Degradation of Some Dyes with Cobalt-Containing Oxidative System

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Abstract

Objectives: The objective of this study is to investigate oxidation of three dyes: indigo carmine, methyl violet and 2, 4-dinitrophenol by two-component system Co$^{2+}$-$\text{H}_{2}\text{O}_{2}$ further analyzing behavior of cobalt in Fenton-like processes.

Method: Oxidative degradation was effected in aqueous solutions of dyes under static conditions. Altering concentrations of substrates were analyzed spectrophotometrically. Dynamic light scattering was used to evaluate the condition of cobalt in the solution. The products of oxidative degradation were studied applying the method of nuclear magnetic resonance.

Findings: The study shows that hydrogen peroxide in presence of ions Co$^{2+}$ is capable of oxidizing indigo carmine. The sulfate ions in the system do not affect the kinetics of the oxidation process. It has been found that oxidation supposedly occurs following the radical mechanism similar to the processes observed in the Fenton system (Fe$^{2+}$ - $\text{H}_{2}\text{O}_{2}$). However, the range of pH values that makes oxidation possible differs considerably from the operating range of the Fenton system: With cobalt ions, the process runs at pH>6. It has been established that intensive oxidation of methyl violet and 2, 4-dinitrophenol also starts when pH value increases up to 6.6-6.8. The formation of cobalt-containing aggregates of cobalt hydroxides in the process of oxidative degradation of indigo carmine has been observed for the first time, i.e. the process occurs in ultra micro heterogeneous system. It has been shown that in presence of cobalt, the substrates are not oxidized in full; the products of oxidation are represented by a complicated set of organic compounds.

Applications/Improvements: In practice, functioning at higher pH values is an important advantage of the cobalt-containing system as compared to the iron-containing one.

Key words: Cobalt Ions, Hydrogen Peroxide, Oxidative Degradation

1. Introduction

Hydrogen peroxide is one of the most widely spread oxidizers that are used in developing Advanced Oxidation Processes implying liquid-phase degradation of organic contaminants by highly active radical particles. Such processes are studied extensively and are applied for the purposes of potable and waste water treatment. Generation of radical particles out of hydrogen peroxide increases redox potential of the system considerably. It is a well-known fact that radicals can be generated by way of introducing the ions of transition metals into the system, for example, ions of iron (II)$^{1}$:

$$\text{Fe}^{2+} + \text{H}_{2}\text{O}_{2} \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^{\cdot}$$

Oxidative system that contains hydrogen peroxide and iron ions (the so-called Fenton system) has been studied profoundly. At the same time, the number of studies dedicated to investigating the interactions between hydrogen peroxide and ions of other iron triad metals is rather scarce. For example, there are three-component oxidative systems based on hydrogen peroxide, cobalt ions and ascorbic acid$^{2}$. It is suggested that the system of cobalt ions – bicarbonate ions should be used for activating hydrogen peroxide$^{3}$. There are few publications dedicated to studying two-component oxidative systems containing hydrogen peroxide and cobalt salt. One of the studies$^{4}$ shows that the formation of radicals is preceded by the coordination of three molecules of hydrogen peroxide at one aquatic
ion of cobalt. Another study investigating the process of xylene orange oxidation by the system Co^{2+}-H_2O_2 in micellar medium suggests the mechanism of oxidative degradation implying the stage of radical breakdown of hydrogen peroxide in presence of double-charged ion of cobalt similar to the Fenton process engaging iron ion. In investigated catalytic capability of ions of some transition metals in Fenton-like systems in the media proximal to neutral; and they have established that at pH 7.7-8.5 cobalt proved to be better catalyst than double-charged ion of iron. According to the studies, catalytic capability of some transition metals decreases at pH 7 as follows: Cu (II) > Cr (III) > Co (II) > Fe (III) > Mn (II) > Ni (II). A detailed review of the Fenton-like systems that do not contain iron has been provided by in.

2. Concept Headings

The objective of this study is to investigate in detail the process of oxidation of indigo carmine, methyl violet and 2, 4-dinitrophenol by two-component system Co^{2+}-H_2O_2. The food grade dye called indigo carmine is a convenient model for the investigations associated with removing organic contaminants from water, insofar as its molecule contains atoms of nitrogen and sulfur. Methyl violet is also used as the model for developing water treatment processes. Nitrophenols belong to the widely spread substrates that are used for the purposes of studying the Fenton-like systems. It was interesting to compare the behavior patterns of iron ions and cobalt in the process of degradation of dyes. Oxidative degradation of methyl violet by the Fenton system has already been described in detail elsewhere. Oxidation of indigo carmine and dinitrophenol by hydrogen peroxide in presence of iron ions has been analyzed by the authors of this study earlier. Discoloration of dyes represents not only methodical but also practical issue, as it is very important to decrease the impact on the environment produced by the wastes of the textile industry.

