Application of Coumarin to Determine and Compare the Rate of Hydroxyl Radical Formation in Aqueous Solutions Irradiated with 172 and 185 nm VUV Light

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Advanced Oxidation Processes (AOPs) include chemical, photochemical, and electrochemical processes, based on the producing reactive species (especially HO•). These species can react with organic pollutants and possibly mineralize those in the presence of dissolved O_2. VUV photolysis, one of the AOPs, is based on high energy UV-radiation (wavelength <200 nm). VUV light has enough energy to break the bound in water molecule and consequently produce HO• and H• reactive species directly from water.

Two typical VUV light sources exist. One of them is the low-pressure mercury vapour lamp, which emits both 254 nm UV and 185 nm VUV light. This lamp is used generally for ultrapure water production. The other light source is the Xe excimer lamp, which emits quasi-monochromatic light with a wavelength maximum at 172 nm. There are several benefits for the Xe excimer lamps, one of the most important is the relative high photon flux comparing to the conventional low-pressure mercury vapour lamp. Although the different between the wavelengths emitted by these two light sources is no more than 13 nm, there are significant difference between the 185 and 172 nm VUV radiated aqueous solutions.

In the case of 172 nm VUV radiation, the VUV irradiated zone is only 0.04 mm deep, because of the high molar absorbance of water at this wavelength. The primary reactive species (HO• and H•), having a short lifetime, form and react within this zone. The carbon centered radicals, which formed due to the reaction of organic pollutants with primary radicals, react with dissolved O_2. Because of the extremely high concentration of HO•, H•, and carbon centered radicals, an O_2 poor layer forms close to the wall of the light source. Thus the 172 nm irradiated solution can be characterized as an extremely inhomogeneous system, since both radical's concentration and dissolved O_2 concentration decreases fast with the distance from the outside of the light source. At the same time 185 nm UV light is able to penetrate 11 mm deep in water, thus this system is less inhomogeneous than the 172 nm VUV light radiated one.

In this work the formation rate of 7-hydroxycoumarin was used for the determination of HO• formation rate. The effect of the initial concentration of coumarin, dissolved O_2 and terc-buthanol as HO• scavenger on the transformation rate of coumarin and formation rate of 7-hydroxycoumarin were investigated and compared in the case of both 172 and 185 nm irradiated solutions. Our results proved that the recombination of primary radicals in 172 nm irradiated solutions is probably has a higher importance than in 185 nm irradiated ones.

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