Budapest University of Technology and Economics
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Ph. D. Theses

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New Dyeing Procedures, Complex Forming Compounds and their Role in the Photoinitiated Conversion of Dyes

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1. Introduction

The analysis of the life-cycle of raw materials and chemicals in the chemical and textile industries are important environmental requirement. The role of dyes proved to be particularly significant in this field.

The reduction of the number of individual dyes in dyeing, the increase in the proportion of the fixed reactive dyes, decolouration and removal of residual dyes in the dye bath, increase in the lifetime of textiles in use have been targets of my work.

In this respect the following has to be considered. Environmental-friendly dyes adequate for trichromatic dyeing have to be selected from the great number of synthetic organic ones. Accurate knowledge about the concentration of the dyebath and that of the wastewater of the dye-house is essential requirement in the elaboration of dyeing technologies as well as that of the wastewater treatment. Photochemical decolouration or complete removal of dyes from wastewater is applied preferably. Complete removal of the dissolved dye by complexation became lately actually instead of nanofiltration.

In agreement with the preceding the aim of my work has been as follows:

- Optimization of method of determination of the fixed proportion of reactive dyes as well as that one remaining in the dyebath by means of ANOVA analysis;
- Determination of the relative efficiency of cations and anions in heterobifunctional reactive azo dyeing used for increase in the proportion of the fixed dyes;
- Elaboration of trendy colours of 2005 spring and summer by means of tri-chromatic reactive dyeing;

- Detailed analysis of interaction between disperse, acid and reactive dyes respectively with complexating organic compounds with respect to the removal of dyes from dye-house wastewater;
- Dependence of lightfastness, decisive in the lifetime of the garments, from the composition of the atmosphere with respect to the presence or absence of air, oxygen, nitrogen and moisture furthermore to the presence or absence of perspiration;
- Determination of the kinetic of photo destruction as well as methyl orange as of three heterobifunctional reactive azodyes and of their complexes formed by cyclodextrin or by crown ether in water and in chloroform, respectively.

2. Device and methods in experiments

MATHIS Labomat BFA-12, LINITEST Hanau and MultiDye have been used in dyeing experiments.

HP UV-VIS 8452A has been served for the determination the light absorption.

DATACOLOR MICROFLASH 200 has served for the determination of color characteristics of the dyeings (Softwares: Datamach 3.0 and Datamaster 2.3.1.).

STATISTICA 7.0 software-pack has been used for the evaluation of the fixed dye proportion.

JASCO-810 *CD*-ORD Spectropolarimeter has been the equipment for measuring the CD/ORD spectra of the dye-cyclodextrin complexes.

Solubility isotherms have been constructed by means of the special laboratory dyeing equipment.

VirFis Sentry 12525 has served for the lyophilisation of dye-cyclodextrin complexes.

BRUKER DRX 500 and VARIAN Inova 500 (with cryogenic probe) have been used for constructing ^{1}H-NMR spectra of dye-cyclodextrin, dye-crown ether and dye-cucurbituril complexes.

Perkin Elmer ESI-MS and Varin MAT 312 FAB-MS have been the tools for measuring the MS spectra of the dye-cyclodextrin complexes.

Kaiser IR Spectrometer and FT-RAMAN has been used for constructing IR and RAMAN spectra of dye-cyclodextrin complexes, while BRUKER Tensor-37 IR Spectrometer was used for those of dye-cucurbituril complexes.

Dyeings have been irradiated to light on Xenotest equipment.

Dye solutions (up to 5 ml) have been irradiated to light on optical bench and over volume have been treated in a photochemical reactor.

Dissolved oxygen has been removed from the dye solution by streaming nitrogen through it.

3. New scientific results

1. The accuracy of the methods determining the fixed proportion of heterobifunctional reactive azodyes on cotton has been compared by of ANOVA methods. Most accurate has been proven indirect I method followed by indirect II method while the direct method was less accurate by one order of magnitude [9, 23].

2. It could be demonstrated that potassium sulphate was the best in supporting the fixation of two heterobifunctional reactive azodyes on cotton fabric among the studied six electrolytes (NaCl,.Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, $MgSO_4$) [1, 11, 12, 16, 18].

