

Studies of the Kinetics of Dye Decomposition in Water Solutions

E. Maćkowska¹, R. Gogolin¹, W. Dumczal², J. Gaca^{1*}

¹Department of Chemistry and Chemical Engineering, University of Technology and Agriculture, Seminaryjna 3, 85 - 326 Bydgoszcz, Poland

²Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Received: 11 September, 2002

Accepted: 12 March, 2003

Abstract

The behavior of water solutions of dyes under the influence of oxidizing agents has been described. Decomposition of the dyes in time was observed on the basis of changes in the adsorption spectra. The obtained spectrophotometrical data were subjected to the factor analysis in order to determine the number and the spectral characteristics of colour components in the systems under study. The correctness of the accepted mechanism of decolouration (parallel and successive reactions) was tested and the number of reaction stages was determined. The rate constants of substrate decomposition and product formation were determined. Moreover, the spectral profiles of intermediate products were obtained.

Keywords: dyes, oxidation, ozone, decolouration, kinetics

Introduction

One of the most dangerous sources of the natural environment pollution are the industrial liquid wastes. The rapid and water-consuming development of industrial production caused surface water pollution and serious waste treatment problems. The dye industry is particularly threatening from the ecological point of view. Any atypical colouration of liquid wastes stimulates a lot of interest for authorities engaged in environment protection, since colouration in the receiving body of water restricts, among other things, light transmittance and self-purification of water. During waste treatment processes, the dyes are practically not subjected to biological decay during their short stay at a sewage treatment plant. They are eliminated in most part by adsorption on sludge and the rest can be removed by sedimentation or in chemical processes.

Our studies aimed to verify whether the chemometric analysis based on the measurements of absorbance changes in the process of dye destruction by various oxidizing agents can be applied for determination of mechanisms of dye decomposition in water solutions.

The gryfacid dyes and gryfalans, i.e. metal complex dyes of 1:2 type, were selected for oxidation. The above-mentioned dyes are produced by chemical plant "Zachem" in Bydgoszcz. They are characterized by high wash-resistance and light-resistance [1]. The near-zero BOD₅ value allows us to state that they are resistant to biodegradation. The significant difficulties in decomposition of dyes by biological methods stimulated the search for possibilities of decolourization. One of the methods of dye degradation involves the use of peroxides [2, 3, 4]. On the grounds of the wide variety of the dyes produced, it is difficult to describe the general kinetic model of their degradation [5]. In the case of metal complex dyes, the additional factor which can have an effect on the course of decolourization reaction is the presence of metal in their molecules [6].

*Corresponding author

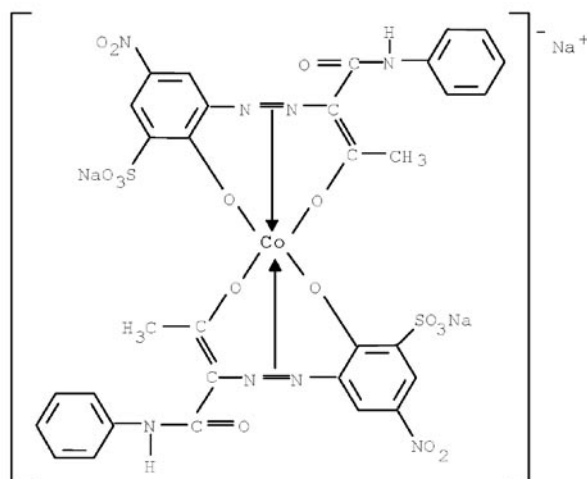
Experimental Procedures

Water solutions of dyes (further called the initial ones) were prepared by selecting concentrations in such a manner that the initial absorbance values of these solutions were near to unity after a ten-fold dilution. Depending on ϵ of the dyes studied, the concentrations of their water solutions were within the range from 10^{-3} to 10^{-4} mol·dm $^{-3}$. The solutions were stored in flasks without access to light. It was found that all the dyes studied are stable in water solutions because no changes in absorbance values occurred during their storage. The effect of H_3O^+ ions on the absorption spectra parameters has also been studied but no relation between the absorption maximum and the pH of the solution was observed.