3. Method

The study made use of analytically clean indigo carmine, methyl violet and 2, 4-dinitrophenol without any additional treatment and “medical” hydrogen peroxide which precise concentration has been determined applying the method of indirect redox titration of iodine by sodium thiosulfate in acid medium. The experiments on oxidative degradation were carried out in 25 ml aqueous solutions of indigo carmine, methyl violet or 2, 4-dinitrophenol. Initial concentrations amounted to the figures as follows: 70.3 µmol/l – for indigo carmine, 17.8 µmol/l – for methyl violet, 100 µmol/l – for dinitrophenol. Concentrations of hydrogen peroxide and cobalt salt was varied. In each experiment hydrogen peroxide was the last to be added to the reaction system. Initial pH values of the reaction systems were adjusted to the preset values by adding the solution of sodium hydroxide. pH values of the reaction mixtures were fixed with pH-meter Mettler Toledo. Electrical conductivity of the solutions was measured with conductivity meter ANION 4100. Oxidation occurred at a temperature of 25°C. Concentrations of the substrates were measured applying the method of spectrophotometry with spectrophotometer Solar CM2203 equipped with thermostatic control of the sample holder. Characteristic wavelengths for the oxidized substrates were as follows: 605 nm – for indigo carmine, 572 nm – for methyl violet, 350 nm – for 2, 4-dinitrophenol. It was necessary to make sure that the change in optical density of the solutions under investigation was not associated with anything other than the decrease in the concentration of the substrates in the course of their degradation. To exclude the effects produced by complex formation in the systems, the authors registered the spectra of the solutions that contained indigo carmine, methyl violet or 2, 4-dinitrophenol and salt of cobalt (II). The comparison of the spectra showed that in presence of cobalt, neither the formation of new maximums nor the shift of the existing absorption bands were observed. The products of oxidation were identified applying the method of nuclear magnetic resonance. One dimension H NMR-spectra were recorded by spectrometer 400-MR (Agilent, USA) at resonance frequency of 399.978 MHz. The measurements were taken at a constant temperature of 25°C. The data of the experiments were analyzed by VNMRj 3.1 and Mest ReNova 6.0 software. Heavy water with isotopic purity of 99.95% was used as solvent within the framework of the experiments registering NMR spectra. In these experiments, the concentrations of all reagents were increased pro rata to achieve the limit value of detection with NMR method. In 20 minutes after the substrate oxidation completion (complete discoloration of the solution) the size and ζ-potential of the particles contained in the systems after the reaction were measured applying the method of dynamic light scattering and electrolysis accordingly with analyzer ZetaSizer Nano ZS. The morphology of
nano-aggregates in the reaction mixtures was investigated applying the method of transmission electron microscopy with JEOL JEM 2100 transmission microscope featuring operating accelerating voltage of 200 kV and resolution of 0.2 nm.