3. It could be demonstrated that selected trendy colours could be reproduced on cotton fabric by trichromatic heterobifunctional reactive azodyeing [2, 3, 4, 5, 21, 22].

4. The complex formation of one azo acid dye and three disperse dyes different in their chromophore group with substituted β-cyclodextrins as well as with 18-crown-6 ether could be justified. Correlation could be established between the stability constant of disperse-dye RAMEB complexes and their dyeing ability [6, 7, 13, 14, 15, 17].

5. New synthesis method could be elaborated for selective production of cucurbit[6]uril and cucurbit[8]uril, respectively. Their complexation capacity with seven different dyes has been determined in the presence and absence of electrolytes, respectively[10, 24].

6. Dominantly radical photodegradation of four azodyes could be justified in polar (water) as well as in nonpolar (chloroform) liquid phase in the presence of different additives (alcohols, cyclodextrins, crown ethers and components of artificial perspiration, respectively) furthermore also on cotton fabric in different atmospheres [7, 8, 14, 17, 19, 20].

4. Possibility of application

- Exact analysis of the fixed reactive dye-content in dyeings.
- Optimisation in textile dyeing technologies by reducing the specific demand in dye consumption.
- Purification of the wastewater of dye-houses.

- Regulation of the rate of photochemical transformation of dyes according to specific requirements.

5. Publications related to the thesis

5.1. Published papers

5.1.1. Published papers in Hungarian

1. Nagy H. J., Rusznák I., Sallay P., Víg A.: Elektrolitok hatása a heterobifunkciós reaktív azoszínezékek szorpciójára és kapcsolódására pamutszöveten
   *Magyar Textiltechnika **56**, 97-101 (2003)*
2. Rusznyák O., Nagy H. J., Jantai T-né., Sallay P., Rusznák I., Víg A.: A rejtélyes türkiz (Divatszínek előállítása trikromatikus színezéssel) I rész
   *Magyar Textiltechnika **57**, 101-103 (2004)*
3. Rusznyák O., Nagy H. J., Jantai T-né., Sallay P., Rusznák I., Víg A.: A rejtélyes türkiz (Divatszínek előállítása trikromatikus színezéssel) II rész
   *Magyar Textiltechnika **57**, 121-123 (2004)*
4. Rusznyák O., Nagy, H. J., Rusznák I., Sallay P., Víg, A.: Pamutcellulóz trikromatikus színezése heterobifunkciós, reaktív színezékekkel I. rész
   *Magyar Textiltechnika **58**, 156-157. p. (2005)*
5. Rusznyák O., Nagy, H. J., Rusznák I., Sallay P., Víg, A.: Pamutcellulóz trikromatikus színezése heterobifunkciós, reaktív színezékekkel II. rész
   *Magyar Textiltechnika **59**, 12-13. (2006)*
6. Nagy H. J., Rusznák I., Sallay P., Víg A.: Poliészter színezése komplexált diszperziós színezékekkel
   *Magyar Textiltechnika **60**,* 143-144. *(2007)*
7. Nagy H. J., Rusznák I., Sallay P., Víg A.: Metilnarancs komplexálás és a komplexek fotokémiája
   *Magyar Kémikusok Lapja **63**,* 4 106-111. *(2008)*

5.1.2. Published papers in English

8. A. Víg, K. Sirbiladze, H. J. Nagy, P. Aranyosi, I. Rusznák, P. Sallay: The light stability of azo dyes and dyeings V.-The impact of the atmosphere on the light stability of dyeings with heterobifunctional reactive azo dyes
   *Dyes and Pigments **72,** 16-22 (2007)*
9. H. J. Nagy, A. Kuvik, I. Rusznák, P. Sallay, Á. Drégelyi Kiss, S. Kemény, K. Sirbiladze, A. Víg: Reliability Studies in the Determination of Quantitative Covalent Fixation of Reactive Dyes on Cellulose
   Periodica Polytechnica (2008) (Accepted.)
10. H. J. Nagy, P. Sallay, M. L. Varga, I Rusznák, P. Bakó[1], A. Víg: Removal of dyes from industrial wastewater by cucurbiturils
    Textile Research Journal (2008) (Accepted.)