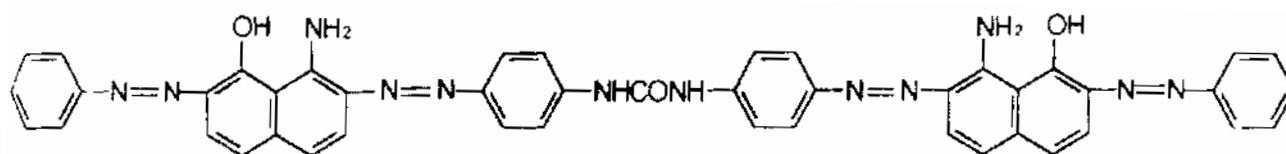
Water solutions of dyes were subjected to the action of the oxidizing agents: $(NH_4)_2S_2O_8$ in concentrations from 10^{-1} to 10^{-2} mol·dm $^{-3}$ and O_3 whose flow rate in solution was 0.153 cm 3 O_3 /min.

The tests were carried out as follows: exactly 8 cm 3 of the initial dye solution and a defined amount of oxidizing agent were introduced into graduated flasks (100 cm 3) and filled up with distilled water to the mark. Changes of absorption in time were measured at wavelengths within the range from 300 to 800 nm for each prepared sample.

The obtained sets of spectrophotometrical data were subjected to the factor analysis in order to determine the number and spectral characteristics of colour components in systems under the study [2].



Scheme 1. C.I. Acid Yellow 194



Scheme 2. C.I. Direct Green 97.

The absorbance of a multicomponent system is (according to the Lambert-Beer law) a sum of absorbances of the individual components, which in the matrix notation (taking into account the experimental errors) can be given by the following formula:

$$A = S \times C + E$$

where:

A - is the matrix of absorbances of j samples measured at i spectral points (size **A** is $i \times j$).

S - is the matrix of molar absorbance coefficients of all the components; its size is $i \times r$, while r represents the number of colour components in the system and the columns of the matrix **S** are spectral profiles of the components in the system.

C - stands for the matrix of component concentrations in a given series of samples; its size is $r \times j$. The rows of matrix **C** represent the concentration profiles of the individual components for a given series.

E - denotes the matrix of errors; its size is $i \times j$. In practice, matrix **E** contains also the discrepancy from the accepted mathematical model of the system, for example deviations from the Lambert – Beer law.

For decomposition of matrix **A** to component matrices and for determination of a number of real and linear independent colour components r (principal component analysis, PCA), the procedure based on NIPALS [7] algorithm and IND function by Malinowski IND [8][9] was applied and the solution was obtained in the form of the following equation:

$$A = T \times P + E$$

where matrices **T** and **P** in contradiction to the matrices **S** and **C** have no physicochemical sense and they describe abstract colour agents. The matrices **T** and **P** are transformed into **S** and **C** applying the operation called rotation or transformation:

$$(T \times R) \times (R^{-1} \times P) = S \times C$$

The elements of matrix **R** were calculated taking into account the dependences resulting from the accepted kinetic models of the studied conversions (target factor analysis) [7]. Evaluation of the model applied was accomplished on the basis of the SPOIL function (formulated by Malinowski) values [10]. The spectral and concentration characteristics of the real independent colour components

Table 1. General characteristics of the dyes studied.