4. Result

Hydrogen peroxide is capable of oxidizing indigo carmine in aqueous solution; however, the speed of this process is negligibly slow within the wide range of pH values from 2 to 8. The presence of cobalt ions does not affect the process at pH values lower than 6. At pH values higher than 6, introduction of ions of cobalt (II) into the reaction system increases the rate of indigo carmine degradation considerably which is manifested through fast discoloration of the solution. Comparing the spectra of the reaction mixture in the process of oxidation with the spectrum of indigo carmine solution it was noted that the intensity of maxima at 605 and 280 nm was decreasing gradually; but the maximum in the range of the wavelengths approximating 218 nm did not disappear and its intensity remained practically unchanged. Apparently, this maximum is characteristic for hydrogen peroxide which amount is excessive as compared to the substrate. Expectedly, the rate and the efficiency of oxidative degradation of indigo carmine depend on the ratio of the concentrations of the components in the oxidative system and the substrate. The results of the experiments on varying the concentrations of hydrogen peroxide and cobalt salt showed that maximum initial rate of indigo carmine degradation was observed in the system that contained the highest concentrations of Co^{2+} and H_2O_2 Figure 1. Notably, the lowest rate of the oxidative degradation was fixed at comparatively high concentration of hydrogen peroxide which is plausibly explained by the insufficient number of ions Co^{2+} to ensure radical decomposition of all amount of H_2O_2. This fact indirectly proves that the process runs according to the mechanisms similar to those observed in the Fenton system. Based on the data of the oxidation kinetic curves, the formal kinetic order of indigo carmine oxidative degradation was calculated. For this purpose, the authors applied the method founded on determining the period of the substrate semi-transformation. The calculations for each of the four curves in Figure 1 result in values in the range of 1.23 to 1.99; thereat, the value approximating 2 was obtained for three out of four curves. It can be assumed that the limiting stage of the process is the stage of the formation of Co (II) complex with hydrogen peroxide and only then the chain reaction starts where the conventional idea of the order of reaction is no longer applicable. Value 1.23 was obtained for curve 4 that reflects the process running at maximum observable rate. It is probable, that the concentration of the active oxidizing particles in this experiment is quite high (in excess) and does not affect the speed of the reaction. Measuring pH value in the process of oxidative degradation applying potentiometer-based method made it possible to establish that in the course of indigo carmine oxidation, pH value changes just slightly. This is a proof of the fact that neither intermediates nor the final products of degradation make any contribution to the acid-base balance in the systems under investigation. Electric conductivity of the reaction mixture remained unchanged in the course of oxidative degradation of indigo carmine proving that the concentration of the charged particles in the solution was constant. It is known that metal salt anion can play a certain part in the process of oxidizing the substrates by the systems based on hydrogen peroxide: Thus, in the case of the Fenton system, chloride and sulfate ions produce inhibiting effect on the process of oxidation, while nitrate ion usually does not affect it in any significant manner. It was found that in case of system Co^{2+}-H_2O_2, the use of cobalt sulfate and cobalt nitrate in indigo carmine
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oxidation process brings about similar results: Kinetic curves of indigo carmine oxidation virtually coincide, no inhibiting effects of anions were observed. In the Fenton-like oxidative processes pH value of the reaction system is very significant and it predetermines the form of the metal and its activity in the reaction of hydrogen peroxide decomposition. It is a well-known fact that the Fenton system (i.e. hydrogen peroxide in combination with double-charged ions of iron) is most efficient within pH range of 2.7–3.5. However, as it has already been noticed above, oxidation of indigo carmine by the cobalt-containing system does not occur in this range of pH values. Alkalizing results in faster discoloration of the solution; the relevant kinetic curves are shown in Figure 2. At the same time, at pH>6.8 in the solution with cobalt sulfate concentration of 1 µmol/l large visually discernible aggregates of cobalt were formed in the very beginning of the oxidation process. Obviously, the process of discoloration of the solutions at pH>6.8 is affected by indigo carmine oxidation as well as by its adsorption on the generated aggregates. Consequently, the conclusions made by in about the behavior of ions in transition metals at pH values higher than 7 can refer not only to oxidation but rather to the sum of several processes. The regularities similar to those established for indigo carmine oxidation by cobalt-containing system are also observed in cases of methyl violet. The dye itself is not oxidized by hydrogen peroxide. When ions of cobalt are introduced into the sub-acid solution, methyl violet is still resistant against oxidation: At pH 5.7 the concentration of the dye in the reaction mixture remains practically the same during several hours. Intensive oxidation of the substrate commences when pH increases up to the values approximating the neutral values of 6.6-6.8. Thereat, the solution becomes discolored and the gas bubbles appear in the reaction mixture. It is most probable that in parallel with the radical breakdown, hydrogen peroxide is also catalytically decomposed into oxygen and water. Interestingly, oxygen is also released if ions of iron (III) are used instead of ions of cobalt. It may be that the contribution of this side reaction becomes apparent due to the relatively low concentration of the substrate. In the experiments described herein, the concentration of methyl violet was 3.5-5 times lower than the concentration of two other dyes. The operating range of the most popular oxidative systems (Fenton or Ruff iron-containing reagents) is limited by quite low pH values, insofar as the hydrolysis of iron ions and the formation of low-solubility iron hydroxide bring iron ions beyond the reaction area. In the case of this study, the fact that the process occurs in the neutral range of pH values represents considerable advantage of the cobalt-containing oxidative system. This fact means that the suggested oxidative system enhances the areas for applying the oxidative degradation method. Now, different kinds of waste water with high pH values can be treated without any preliminary processing. Oxidation of 2, 4-dinitrophenol in presence of cobalt ions at pH = 5.8-6.2 also runs at considerable rate which, similar to the two cases described above, depends on the concentration of hydrogen peroxide and on the concentration of cobalt ions. However, the rate and the depth of 2, 4-dinitrophenol degradation are lower than those observed in cases of two other dyes. Upon 2 hours of oxidation, 2, 4-dinitrophenol concentration becomes two times lower, while other substrates are subject to almost complete degradation by that time. One more difference of dinitrophenol process is represented by the explicit effect produced by the anion of cobalt salt on the efficiency of the process: Dinitrophenol oxidation by hydrogen peroxide in presence of sulfate of cobalt (II) runs faster as compared to the oxidation where nitrate of cobalt (II) is used as the source of Co

