

Investigation of the persistence of metal complex dyes

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Introduction

Every technological process, in any sector of industry, generates by-products which enter the environment and pollute water bodies and bottom deposits. Rapid expansion of the production of dyes, pigments, paints, inks and varnishes has created many threats to the environment, resulting from the use of colour substances in the manufacture of these products. Any unusual colouring of wastewater arouses the interest of environmental authorities, as the coloration of water bodies reduces light transmittance and self-cleaning capacity of water.

Most dyes applied and used in proper manner do not pose a significant threat to the environment. However, the dyestuffs industry uses thousands of raw materials and intermediates, among which substances posing toxicological and ecological threat can always be found [1]. Dyes are organic compounds of diverse and complex chemical structure. More than half of them are azo dyes. Usually the main constituents of their chemical structure are substituted aromatic or heteroaromatic groups, linked by one or more azo bonds [2]. Azo derivatives pose a particularly high toxicological, carcinogenic and mutagenic threat [1]. Hence the questions raised about the harmfulness of the dyestuff industry products. However, most dyes applied and used in proper manner do not pose a significant threat. The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers has assessed the toxicity of several thousand commercial dyestuffs, derived from various chemical groups, and found that only about 1% of them show elevated toxicity. Thus, dyes generally are not harmful and under normal conditions of use and manufacture should not cause poisoning. For a layman the colouring of water may be a sign of its high contamination, even when the concentration of the dye is not more than $4 \times 10^{-5} \text{ g/dm}^3$ and is harmless. It is often more important to decolorize wastewater before its discharge to a river, a lake or a pond, than to remove colourless, soluble organic substances that in fact are usually biologically non-degradable and cause high chemical oxygen demand. Dyes do not undergo biological decomposition during their short residence time in a wastewater treatment plant. Large fraction is eliminated by absorption on sewage sludge, the remainder may be removed by precipitation or by means of chemical processes. The purpose of the treatment of coloured wastewater is therefore to change its composition and properties so that the discharge of such wastewater does not disturb the natural biological equilibrium, allows for reuse of the water and does not pose a threat to human health. The effects of processing textile industry wastewater depend not only on the method of processing, but in the first place on the type of chemicals that form the colour composition.

The diversity of wastewater compositions is the reason for a lack of unity in the approach to the treatment of such wastewater.

Experimental

Water and wastewater decolorization is now conducted in a multitude of ways, which clearly shows that none of the existing processes is 100% efficient. Studies [3, 4, 5, 6] have shown that dyes are most readily destroyed by means of various oxidizers and deep oxidation systems, such as: $\text{UV} + \text{H}_2\text{O}_2$, $\text{UV} + \text{O}_3$ or $\text{UV} + \text{S}_2\text{O}_8^{2-}$. Chemical oxidation transforms organic compounds, including dyes, into

simpler, usually colourless substances, and the oxidizers applied are decomposed into by-products that are harmless to the environment.

In the investigations presented here we compared the efficiency of decolorization of coloured solutions by various oxidizing systems in order to assess which of them could constitute a useful method of decomposing these solutions. Oxidation was applied to coloured 1:2 metal complex compounds, which are very competitive in relation to acid dyes. Progress in the development of polyamide fibres and increasing requirements for the resistance of dyed products to wet media and to light have led to a significant drop in demand for acid dyes. These have been replaced by 1:2 metal complex dyes, which provide high fastness and acceptable levelling. In previous studies [3-6] we have analysed in detail the persistence of aqueous solutions of 1:2 metal complex dyes manufactured by BORUTA-ZACHEM KOLOR Sp. z o. o. in Bydgoszcz. The dyes studied included Gryfalan Violet RL and Gryfalan Navy Blue RL. These dyes have identical coordination sphere with different central ions: Co and Cr. It was found that decolorization of both dyes could be effected quite rapidly using hydrogen peroxide in an acidic medium or using Fenton's reagent ($\text{H}_2\text{O}_2 + \text{H}_3\text{O}^+ + \text{Fe}^{2+}$). Decolorization reaction run much faster when ozone was used. Chemometric analysis of absorbance change in time was applied to determine the mechanism of dye decomposition reaction in aqueous solutions. In the chemometric analysis of the systems studied, the best fit of concentration profiles of the studied systems to reference profiles was achieved when it was assumed that the reactions of each of the dyes are ruled by different mechanisms. A decision was made to synthesize other complexes of identical coordination sphere, but with different central ion (Fe, Cu, Ni) and verify the mechanism of their decomposition using chemometric analysis.