Dye	Molecular formula	Molar mass	Concentration of solution studied [mole/dm ³]	Absorption maximum [nm]
Direct Green 97	C ₄₅ H ₃₄ O ₃ N ₁₂	790	2.74 · 10 ⁻⁴	616
Acid Yellow 194	C ₃₂ H ₂₂ N ₂ O ₁₆ S ₂ CoNa	966	5.75 · 10 ⁻⁴	446

present in the system as well as the rate constants of conversion of these components were obtained. The spectral data were analyzed applying Excel 5.0, using Solver tool and macros developed especially for this purpose. On account of the presence of the considerable excess of oxidizing agent in the samples, the system of first-order successive reactions was accepted as a kinetic model. Standard deviations of the rate constants were evaluated by using the procedure developed on the basis of the algorithm described by de Levie [11].

Absorption was measured by spectrophotometer Handbook HP 8452A Diode-Array and ozone was generated by ozonator with a lamp (20W) produced by Osram.

The structural formulas and trade names of the dyes chosen for experiments are presented on Schemes 1 and 2.

Results

The effect of diammonium peroxydisulfate(VI) on decolouration of Direct Green 97 is presented below. Absorbance was measured in 1 min intervals for 20 min.

The mechanism of the reaction under the study was identified on the basis of the results of factor analysis of the result set obtained during measurements, evaluation of the character of concentration profiles and statistical evaluation of other models fitting experimental data.

Factor analysis of the result set obtained during measurements showed that there were only three colour com-

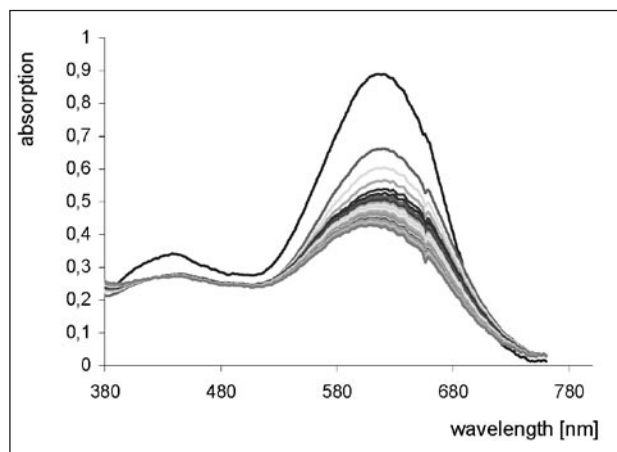


Fig.1. Changes in absorption spectra of Direct Green 97 in time under influence of ozone.

Table 2. Numerical results of the chemometric analysis of the system: Direct Green 97 – (NH₄)₂S₂O₈.

	k [1/min]	σk	SPOIL
Stage I	2.16	0.34	5.37874
Stage II	0.02244	0.00063	1.10094
Stage III	0.0908	0.0031	3.93981

ponents in the system. The transformation of the abstract concentration profiles taking into regard only the condition of non-negativity of concentrations of all the components leads to the profiles whose shape (maximum on the profile of product 1, inflexion on the profile of product 2) suggests a mechanism corresponding not to parallel but to the two-stage successive reaction:



However, the fit to the theoretical concentration profiles corresponding to this model gives the SPOIL function values over 10, which made us reject the model [5]. For the same reason, the model of two-stage successive reaction with one or two reversible stages cannot be accepted. Yet the completion of the model with the conversion of the last colour product into transparent substances:

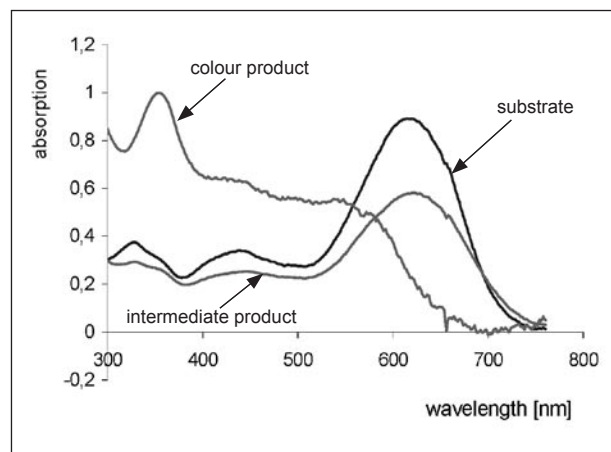


Fig.2. Spectral profiles of the real components of the system: Direct Green 97 – (NH₄)₂S₂O₈.

