Wastewater containing emissions from textile production poses an environmental hazard due to the refractory carcinogenic nature of dyes. Crystal Violet (CV) is a typical representative of the triphenylmethane dye, is toxic to living organisms, and is a mutagenic and mitotic poison [7]. On the other hand, the dye molecule is of scientific interest in the field of nonlinear properties. The interaction of the dye with ferroelectric crystals results in outstanding optical properties and is of great interest due to its potential applications in displays and electrooptical devices.

The chemical coagulation process can reasonably remove dyes from wastewater, but it will generate a large amount of secondary waste. The use of activated carbon can help remove the dye in aqueous solution efficiently, but further processing of the spent carbon is costly. There are works devoted to the study of wastewater treatment from dyes by photolytic oxidation (TiO_2/UV , ZnO/UV , $\text{H}_2\text{O}_2/\text{UV}$, $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$) [8–10]. Pulsed electron beams are capable of penetrating deeper layers than UV radiation. The penetration depth of the electron beam depends on the beam energy and the nature of the material being irradiated. The luminescence study of organic compound solutions under the impact of an electron beam contributes to solving the problem of diagnostics and utilization of dissolved organic compounds. The main goals of our study are to investigate the transformation of CV in water under various excitations, to measure the luminescence of the surrounding air and aqueous solutions of CV when they are irradiated with a high-current pulsed electron beam with an average energy of $E_e = 170$ keV and a duration of 2 ns, formed by the RADAN-303 accelerator [11].

2. Materials and methods

2.1 Reagents

The object of our study was the dye N, N, N', N', N'', N''-hexamethylpararosaniline (Crystal Violet, CV (Fig.1)). CV and hydrogen peroxide (35%) were purchased from Sigma-Aldrich Co.

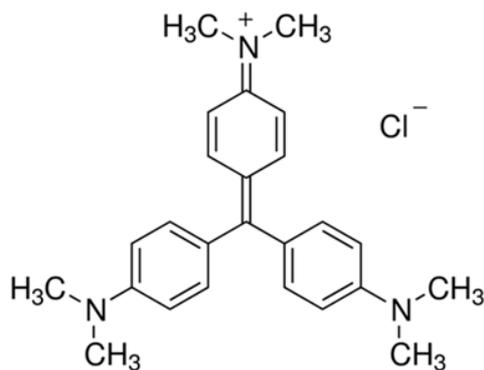


Fig.1. The structure of Crystal Violet.

2.2. Instruments and methods

2.2.1 UV irradiation and technique

Experiments with UV irradiation were carried out using KrCl and XeBr excilamps [12]. The KrCl excilamp has a maximum emission wavelength of about 222 nm and an emission power of 6.5 mW/cm². The XeBr excilamp has a maximum emission wavelength of about 283 nm with an average emission power of 17.12 mW/cm² [12]. Experiments with the KrCl excilamp were carried out using flow [7] and stationary [13] reactors. Experiments with XeBr and KrCl+XeBr excilamps were carried out using a stationary reactor. The decrease of CV concentration in water was recorded from changes in the absorption spectra. Spectrophotometric studies were performed with a CM2203 (SOLAR Co., Belarus). To obtain CV dissolved in water with an initial CV concentration of $C = 1$ mM, a dry sample was placed in distilled water and until completely dissolved in an ultrasonic mixer. The resulting sample was diluted to 0.05 mM and poured into a container with a magnetic stirrer in a photoreactor, in which the effluent was continuously recycled, so that the system acted as a batch reactor (flow reactor). In UV/H₂O₂ analyzes, hydrogen peroxide was added to a glass container along with the dye at the required initial concentration. All experiments were carried out at room temperature (23–25 °C), the operating time was 120 min (except for a series of experiments with hydrogen peroxide, 60 min). The samples were analyzed during irradiation at different times (0, 2.5, 5, 10, 20, 40, 60, 90, and 120 min). Repeated experiments were carried out and average values were obtained. The standard deviation calculated for the entire data set was no more than 2%.