Aqueous solutions of the coloured metal complexes of the formula given in Figure 1 were prepared in measuring flasks. Molar concentrations of the solutions ranged from 2×10^{-5} to $7 \times 10^{-5} \text{ mol/dm}^3$.

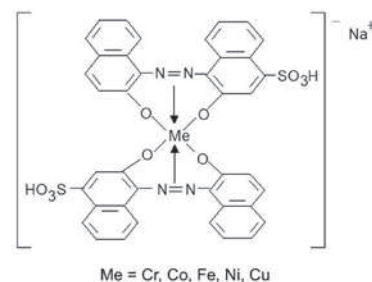


Fig. 1. Formula of 1:2 metal complex dyes

The following oxidizing agents were added to the solutions: H_2O_2 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{H}_2\text{O}_2 + \text{Fe(II)}$ and O_3 , the flasks were made up to the mark with distilled water and thoroughly agitated. Afterwards absorption in the 200–800 nm range was measured. Tests were conducted in both neutral as well as acidic medium. The loss of dye was calculated from formula 1:

$$\alpha = \frac{A_0 - A_t}{A_0} \cdot 100\% \quad (1)$$

where:

α – degree of solution decolorization

A_0 – absorption at time 0

A_t – absorption at time t

Discussion of results

The results obtained indicate that aqueous solutions of the synthesized coloured complex compounds, under the action of oxidizers, show persistence similar to that of dyes manufactured by BORUTA-ZACHEM KOLOR Sp. z o. o. in Bydgoszcz. It was found that the solutions were most resistant to decolorization by hydrogen peroxide in a neutral medium (an average colour loss of 20% after 90 minutes), less resistant in acidic medium (60% after 90 minutes). A 90% colour loss was determined after 50 minutes of reaction with diammonium peroxydisulphate. The most efficient decolorizing agent was the Fenton's reagent (hydrogen peroxide and Fe^{2+}). Complete decolorization occurred after 20 minutes. Good results were also obtained with ozone. After 40 minutes the solution was decolorized in 90%.

The reaction between the complex compounds and diammonium peroxydisulphate was selected for the determination of the decolorization mechanism by means of chemometric analysis. Examples of graphs of spectral changes used in the chemometric analysis are shown below.