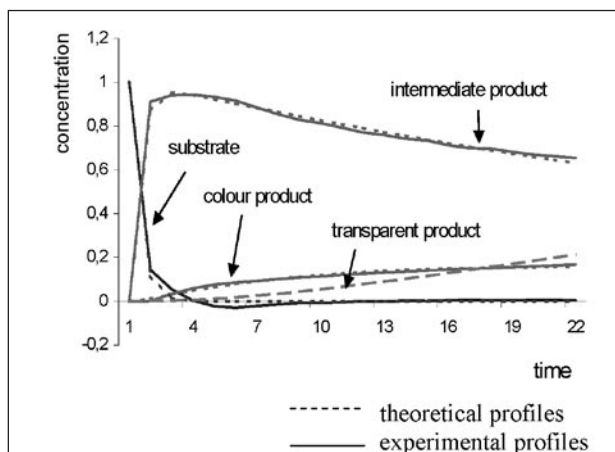


Fig. 3. Concentration profiles of the real components of the system: Direct Green 97 – $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

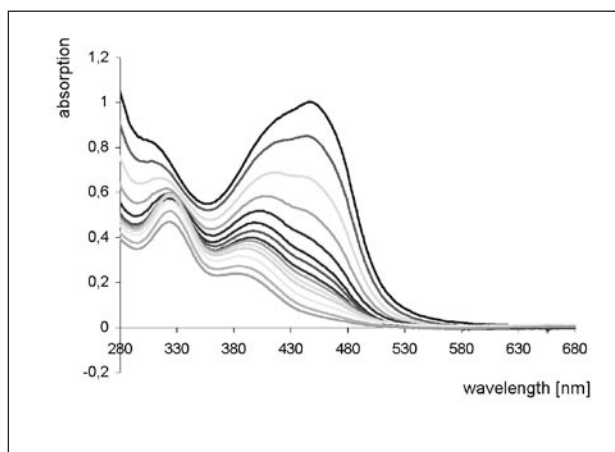


Fig. 4. Changes in absorption spectra of Acid Yellow 196 in time under influence of ozone.

substrate \rightarrow product 1 \rightarrow product 2 \rightarrow transparent products

allowed us to obtain-lower than 6 values of the SPOIL function (Table 2), i.e. statistically acceptable models. Spectral profiles of the real components of the system are presented in Fig. 2. Theoretical and experimental concentration profiles of the system are presented in Fig. 3.

In the next stage of experiments, the effect of ozone action on the water solution of Acid Yellow 194 was determined. The experiment was carried out at the ozone flow of $0.153 \text{ cm}^3 \text{ O}_3 \cdot \text{min}^{-1}$. The adsorption values were measured at 5 min intervals for 80 min.

The results of the factor analysis proved that reaction under study runs according to the analogous kinetic model as the decomposition of Direct Green 97:

substrate \rightarrow product 1 \rightarrow product 2 \rightarrow transparent products

However, both systems were distinctly different with respect to the first stage and the stability of the second intermediate product (Table 3).

Conclusions

It was found that the chemometric analysis can be successfully applied for examination of the mechanism of decolourization of dyes with the use of oxidizing agents. The results suggest the mechanism of these reactions (parallel, successive reactions) and permit estimation of the number of the reaction stages. The rate constants of substrate decomposition and product formation can also be determined to a high accuracy and, moreover, the spectral profiles of the interme-

Table 3. Numerical results of the chemometric analysis of the system: Acid Yellow 194 – ozone .

	k [1/min]	σk	SPOIL
Stage I	0,0697	0,0017	4,10446
Stage II	0,0335	0,0021	3,94878
Stage III	0,01003	0,00061	1,1681

