

Summary

The habilitation thesis is structured in two parts. In the field described, 15 personal scientific articles have been published to date, as principal author or co-author, in journals with an impact factor, 7 in other indexed databases, as well as numerous articles presented at various international symposia, national symposia with international participation, and national conferences (full papers or abstracts).

The first part of the habilitation thesis concisely presents the main professional achievements to date.

The scientific research domains addressed have focused on environmental engineering. The entire scientific activity has been closely linked to the topic of the doctoral thesis (2009), entitled “*Contributions to the synthesis of non-benzidine direct dyes,*” completed under the supervision of Professor Dr. Eng. Alfa Xenia Lupea.

In this regard, the work began with experimental studies related to the synthesis of a considerable number of dis- and tris-azo direct dyes, alternatives to benzidine-based dyes, using as central components two diamines considered non-carcinogenic compared to benzidine: *4,4'-diaminostilbene-2,2'-disulfonic acid* and *4,4'-diaminobenzanilide*. The practical part consisted of applying these dyes both on cellulosic fibers and by incorporating them into acrylic films. Naturally, these steps were followed by determinations of fastness properties and color parameters of the dyeings, performed in the *CIE L*a*b** system. The color of the films was also studied in the same color space.

The investigation of the toxicity of several dyes derived from 4,4'-diaminobenzanilide began with studies on colonies of *Hydractinia echinata* (H. echinata) and continued with research on heterotrophic bacteria. Here, one may also mention *in vivo* imaging examinations on human skin, as well as the antibacterial properties of several dyes belonging to both classes.

As expected, the need for the treatment of textile wastewater became inevitable. Therefore, physical treatment methods for laboratory wastewater containing some commercial dyes (adsorption on various natural and synthetic substrates) were followed by chemical

treatment methods (advanced oxidation processes, electrochemical processes) applied to a series of newly synthesized dyes.

Accordingly, a literature review is presented, covering concepts related to the synthesis, applications, and toxicity of the above-mentioned alternative direct azo dyes—replacements for benzidine-based dyes—as well as their removal from wastewater.

This is followed by the presentation of original results concerning the aspects mentioned above.

It is well known that azo dyes represent the largest and most diverse class of organic dyes used industrially. They contain one or more azo groups ($-N=N-$), responsible for their intense color and stability. Their synthesis is accessible and covers almost the entire color spectrum. Major industrial applications include the textile industry, pigment production for paints and varnishes, inks, plastics, cosmetics, food products, etc.

Therefore, the original part is divided into two sections: the first dedicated to direct azo dyes derived from *4,4'-diaminostilbene-2,2'-disulfonic acid*, and the second focusing on direct azo dyes derived from *4,4'-diaminobenzanilide*.

Thus, *nine* dyes were synthesized using *4,4'-diaminostilbene-2,2'-disulfonic acid* as the central component, *seven* of which are new and not previously reported in the literature. Subsequently, many of these dyes were incorporated into acrylic-based films, mixed with a standard pigment (TiO_2 , Pigment 6, C.I. 77891), and applied to a cellulosic substrate. The spectrophotometric color study in the *CIE $L^*a^*b^*$* system (under the influence of the three classical illuminants: D65—daylight, A—incandescent light, and F2—cool fluorescent light, using a 10° observer) yielded results supporting their appreciable coloring power. Simultaneously, the classical phenomenon of metamerism—expressing the dependence of color parameters on the illuminant—was clearly highlighted, its commercial importance being well recognized.

Similar conclusions were reached when applying the same protocol, accompanied by fastness determinations on cotton fibers, for a smaller number of *new* dyes derived from *4,4'*-

diaminobenzanilide. Literature data regarding color analysis of dyes belonging to these two classes are extremely limited.

It can be concluded that these compounds may be used as alternative dyes to benzidine-based ones. Furthermore, *two new* dyes with *4,4'-diaminostilbene-2,2'-disulfonic acid* as the central component and *one new* dye derived from *4,4'-diaminobenzanilide* were monitored through *in vivo* imaging analysis on human skin, to evaluate individual tolerance. The results proved encouraging, as no changes in skin color or texture were recorded, nor any cases of contact dermatitis following their application.

At the same time, their antimicrobial activity was tested against two Gram-positive bacteria (*Staphylococcus aureus* and *Streptococcus pyogenes*) and three Gram-negative bacteria (*Pseudomonas aeruginosa*, *Proteus vulgaris*, and *Escherichia coli*), using the disk diffusion method. The data indicate that these compounds exhibit notable antimicrobial activity against the tested species, with a more pronounced effect on *Staphylococcus aureus* and *Escherichia coli*—an unconventional and interesting application.

It is known that determining the toxicity of compounds on environmental microorganisms requires establishing their minimum toxic concentration. In this regard, toxicity tests were performed on heterotrophic bacterial cultures obtained from the Bega River, using a series of *five new* dyes derived from *4,4'-diaminobenzanilide*. After testing the dyes at increasing concentrations and comparing them with a control, the results indicate a low degree of toxicity. It is known that toxicity is mainly determined by dye stability, biodegradability, and the toxicity of degradation products. To complete the studies, the final part addressed the treatment of colored wastewater containing some of the dyes mentioned above. Two different chemical pathways were investigated: the first based on advanced oxidation processes, and the second on electrochemical methods.

Thus, a photocatalytic treatment ($\text{TiO}_2\text{--MoO}_3$ and UV light) was applied for the depollution of synthetic wastewater, each containing *one* of the new dyes. One of these dyes contains *4,4'-diaminostilbene-2,2'-disulfonic acid* as the central component, while two are derived from *4,4'-diaminobenzanilide*. Monitoring of the mixed treatment, performed by UV-Vis

spectroscopy and chemical oxygen demand measurements, indicated efficient degradation of the compounds.

Finally, the electrochemical behavior in a non-aqueous medium of a series of *five new* dyes derived from *4,4'-diaminostilbene-2,2'-disulfonic acid* was investigated using cyclic voltammetry. This analytical technique was used to elucidate potential oxidative degradation pathways. The collected data showed that the anodic oxidation of the studied chromophoric structures follows an irreversible pathway, most likely occurring at the amide nitrogen common to all structures.

The valorization of these results materialized in 8 personal scientific articles, as principal author or co-author, published in journals with an impact factor, as well as numerous articles presented in other indexed databases and at international, national with international participation, and national symposia (full papers or abstracts).

The second part of the habilitation thesis presents the objectives from the perspective of scientific and academic career development.

The thesis concludes with a list of 208 bibliographic references.