# A combined electron-beam and coagulation method of purification of water from dyes

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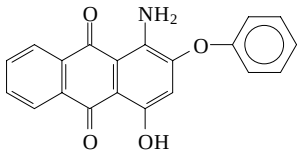
A combined electron-beam and coagulation method has been developed for the purification of water from dyes present in soluble and disperse forms.

Various combined methods of electron beam applications for the purification of water and wastewater (see, *e.g.*, refs. 1–4) are known. In particular, the combined electron-beam methods for removal of heavy metals (lead, cadmium, mercury, chromium) from water were described in refs. 5–8, carried out with the participation of several of the authors in this paper. The present publication is devoted to the description of the results from a study on combined electron-beam and coagulation methods for the removal of dyes from water. In this method, irradiation is used for the decomposition of soluble dyes and coagulation for removal of dye present in water in disperse form.

An electron accelerator of type ELV (electron energy 1 MeV, maximum beam power 50 kW) located in the Daeduk R & D Centre was used as a source of ionizing radiation. Model aqueous solutions of the following dyes: Disperse Red 60 (a dye of anthraquinone type **1**), Acid Red 172 (monoazo dye, 1:2 metal complex) and Reactive Red 21 (monoazo dye with vinyl sulfonate functional group) were studied. The first of these is insoluble in water and is present in disperse form. Two other dyes are soluble in water. The content of each dye in the solution under investigation was 50 mg $dm^{-3}$. This amount is close to the content of dye in industrial wastewater.

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For electron beam treatment, solution (volume 0.8 $dm^3$) was placed in a flat vessel which was moved by remote control through the zone of irradiation (area *ca.* 100×10 cm) by scanned electron beam. The irradiation time was ~1 s. Just before and upon electron-beam treatment, the solution was bubbled with air or argon to saturation and with stirring. Dosimetry was conducted with the dichromate dosimetric system.[9] The dosimetric solution was irradiated under the same conditions as the solution of dye. Dose rates were 1–10 kGy.

Optical measurements were performed on a spectrophotometer 'Cary-13E' ('Varian'). The COD (Cr) values were determined by a standard procedure.[10] Total organic carbon (TOC) values were obtained with an analyser 'TOC-5000A' ('Shimadzu', Japan) from the difference between the total carbon content and the total content of inorganic carbon. Two solutions were utilized for coagulation. One contained 200 g $dm^{-3}$ $Fe_2(SO_4)_3$ and the second 42 g $dm^{-3}$ $Ca(OH)_2$. An 0.2% aqueous solution of polyacrylamide served as a flocculant. For coagulation and flocculation, 1.6 $cm^3$ of $Fe_2(SO_4)_3$ solution and 0.5 $cm^3$ of polyacrylamide solution, respectively, were added to 200 $cm^3$ of the solution studied.

It was found that both dyes soluble in water were not removed by coagulation and flocculation. However, their solutions were almost completely discoloured as a result of irradiation at doses < 10 kGy, Figure 1. Electron-beam treatment of the solutions of these dyes at such doses led simultaneously to a considerable decrease in TOC and COD (Cr) values (Figure 2). At the same doses, the degree of purification was higher in aerated solutions than in deaerated ones. The result of an electron-beam treatment of the solutions of the dyes under consideration was also formation of disperse precipitates which were removed by filtration.

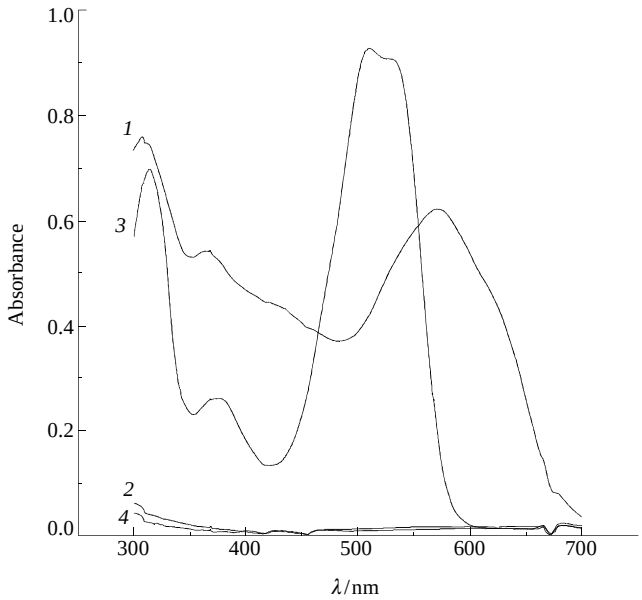


**Figure 1** Optical absorption spectra of aerated aqueous solutions (50 mg $dm^{-3}$) of Acid Red 172: *1*, unirradiated, *2*, irradiated (dose 9 kGy) and Reactive Red 21: *3*, unirradiated, *4*, irradiated (dose 7 kGy).

Disperse Red 60 in water is stable to electron irradiation (Figure 3). The colour intensity of this system in the absence and in the presence of air did not change upon irradiation to dose 30 kGy; the system remained brightly-red, and the TOC value decreased by only 34%.