5. Discussion

The inhibiting effect of the nitrate ion has not been observed by the authors of this study before and it is not known to be described in the literature. On the contrary, in¹⁵ believe that the rates of oxidation of organic substrates by the Fenton system depend on the nature of anion, but perchlorate and nitrate ions are not prone to forming stable coordination compounds and therefore, they cannot affect the process of oxidation. It has to be
acknowledged that the effect produced by the nitrate ion on the process of degradation is a specific feature of the cobalt-containing oxidative system. In the framework of special experiments on indigo carmine oxidation by the Fenton systems (double-charged ions of iron) and Ruff systems (triple-charged ions of iron) magnesium salts were introduced into the solutions under investigation at concentrations of 7 µmol/l. In presence of magnesium sulfate, the rate of indigo carmine degradation by the Fenton system proved to be considerably lower than that in the system without the additive and it took much longer to achieve complete degradation than in the system with no additive. At the same time, the kinetic curve obtained in presence of magnesium nitrate virtually coincided with the curve for the system without magnesium salt. The results of comparing two salts of magnesium unambiguously testify of the effects produced on the process by the anion; magnesium cation, expectedly, is inert in the process under investigation. Nitrate does not affect the course of oxidative degradation of indigo carmine. Similar conclusions were made based on the results of oxidizing indigo carmine by the Ruff system: magnesium nitrate did not affect the profile of the kinetic curve, while, upon introducing magnesium sulfate into the system, the indicators of inhibition in the process of indigo carmine oxidation became clearly visible. In explain the inhibiting ability of the sulfate ions by their interaction with oxidizing radicals that results in lower number of the active particles in the system. It is probable that in the case of this study similar ability of nitrate ions to interact with active radical particles was observed. At the same time, the newly generated radical particles SO₄⁻ are sufficiently active and they can make their contributions to substrate oxidation. Thus, experimentally observed effects of foreign anions represent the averaged result of several parallel processes: destruction of hydroxyl (hydroperoxyl) radicals upon interacting with the introduced substance or with the reaction intermediates and the destruction of the substrate affected not only by the oxidizing particles but also by the newly generated reaction intermediates. Consequently, the final result depends upon the ratio between the reaction ability of hydroxyl (hydroperoxyl) radicals and the radicals generated with anions and also upon the resistance of the substrate against destruction. The issue of the products of oxidative degradation is of principal importance, insofar as any toxic or highly stable intermediates are unwanted in the processes of water treatment. The optimum option should be to mineralize the organic contaminants completely implying deep oxidation to carbon dioxide and water. H NMR spectrum of methyl violet solution in deuterated water consists of the set of the signals in the range over 6 ppm that are characteristic for protons of benzene ring and two singlets that characterize the protons of aliphatic groups. Also, in the spectrum there is a broad signal with chemical shift of 4.5–4.75 ppm that is characteristic for the protons of common water Figure 3. Small amounts of water are present in all solutions; it is a product of oxidation of the organic compounds. The signals of the protons of water are observed in all registered spectra and are preserved (sometimes as inverted signals) after special instrumental “suppression”. It was found that H NMR spectrum registered upon oxidation of methyl violet by system Co²⁺/H₂O₂ contained considerable number of signals Figure 4 that evidently corresponded to the whole set of products. Identification

Figure 3. ¹H NMR spectrum of methyl violet solution.

Figure 4. ¹H NMR spectrum of products of oxidation of methyl violet by system Co²⁺/H₂O₂ (C(mv) = 2.6 mmol/l, C(CoSO₄) = 3.7 mmol/l, C(H₂O₂) = 0.66 mol/l).
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intermediates at the surface of cobalt hydroxide cannot be altogether excluded from consideration, though the sign and the value of ζ-potential testify of forming hydroxide complexes in the first place.

