Characterization of carbonyl by-products during Uniblu-A ozonation by liquid chromatography/hybrid quadrupole time-of-flight/mass spectrometry

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The structural elucidation of carbonyl-containing by-products arising from Uniblu-OH ozonation has been investigated by liquid chromatography/electrospray ionization tandem mass spectrometry (LC/ESI-MS/MS) employing a quadrupole time-of-flight mass spectrometer. The by-products were derivatized with 2,4-dinitrophenylhydrazine, allowing the formation of [M–H]− ions of the derivatives in the electrospray source. Exact mass measurements of both the [M–H]− ions and their product ions allowed the elemental formulae and related structures of ten by-products to be determined confidently. The main degradation pathway were decarboxylation followed by further oxidation. It is noteworthy that the experimental procedure employed allowed the identification of both nitrogen- and sulphur-containing carbonyl by-products during Uniblu-OH ozonation. This result is of environmental relevance for monitoring the balance of organic nitrogen and sulphur during the ozonation of organic pollutants. These atoms, in fact, do not undergo complete mineralization. Copyright © 2011 John Wiley & Sons, Ltd.

Textile dyes and other dyestuffs represent a major source of industrial water pollution in many countries due to their persistence, acute toxicity or mutagenic effects to exposed aquatic organisms. A major issue of discussion and regulation in the developed countries is the removal of color from textile wastewater, also including the requirement to recycle the rinsing water from dye baths.

Conventional textile wastewater treatment plants that rely on biological oxidation (biodegradation)[3] and/or simple physicochemical (adsorption)[3] strategies are ineffective in achieving complete decolorization and the removal of dye residues because most dyestuffs are both resistant to biological degradation and highly water soluble. It follows that the employment of more powerful chemical methods, namely those known as advanced oxidation processes (AOPs), is necessary to reach the target legal limit for effluent discharge. AOPs are chemical methods based on the generation of hydroxyl radicals (•OH) able to oxidize contaminants in a non-selective manner.[3–8]

It has been reported that ozonation is one of the most effective technologies for the remediation of textile wastewater containing bio-recalcitrant dyes and other persistent organic compounds.[9,10] Several studies have been carried out that demonstrate the efficiency of ozone treatment for removal of dyes and some of them were also aimed at identifying the resulting by-products.[11–15] Due to its high oxidation potential, ozone can effectively break down the conjugated double bonds of the chromophores of dyestuffs as well as other functional groups such as their complex aromatic rings.[16–18] This ultimately leads to the formation of smaller molecules with fewer conjugated double bonds, thereby decreasing the color of effluent. However, although the removal of dyes by ozonation is often successfully achieved, their complete oxidation (i.e., the total mineralization of organic carbon to carbon dioxide) is seldom obtained. Therefore, ozonation by-products should usually be expected in ozonation effluents.

Reactive dyestuffs based on the anthraquinone structure have long been used in cellulose fiber dyeing. They are more resistant to biodegradation due to their fused aromatic structures than azo-based dyes.[19] The anthraquinone-based dyes represent an environmental problem as it is not possible to recover them from spent baths because the reaction carried out to link them to fibers leads to the formation, through a side reaction, of the hydrolyzed dyes. As the fixation rate between the reactive dye and the fiber is usually below 90% it follows that the resulting spent waters cannot be further used and should be disposed of properly. However, little information about the ozonation products of anthraquinone reactive dyes is available.[20–25] In general, as degradation by-products are more polar than the parent compounds their identification is often carried out by liquid chromatography/electrospray ionization mass spectrometry (LC/ESI-MS), often employing accurate mass measurement.[26,27] It is known that such by-products are transient compounds as they are further degraded, leading to the formation of low molecular weight carbonyl compounds which, in turn, are finally degraded to low molecular weight organic acids. However, the identification of low molecular weight aldehydes and ketones only on the basis of comparison with authentic standards fails to account for the total organic carbon present in the ozonated aqueous solution.[28] It follows that unknown low molecular

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