Virtually complete purification of water from dye Disperse Red 60 was achieved by the coagulation and flocculation method. For example, the initial aerated water with this dye had a TOC value of 26–27 mg $dm^{-3}$. The TOC value became equal to 3.1–4.5 mg $dm^{-3}$ after electron-beam treatment at dose 3–10 kGy, subsequent addition of aqueous $Fe_2(SO_4)_3$, neutralization to pH ~7 with $Ca(OH)_2$ solution and stirring in the presence of flocculant and filtration. Note that a considerable part of the residual TOC value was due to polyacrylamide penetration to the mother solution through the filter. The colour of the system after such a combined treatment was ≤ 16 units.

A decrease in the TOC value to 2.5–2.6 mg $dm^{-3}$ for aerated water with Disperse Red 60 was observed upon irradiation of the system in the presence of $Fe_2(SO_4)_3$. In this case,

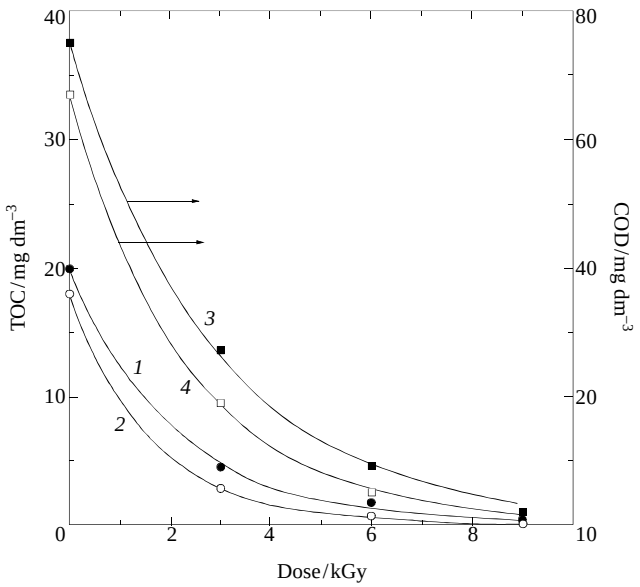


**Figure 2** Dependence of TOC (*1*, *2*) and COD (Cr) (*3*, *4*) values of aerated aqueous solutions (50 mg dm$^{-3}$) of Acid Red 172 (*1*, *3*) and Reactive Red 21 (*2*, *4*) on receiving a dose of electron radiation.

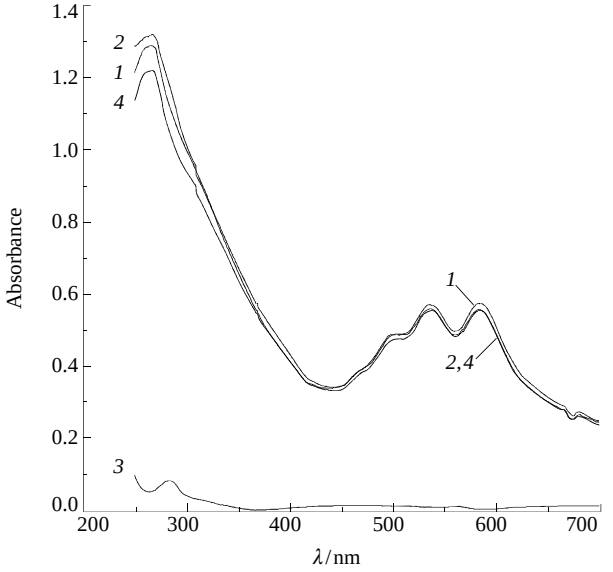


**Figure 3** Optical absorption spectra of aerated water containing 50 mg dm$^{-3}$ of Disperse Red 60 before electron-beam treatment (*1*), after electron-beam treatment to dose 3.5 kGy (*2*), after electron-beam treatment to dose 3.5 kGy and subsequent coagulation and flocculation (*3*) and deaerated water containing the same amount of the dye and irradiated to dose 3.5 kGy (*4*).

neutralization, stirring with flocculant solution and filtration were performed after irradiation. If water containing the dye and flocculant was exposed to electron-beam treatment, then the TOC value decreased to only 10–12 mg dm$^{-3}$.

We must emphasize that coagulation and flocculation led to the same results both in the case of irradiated and unirradiated solutions. Thus, a solution containing all the three dyes can be exposed to electron-beam treatment both before coagulation and flocculation and after this procedure.

Obviously, the discoloration of dyes soluble in water mainly occurs as a result of their interaction with OH radicals formed from radiolytic decomposition of water. This is confirmed by the fact that the degree of purification is higher in aerated solutions than in deaerated ones. In the latter, hydrated electrons reacting with dye give rise to the formation of a semireduced form which can in its turn partially react with the product of reaction between dye and OH radical regenerating the dye. In aerated solutions, a reaction between oxygen and hydrated electron takes place; the $HO_2$ or $O_2^-$ radical formed shows low, even no reactivity, towards the dye.

The dye Disperse Red 60 is present in the water in a separate phase. Because of it its reactions with water radiolysis products are suppressed, and the dye is characterized by its comparatively high radiation stability. However, it is easily captured by coagulant.

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