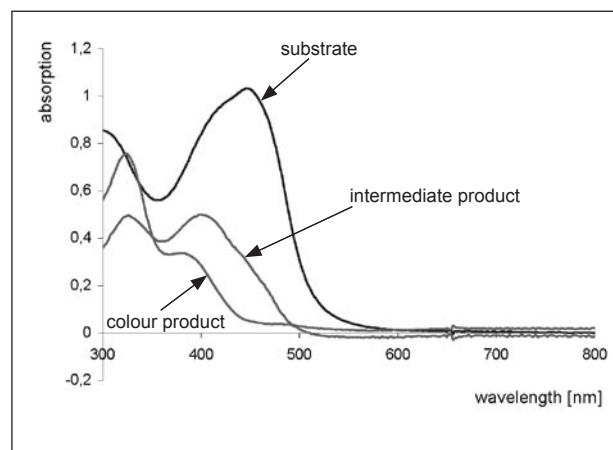


Fig. 5. Spectral profiles of the real components of the system: Acid Yellow 194 – ozone.

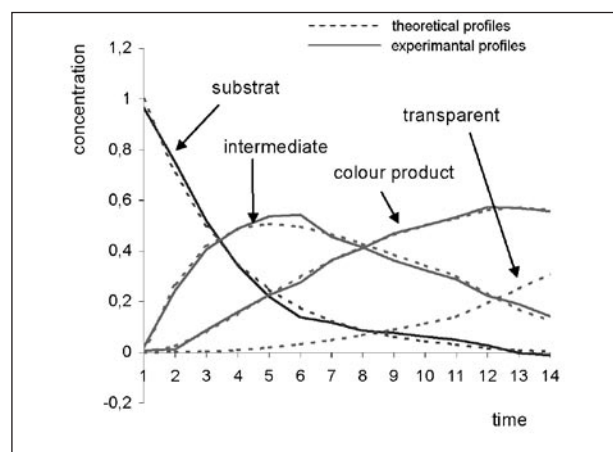


Fig. 6. Concentration profiles of the real components of the system: Acid Yellow 194 – ozone.

diate products can be obtained, which helps identification or determination of the structure of the products.

Determination of the number of products allows us to describe the mechanism of the reaction in the system, which allows us to determine k constants. Knowledge of k values for the individual stages of reaction implies the possibility of foreseeing the stability of the individual products of decomposition formed in the environment and moreover, the possibility of controlling the individual stages of the process.

References

1. PRZYBYLEK M., Barwniki i Środki Pomocnicze, **2**, 50, **1985**.
2. THOMPSON K. M., GRIFFITH W. P., M Spiro, Journal of the Chemical Society - Faraday Transactions **90**,(8), 1105, **1994**.
3. DO J.S., YEH W.C., Journal of Applied Electrochemistry **26**, (6), 673, **1996**.
4. ARTEMEV, ARTEMEVA M.A., VINOGRADOV M.G., ILIKA T.I., Russian Journal of Applied Chemistry Part 2, **67**, (9), 1354, **1994**.
5. HACHEM C., BOCQUILLON F., ZAHRAA O., BOUCHY M., Dyes Pigm., **49**(2), 117, **2001**.
6. BANASZCZYK K., RADZYMIŃSKA E., GACA J., Gaz, Woda i Technika Sanitarna, **8**, 233, **1994**.
7. MALINOWSKI E.R., Factor Analysis in Chemistry, Wiley - Interscience, New York **2002**.
8. ALBERGALI A., NYGERN J., KUBISTA M., Anal. Chim. Acta, **379**, 143, **1999**.
9. OTTO M., Chemometrics, Wiley - VCH Verlag GmbH, Weinheim, **1999**.
10. MALINOWSKI E. R, Anal. Chim. Acta, **103**, 339, **1978**.
11. DE LEVIE R., J.Chem.Educ., **76**, 1594, **1999**,