5.2. Presentations

5.2.1. Presentation (full text)

11. Nagy H. J., Rusznák I., Farkas L., Sallay P., Víg A.: Elektrolitok hatása a reaktív azoszínezések részfolyamataira
    XXIX. Kolorisztikai Szimpózium, Eger (2003.)
12. Nagy H. J., Rusznák I., Sallay P., Víg A.: The role of quality and concentration of electrolytes in estabilishing environmental-friendly reactive dyeing (low salt (LS), high fixation (HF))
    IV. Nemzetközi Textilvegyész és Kolorista Szakember-Találkozó, Budapest (2003.)
13. Nagy H.J., Rusznák. I., Víg A., Sallay P.: Poliészter színezése ciklodextrin-diszperziós színezék inklúziós komplexekkel
    XXX. Jubileumi Kolorisztikai Szimpózium, Eger (2005.)
14. Nagy H. J., Rusznák I., Sallay P., Víg A.: Metilnarancs komplexálás és a komplexek fotokémiája
    XXXI. Kolorisztikai Szimpózium, Eger (2007.)

5.2.2. Presentation (abbreviated)

15. Nagy, H. J.: Poliészter színezése diszperziós színezék-ciklodextrin inklúziós komplexekkel
    BME Vegyészmérnöki Kar 2. Doktoráns konferenciája (2004.)

5.2.3. Presentation (no printed publcation)

16. Nagy H. J.: Elektrolitok hatása a heterobifunkciós reaktív azoszínezékek szorpciójára pamutszöveten
    MTA Természetes Polimerek Munkabizottságának Ülése, Sopron (2002.)
17. Nagy H. J., Rusznák I., Sallay P., Víg A.: Részletek a színezékek komplexeiről és egyikük fotokémiájáról
    MTA Természetes Polimerek Munkabizottságának Ülése, Budapest (2006.)

5.3. Presentation (published in CD-Rom)

18. Víg A., Nagy H., Sallay P., Farkas L., Sirbiladze K., Hernádi S., Rusznák I.: The impact of the electrokinetic-potencial at the cellulosics fabric surface on the reproducibility of reactive dying
    CD of IFATCC XIX.Congress, Paris (2002.)
19. Víg A., Sirbiladze K., Nagy H. J., Aranyosi P., Rusznák I., Sallay P.: Az atmoszféra összetevőinek hatása a heterobifunkciós reaktív színezések fényállóságára
    XXIX. Kolorisztikai Szimpózium, Eger (2003.)
20. Rusznyák O., Nagy H. J., Rusznák I., Sallay P., Víg A.: Heterobifunkciós reaktív színezékek trikromatikus megkötődése pamutcellulózon
    XXX. Jubileumi Kolorisztikai Szimpózium, Eger (2005.)
21. A. Víg, P. Pataki, K. Sirbiladze, H. J. Nagy, P. Aranyosi, I. Rusznák, P. Sallay: Impact of environmental factors on lightfastness of reactive azo dyes
    TEXCHEM lektorált előadás szöveg, Dvore Králové (2003.)
22. Rusznyák O., Nagy, H. J., Rusznák, I., Sallay, P., Víg, A.: Divatszínek trikromatikus előállítása reaktív színezékekkel
    Nemzetközi Textilvegyész és Kolorista Szakember Találkozó, Budapest (2005.)

23. Nagy H. J., Kuvik A., Drégelyi Kiss Á., Kemény S., Rusznák I. Sallay P. Víg A.: Cellulózon rögzített reaktív színezékmennyiség megkötődését meghatározó vizsgálati módszerek összehasonlító megbízhatósági elemzése
    XXXI. Kolorisztikai Szimpózium, Eger (2007.)
24. A. Víg, P. Sallay, H. J. Nagy, M. L. Varga, I. Rusznák: The role of the difference in the internal cavity of cucurbituril rings in complexation of acid, reactive and disperse dyes respectively
    21th IFATCC Congress
    CD of IFATCC XXI. Congress, Barcelona, (2008.)

6. Other publication

1. A. Víg, H. J. Nagy, P. Sallay, I. Rusznák: The mechanism of production and alkali-sensitivity of glucuronic acid-glucose copolymer fibres, yearns and fabrics of cellulosic origin useful in human surgery
   Cellulose Chemistry and Technology ***40****, 353-358 (2006)*