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Aquatic toxicity evaluation of copper-complexed direct dyes to the *Daphnia magna*

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Abstract

The aquatic toxicity of a series of copper-complexed direct dyes based on benzidine congeners, 2,2′-dimethyl-5,5′-dipropoxybenzidine and 5,5′-dipropoxybenzidine, were evaluated in acute toxicity studies using *Daphnia magna*. The purpose of the research described in this paper was to use bioassays with daphnids to determine the aquatic toxicity of metallized direct dyes synthesized. The results clearly show that all of the copper-complexed dyes examined were highly toxic to daphnids and more toxic than unmetallized new direct dyes as expected. The study also suggested that the assay with *D. magna* was an excellent method for evaluation of dyes for aquatic toxicity.

Keywords: Direct dyes; Aquatic toxicity; *Daphnia magna*; Genotoxicity; Copper complex dyes; Benzidine

1. Introduction

Copper is the third most used metal in the world [1] and is known to have a number of negative effects both on crops [2] and the microorganisms in the soil, which could have a negative effect on the fertility of the soil [3]. Bioavailability and toxicity of most metals, and certainly of copper, is controlled by the speciation in the pore water, and therefore it is crucial to test the toxicity of the solution. Heavy metals in general have a low solubility in water, and the concentration of metals in water depends on parameters such as pH, redox potential, organic matter content and the amount of metal present in the solution [4].

It has long been known that after-treatment with salts of metals, such as chromium, aluminum, iron, etc., can give not only varied shades, but can also improve the light and washfastness properties of many direct dyes [5–16]. Probably, in all cases, the dye is in a position to form a chelate with the metal ion, forming a large molecular complex, which might be less soluble in water (which is responsible for improved washfastness properties). Also, the newly formed complex may be more stable photolytically than the original dye. Thus there is an increase in the lightfastness of dyes with certain specific structures when complexing occurs. Many attempts [5–16] have been made in the past to improve the lightfastness properties of direct dyes on textile materials by after-treatment methods. Among the various after-treatments mentioned in the literature, treatment with metallic salts and particularly with copper sulfate is of commercial importance.

Metallization of dyes originally occurred during the mordanting process to help fix the dye to the substrate. Premetallized dyes are now used widely in various outlets to improve the properties of dyes, particularly its lightfastness. However, this is at the expense of brightness since metallized azo dyes are duller than nonmetallized dyes. A major application for copper complexes is in the prior metallization or after-treatment of direct dyes containing at least one *ortho*, *ortho′*-dihydroxyazo or *ortho*-methoxy-*ortho′*-hydroxyazo chromophoric system

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[9–16]. The best-known example is C.I. Direct Blue 76 and C.I. Direct Blue 218, a copper complex derived from C.I. Direct Blue 1 and 15 by metallization with cuprammonium sulfate in the presence of an alkanolamine (Fig. 1).

Most direct dyes have disazo and trisazo structures, with each color dominated by unmetallized structures [16,17]. Azo dyes consist of a diazotized amine coupled to an amine or a phenol, and contain one or more azo linkages. They are the largest class (60–70%) of dyes with the greatest variety of colors [18].

Approximately 10–15% of the dyes are released into the environment during dyeing of different substrates, such as synthetic and natural textile fibers, plastics, leather, paper, mineral oils, waxes, and even (with selected types) foodstuffs and cosmetics [19]. Even at very low concentrations (10–50 mg/L) water-soluble azo dyes can cause waste streams to become highly colored. Aside from their negative aesthetic effects certain azo dyes and biotransformation products have been shown to be toxic, and in some cases these compounds are carcinogenic and mutagenic [20–26]. Approximately, it was determined that 130 of 3200 azo dyes in use have produced carcinogenic aromatic amines because of reductive degradation [27].

The commercial utility of benzidine-based azo colorants and concern over their potential health risks have caused the search for viable nonmutagenic analogs of benzidines to be an important research problem in the past [28–34]. However, researches concerning the aquatic toxicity of metallized azo dyes were not performed seriously by textile chemists. For dyes that contain metals as an integral part of its molecule, the metallic content is essential to the dye's performance as a textile colorant. The metals most commonly found in dyes as part of the dye structure are shown in Table 1.

Textile plants are very important sources of toxic discharges [35,36]. They usually employ cotton and synthetic fibers and include integrated printing and dyeing operations, applying a wide variety of organic dyes and full range stages of fabric processes [37–43]. Therefore, the aquatic toxicological investigation of metallized azo dyes can be very beneficial to the

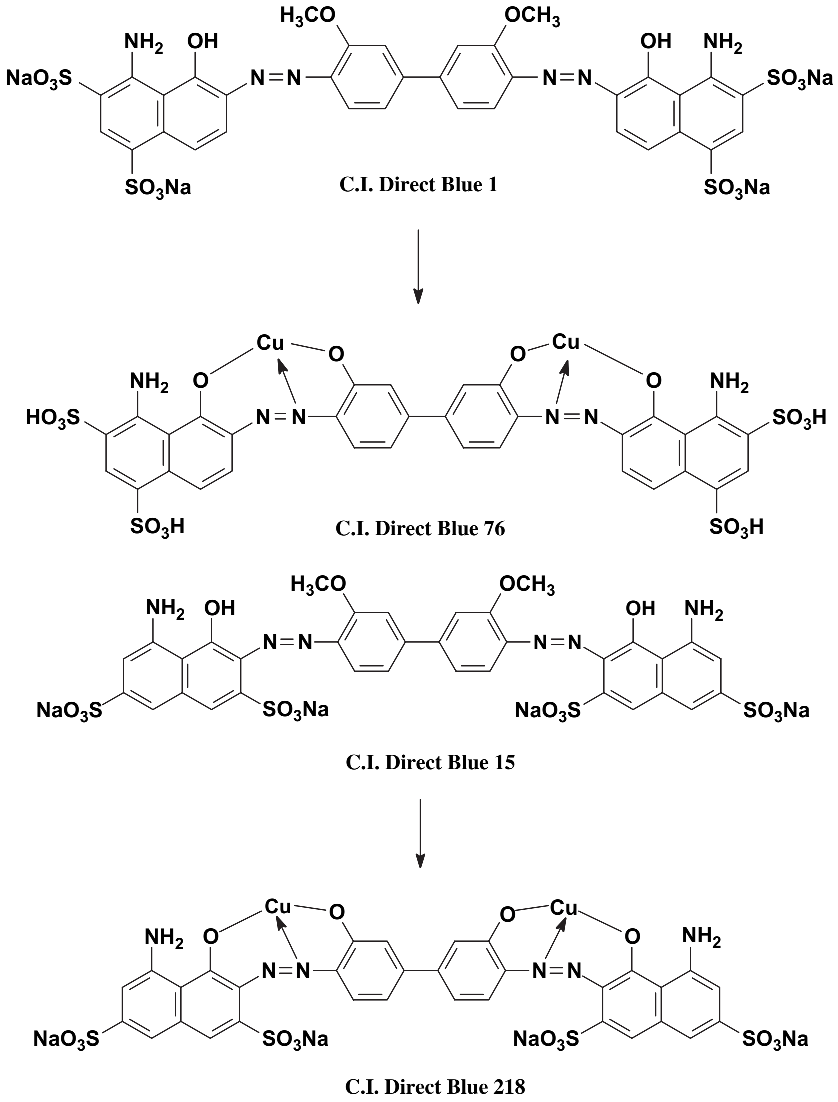

Fig. 1. Metallization of C.I. Direct Blue 1 and C.I. Direct Blue 15.