6. Conclusion

Thus, oxidative system that contains hydrogen peroxide and cobalt ions ensures degradation of the model organic contaminants of different classes: Indigo carmine, methyl violet, 2, 4-dinitrophenol. Apparently, oxidation occurs according to the radical mechanism similar to the processes running in the Fenton system (Fe²⁺ - H₂O₂). From practical perspectives, the important advantages of this system, as compared to the iron-containing system, are represented by operability at higher pH values and also by the absence of any inhibiting effects of sulfates. Stable intermediates can be regarded as disadvantage; insofar as the complete oxidation of dyes is not achieved, extra processing will be required for final water treatment in this system. Importantly, oxidation of dyes occurs in ultra micro heterogeneous system. Radical decomposition of hydrogen peroxide engages the particles of cobalt hydroxide.

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8. References

1. Barb WG, Baxendale JH, George P, Hargrave KR. Reactions of ferrous and ferric ions with hydrogen peroxide. Nature. 1949 Apr; 163:692–4.
2. Verma P, Baldrian P, Nerud F. Discoloration of structurally different synthetic dyes using Co (II)/ascorbic acid/hydrogen peroxide system. Chemosphere. 2003; 50(8):975–9.
3. Long X, Yang Z, Wang H, Chen M, Peng K, Zeng Q, Xu A. Selective degradation of orange II with the Cobalt (II) – Bicarbonate - Hydrogen Peroxide System. Industrial and Engineering Chemistry Research. 2012 Aug; 51(37):11998–2003.
4. Burg A, Shusterman I, Kornweitz H, Meyerstein D. Three H₂O₂ molecules are involved in the Fenton-like reaction between Co (H₂O)₆²⁺ and H₂O₂. Dalton Transactions. 2014 May; 43:9111–5.
5. Nasiruddin KM, Bhutto S. Kinetic study of the oxidative discoloration of xylene orange by hydrogen peroxide in
micellar medium. Journal of Chilean Chemistry Society. 2010; 55(2):170–5.

6. Strlič M, Kolar J, Šelih V, Kocar D, Pihlar B. A comparative study of several transition metals in Fenton-like reaction systems at circum-neutral pH. Acta Chim Slov. 2003; 50(4):619–32.

7. Bokare AD, Choi W. Review of iron-free Fenton-like systems for activating H$_2$O$_2$ in advanced oxidation processes. Journal of Hazard Materials. 2014 Jun; 275:121–35.

8. Goi A, Trapido M. Hydrogen peroxide photolysis, Fenton reagent and photo-Fenton for the degradation of nitrophenols: A comparative study. Chemosphere. 2002 Feb; 46(6):913–22.

9. Hashemian S, Tabatabaee M, Gafari M. Fenton oxidation of methyl violet in aqueous solution. Journal of Chemistry. 2012 Aug; 2013:1–6.

10. Erokhin KS, Tikhova AA, Lebedeva OE. Ferrum condition in Fenton and Ruff’s systems in the course of indigo carmine and nitrophenol oxidation at different pH values. Advances Environmental Biology. 2014 Aug; 8(13):17–9.

11. Solovyov AA, Pashina MA, Lebedeva OE. Oxidative destruction of dinitrophenols by Fenton’s reagent in the presence of inorganic salts. Russian Journal of Applied Chemistry. 2007 Feb; 80(2):275–8.

12. Kremer ML. The Fenton reaction. Dependence of the rate on pH. Journal of Physical Chemistry A. 2003 Feb; 107(11):1734–41.

13. Siedlecka EM, Stepnowski P. Phenols degradation by Fenton reaction in presence of chlorides and sulfates. Polish Journal of Environmental Studies. 2005 Feb; 14(6):823–8.

14. Tikhova AA, Glukhareva NA, Lebedeva OE. Oxidative degradation of polyglycols by the ruff’s system in the aqueous solutions. Russian Journal of General Chemistry. 2014 Sep; 84(9):1806–9.

15. Yi Shen Y, Zhang A, Xiao K. Evaluation of Cobalt oxide, copper oxide and their solid solutions as heterogeneous catalysts for Fenton-degradation of dye contaminants. RSC Advances. An International Journal to Further the Chemical Sciences. 2015 Oct; 5:91846–54.

16. Mashaly HM, Abdelghaffar RA, Kamel MM, Youssef BM. Dyeing of polyester fabric using nano disperse dyes and improving their light fastness using ZnO nano powder. IJST. 2014; 7(7).

17. Youssef BM, Ahmed MHM, Arief MMH, Mashaly HM, Abdelghaffar RA, Mahmoud SA. Synthesis and application of functional (anti-uv) Azo-dyes based on γ-acid on wool fabrics. IJST. 2014; 7(7).