In stationary reactor, the solutions were located in glass beakers with a diameter of 4.6 cm and they were constantly mixed using a magnetic stirrer. These samples were irradiated with XeBr or KrCl excilamps. The volume of the irradiated solution was $V = 50$ ml. During irradiation, the maximum energy absorbed by the solution under study was no more than 10 J/cm³. Changes in volume and temperature were recorded during irradiation. The decrease of dye concentration was monitored by the change in optical density in the absorption spectra at the wavelength of the absorption maximum of the long-wavelength band (measurement error did not exceed 10%).

2.2.2 Exposure to an electron beam. Air plasma luminescence above the solution surface

The characteristics of luminescence in the region from 400 to 850 nm of an air plasma above the surface of a liquid and of the liquid itself were studied using a KLAVI type setup [14]. An aqueous solution of CV ($C = 0.05$ mM) was irradiated with a pulsed electron beam with a duration of 2 ns, and an average electron energy of 170 keV and a current density of 130 A/cm². The number of irradiation pulses following with a repetition rate of 1 Hz varied from 1 to 1600. The layout of the experimental setup is described in detail in [15]. The time-integrated emission spectrum in the

range of 400–850 nm was recorded by a multichannel photodetector. The absorption spectra of the CV after exposure to an electron beam were recorded on a two-beam Shimadzu UV-1700 spectrophotometer in the region of 200–800 nm at room temperature. To diagnose the CV decay in a solution, we explored changes in the spectra and intensity of the volume radiation of liquid and air localized near the surface of the solution and simultaneously excited by the same irradiating electron beam.

Beam electrons penetrate the solution to a depth of 100–150 μm , and the bremsstrahlung generated by them penetrates to a depth of 1.5–2.0 mm. Thus, the effect of electron beams is of a volumetric nature. It is assumed that under such exposure, the dissolved dye will undergo transformation due to the formation of solvated electrons and reactive oxidants in solution. In this case, part of the reactive particles remains in the solution, while the other part leaves it through the solution-air interface and enters the near-surface air layer.

3. Results and discussion

Fig.2 shows the dependence of the CV conversion in water on the concentration of hydrogen peroxide when exposed to KrCl excilamp radiation in a flow reactor. It can be seen from the figure that without the addition of an oxidizing agent (Fig.2, black curve), phototransformation virtually does not occur under these conditions. At the maximum irradiation time of 120 min, the dye loss was 2%. Under the conditions of a flow reactor, the addition of hydrogen peroxide slightly increased the CV conversion. The maximum conversion was achieved under these conditions at a dye:H₂O₂ ratio of 1:2 (Fig.2, curve c). Increasing the concentration of hydrogen peroxide in a ratio of 1:8 even worsened the conversion of CV compared to the aqueous solution (Fig.2, curve f).

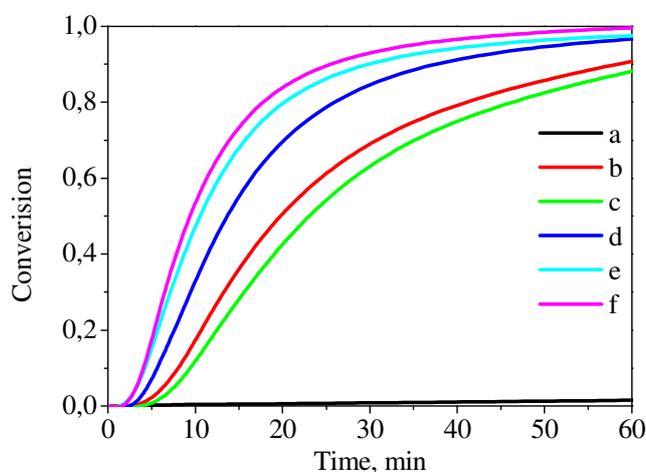


Fig.2. CV conversion in KrCl stationary reactor depending on hydrogen peroxide concentration: a) without H₂O₂, b) 1.25 ml H₂O₂; c) 2.5 ml H₂O₂; d) 5 ml H₂O₂; e) 7.5 ml H₂O₂; f) 10 ml H₂O₂.

To reveal the effect of the radiation wavelength on the phototransformation of CV in water stationary photoreactors were assembled. Fig.3 shows the results of irradiation of an aqueous solution of CV under the action of radiation at 222 and 283 nm. Curves of decrease in CV in Fig.3 were plotted from absorption spectra data. CV decay curves were constructed from the decrease in absorption intensity at the maximum of the long-wavelength band, where D is the optical density of dissolved in water CV absorption after irradiation at a wavelength at 591 nm; D_{max} is the optical density of dissolved in water CV absorption without irradiation at a wavelength at 591 nm.