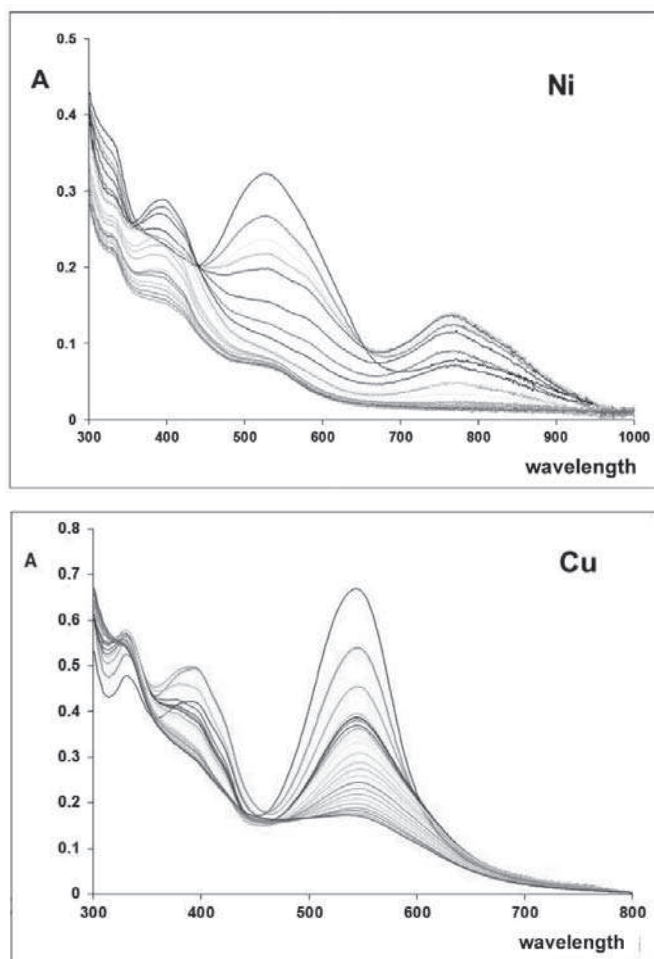


Fig. 2. Examples of changes in time in absorption spectra of coloured complexes under the action of $(\text{NH}_4)_2\text{S}_2\text{O}_8$

The interpretation of a collection of spectrophotometric data registered as spectra of systems of variable composition is difficult. However, the advantage of the spectrophotometric method is the ability to apply it in the case of very dilute solution ($\sim 10^{-5}$ M) and in the study of fast and extremely fast reactions, as well as in the study of unstable systems, when intermediate species cannot be observed.

The obtained collections of spectrophotometric data (Fig. 2) were subjected to factor analysis in order to determine the number and spectral characteristics of coloured constituents of the systems studied [7]. Spectral data were analysed using Microsoft Excel spreadsheet with Solver tool and macros created for this particular purpose [8, 9]. As

the samples contained large excess of the oxidizing agents, the system of first order consecutive reactions was adopted as the kinetic model.

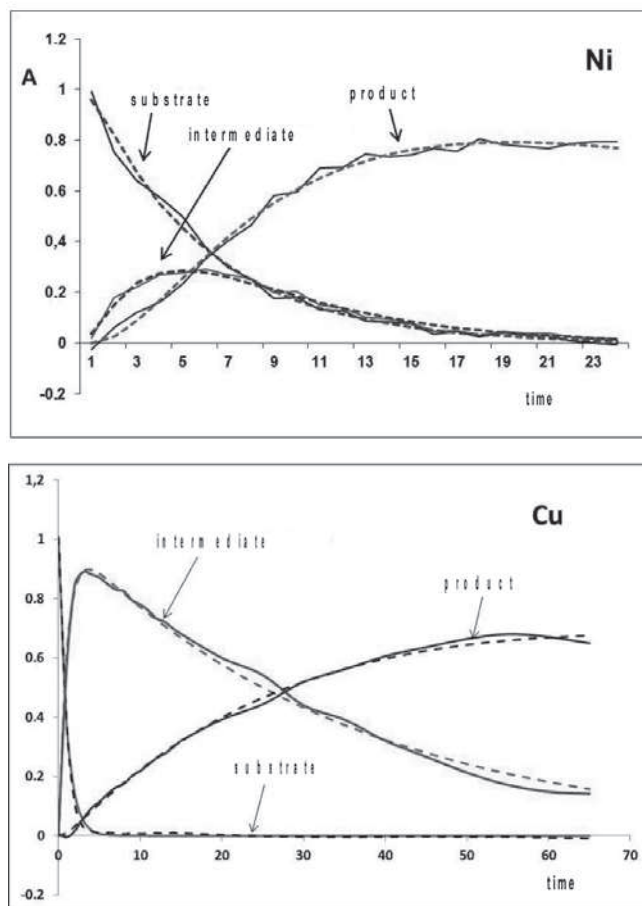


Fig. 3. Fitting matrices of the systems studied to reference matrices

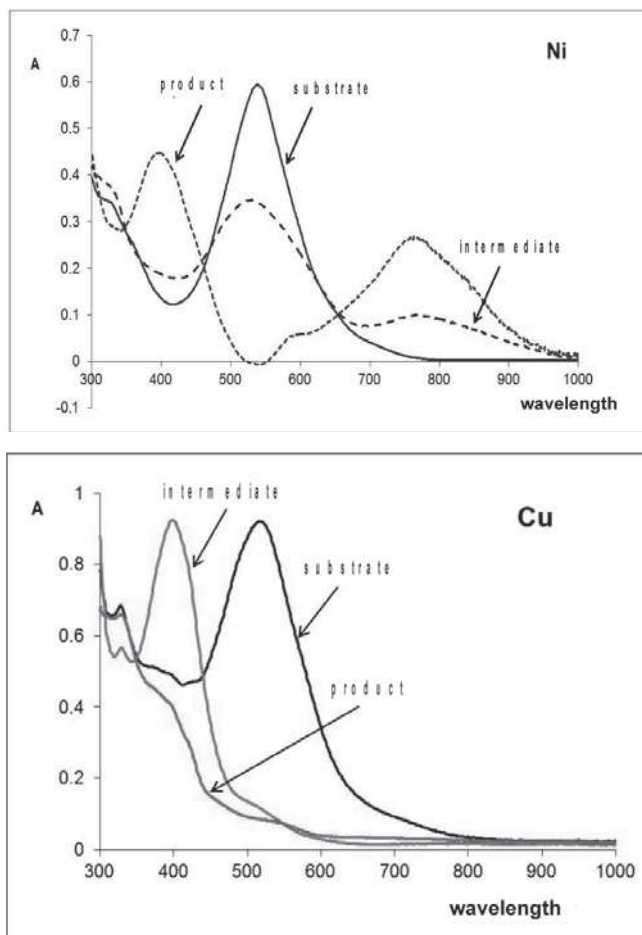
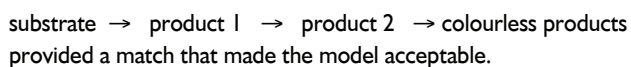


Fig. 4. Spectral profiles of the constituents of dye - $(\text{NH}_4)_2\text{S}_2\text{O}_8$ system

The factor analysis of the collection of measurement data indicated that there were three coloured species in the system. Transformation of abstract concentration profiles to a reference corresponding to a two-stage consecutive reaction:



did not provide a satisfactory match (SPOIL function values above 10), and indicated that the adopted model could not be accepted. Supplementing the model with the transformation of the last coloured product into colourless substances:



provided a match that made the model acceptable.

Examples of theoretical and experimental profiles of the system constituents are shown in Figure 3.

Numerical results of the chemometric analysis and calculated rate constants of the individual stages of the decolorization reaction are shown below.

Table I
Rate constants of the individual stages of the complex oxidation reaction

Metal complex compound	k_1, min^{-1}	k_2, min^{-1}	k_3, min^{-1}
$\text{C}_{40}\text{H}_{24}\text{N}_4\text{O}_{10}\text{S}_2\text{FeNa}$	1.41147	0.04243	0.00296
$\text{C}_{40}\text{H}_{24}\text{N}_4\text{O}_{10}\text{S}_2\text{NiNa}$	1.13488	0.02606	0.00835
$\text{C}_{40}\text{H}_{24}\text{N}_4\text{O}_{10}\text{S}_2\text{CuNa}$	1.09020	0.01030	0.01020
$\text{C}_{40}\text{H}_{24}\text{N}_4\text{O}_{10}\text{S}_2\text{CoNa}$	0.97893	0.02896	0.00550
$\text{C}_{40}\text{H}_{24}\text{N}_4\text{O}_{10}\text{S}_2\text{CrNa}$	0.55285	0.02682	0.00112

Summary

The results obtained indicate that changing the central ion in a 1:2 metal complex compound, the coordination sphere being identical, has no significant effect on the stability of that complex in aqueous solutions. All compounds tested can be decomposed by oxidizing with various agents, e.g.: H_2O_2 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{H}_2\text{O}_2 + \text{Fe(II)}$ or O_3 . It was found that decolorization of solutions under the action of diammonium peroxydisulphate proceeded according to the same mechanism. Decomposition products include both coloured, as well as colourless species. Chemometric analysis shows that intermediate products are formed in the reaction. Rate constants were determined for all stages of the reaction (substrate \rightarrow intermediate product \rightarrow coloured product \rightarrow colourless product) enabling the determination of the persistence of the compounds studied. The aim of the studies conducted is to find the best method of decolorizing wastewater containing 1:2 metal complex dyes.

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