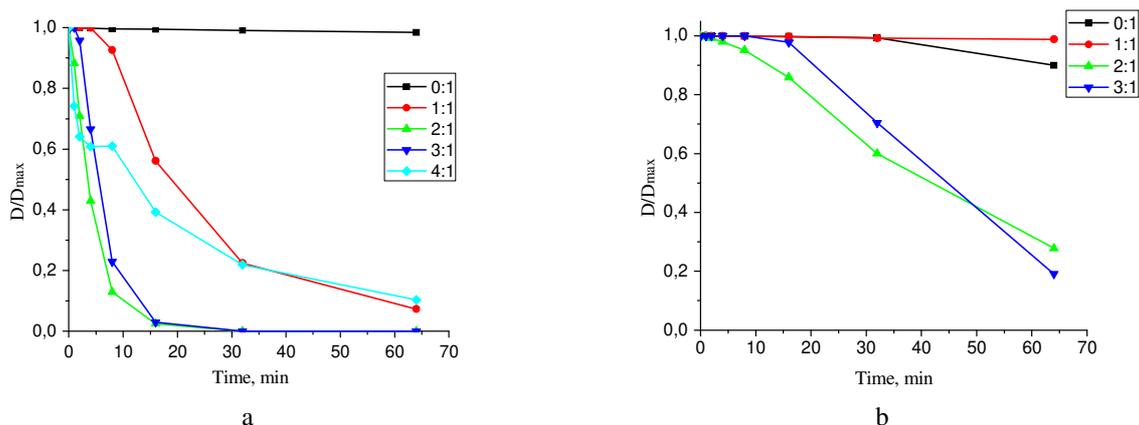


Fig.3. Disappearance of CV in a stationary reactor depending on the concentration of hydrogen peroxide: KrCl (a); XeBr (b).

Note that irradiation with a KrCl lamp without adding H_2O_2 to the studied CV solution does not lead to any significant results. However, the addition of a small amount of hydrogen peroxide (1.25 ml) led to a sharp increase in conversion, i.e., faster phototransformation of CV than in a flow reactor. Thus, the presence of H_2O_2 is the determining factor for achieving high conversion values. However, for higher percentages of H_2O_2 , no significant increase in CV degradation is observed.

To achieve a higher rate of decomposition of an organic compound, we carried out studies aimed at considering of influence of electron beam impact on CV degradation. As a result of CV transformation reactions under the action of an electron beam, the composition of the solution and its absorption coefficient change. This process manifests itself by way of of a decrease in the intensity of the air luminescence bands relative to the background value due to the partial absorption by the CV solution of the air radiation reflected from the bottom of the cuvette (Fig. 4). With an increase in the number of pulses, visible changes in the color of the solution are noticeable - discoloration is recorded (Fig.5a). Based on the data in Fig. 5, it can be argued that under the action of electron beam irradiation, an intensive transformation of the organic compound in water occurs. A decrease in the absorption intensity in the regions of 250–300 and 500–700 nm indicates active degradation of the dye (Fig.5b). In the range from 350 nm to 450 nm, with an increase in the number of pulses to 800, an increase in the absorption intensity was recorded. This indicates the active formation of CV decay products. With a further increase in the number of pulses (Fig.5b), the absorption intensity in this region decreases, which indicates the disappearance of the CV transformation products under the action of electron beam radiation.

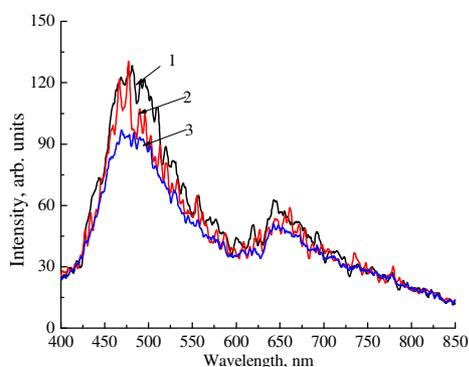


Fig.4. Luminescence: empty cuvette (1); CV in distilled water after preliminary irradiation with 50 (2) and 1600 (3) electron beam pulses.

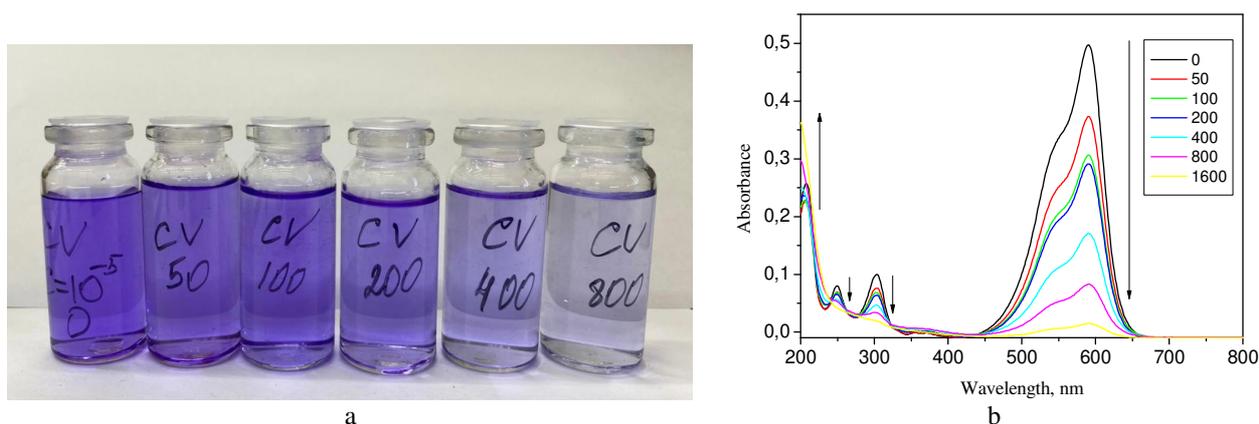


Fig.5. Colors change (a) and absorption spectrum (b) of CV aqueous solutions: before and after exposure to an electron beam of $50 \div 1600$ pulses.

Fig.6 presents the results of comparing the effectiveness of the impact of various irradiation sources on an aqueous solution of the dye. The data indicate an efficient transformation of CV in water upon exposure to an electron beam compared to UV radiation sources. However, the addition of an oxidizing agent to an aqueous solution of CV leads to comparable efficiencies of CV transformation under the actions of an electron beam and a KrCl excilamp.

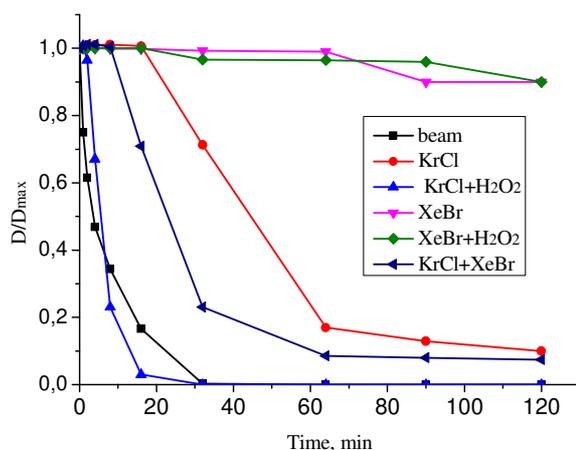


Fig.6. Disappearance of CV upon exposure to UV radiation from excilamps and an electron beam.

4. Concluding remarks

The results obtained can be used in ecological studies on the influence of primary organic molecules and products of their transformation under the action of short-term electron beams on the environment. The use of luminescence, as a consequence of the interaction of an electron beam with air and a solution of organic molecules, called pulsed cathodoluminescence, makes it possible, virtually, in real time, to observe the processes of transformation of solutions and to detect volatile reactive particles coming from solutions into the air. As a result, the following conclusions can be drawn:

- UV radiation can destroy the dissolved dye – crystal violet through direct and indirect photolysis.
- Under the influence of UV radiation from excilamps, the efficiency of CV degradation without the addition of an oxidizing agent in water is only 2%.

- The addition of hydrogen peroxide (1:2) reduces the amount of dye in the water, and the conversion is 93%.
- Exposure to an electron beam made it possible to achieve a decrease in Crystal Violet dissolved in water without the addition of an oxidizing agent.

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5. References

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