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## THE PROCESS OF WASTEWATER TREATMENT WITH ADVANCED OXIDATION METHODS TO REMOVE DYE

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**Abstract.** The research revealed that Fenton reagent is to be utilized to remove the dye (active bright orange CS/5K) from industrial sewage. Hypercube Hyperchem Professional v8.01 software (trial) was used to carry out the quantum-chemical calculation of colouring agent structure and heat energy. Based on the information from references and the received experimental data, the oxidation mechanism of colouring agent (active bright orange CS/5K) by photo-Fenton system has been introduced.

**Keywords:** dye, advanced oxidation processes, kinetics, quantum-chemical calculation, mechanism.

### 1. Introduction

The composition of industrial sewage (IS) fluctuates significantly, but it is always highly coloured and contains a significant amount of organic dyes and surfactants of various type and origin. For purification of industrial sewage both coagulative, sorption and oxidation methods are utilized. However, the application of each of them has a range of deficiencies. When purification is carried out with the help of coagulative methods, a significant amount of organometallic precipitates, which need salvaging, are formed. The disposal of waste with the major interior specific surface as a sorbent, allows removing effectively the organic matter from sewage. However, the sorbent demands regeneration, therefore, oxidative methods with hydrogen dioxide, ozone, UV-radiation are considered to be the most eco-friendly and efficient. The advantage of peroxide compound of hydrogen as a redox-agent, in comparison with other oxidation agents, lies in its miscibility in water solutions with various pH as well as it proves to have high redox potential.

When conducting the purification of textile sewage with hydrogen peroxide it is not always possible to attain

the proper purification efficiency, since such organic compounds as benzene, toluene, ethanol and others, are resistant to peroxide reaction, and oxidation rate in diluted sewage is rather low. The main problem with purification of textile sewage is the removal of colouring agents, which varies depending on the type and origin of colouring agent. Such colorants as disperse, substantive dyes, lead-acid and active are the most widespread and the most difficult to remove. The efficiency of oxidative degradation of dyes was performed using active bright orange, which is a typical representative of active dyes and one of the most common pollutants of wastewater of textile industry.

To remove the colouring agents from sewage, the oxidative methods were widely utilized, based on the disproportion of peroxide compound of hydrogen with formation is reactionary-capable hydroxide radicals  $\text{OH}^\bullet$  ( $E^0 = 2.38 \text{ B}$ ), namely: photolysis of peroxide and its catalytic decomposition under the influence of ions  $\text{Fe}^{2+}$  (Fenton system). Photodissociations along with photochemical methods (photocatalysis in  $\text{TiO}_2$ ,  $\text{UV/O}_3$ , etc.) refer to the so-called "advanced oxidation processes" (AOPs), based on oxidation decomposition of the organic compounds, initiated by hydroxide radicals  $\text{OH}^\bullet$  [1-3]. However, the efficiency of these methods depends on requirements and the composition of sewage, therefore, in each specific case, it is necessary to select requirements and proper catalytic system, which would remove colouring agents completely.

The research [4] also covers the efficiency of  $\text{TiO}_2$  as a catalytic agent in the process of removal in addition to oxidative systems with UV-radiation. The research revealed the high quality of photo-Fenton and  $\text{TiO}_2$  treatment of sewage, polluted with organic matter. It has also been noted that the mechanism of Fenton system shows much more complex kinetics, rather than oxidation treatment solely with  $\text{TiO}_2$ . B. Tryba [5] observed the

processes of phenol decomposition at UV-radiation with and without hydrogen peroxide compound on photocatalytic agents:  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-Fe}$ ,  $\text{TiO}_2\text{-C-Fe}$ . It has been discovered that the utilization of peroxide together with  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-Fe}$  decreases the formation of oxyhydroxides-radicals on their surfaces, and photodecomposition is rather low. Phenol decomposition on the photocatalytic agent at UV-radiation with the addition of hydrogen peroxide compound increases the “photo-Fenton” reaction:  $\text{Fe}^{2+}$  is acidified to  $\text{Fe}^{3+}$ , which then effectively recirculates to  $\text{Fe}^{2+}$ , shaping in the course of decomposition of phenol, intermediate products, such as hydroquinone and catechol. In comparison with photocatalytic agent  $\text{TiO}_2\text{-C-Fe}$ , phenol decomposition proceeds more slowly on the photocatalytic agent  $\text{TiO}_2\text{-Fe}$ . Photocatalytic agents presented in the research [5] are active “photo-Fenton” reaction with UV-radiation. The greatest possible exponents of fracture of phenol and extent of its mineralization are observed in the system  $\text{H}_2\text{O}_2/\text{Fe-C-TiO}_2/\text{UV}$ .

The objective of the present research is the identification of oxidation kinetics of the colouring agent, the selection of new oxidation system based on Fenton reagent and revealing the mechanism of oxidation decomposition of the colouring agent active bright orange CS/5K with the help of Fenton reagent system.

## 2. Experimental

### 2.1. Materials

Sample of sewage taken from the textile factories of Ukraine polluted by the colouring agent – colouring agent active bright orange CS/5K ( $\text{C}_{18}\text{H}_{12}\text{O}_4\text{N}_2\text{SNa}(\text{SO}_3\text{Na})_3$ ) concentration of 10–50  $\text{mg}/\text{dm}^3$ .

Solution  $\text{FeSO}_4$ ; Photocatalytic agents:  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{MnO}_2$ , UV-radiations  $\lambda = 254$  nm.

Quantum-chemical calculation of the composition and thermodynamic features of the colouring agent carried out by means of Hypercube Hyperchem Professional v8.01 software (trial).

### 2.2. Methods

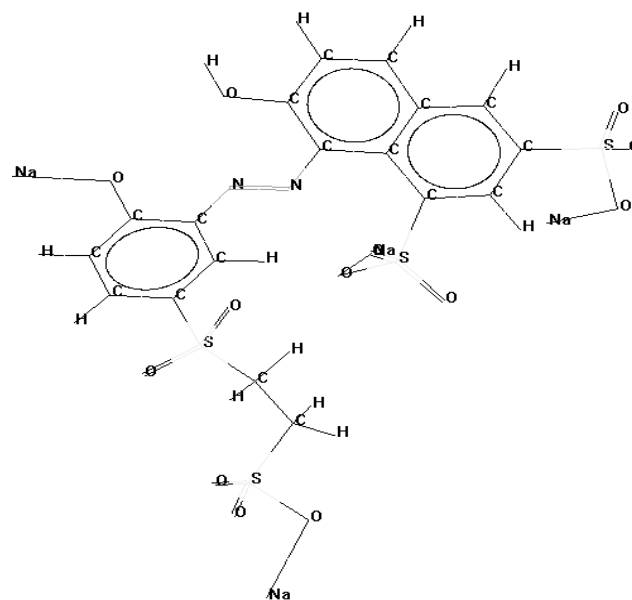
Samples of sewage of the textile factories of Ukraine with the colorant active bright orange CS/5K concentration of 10  $\text{mg}/\text{dm}^3$  were the subject of the research. The oxidation of sample solutions of sewage with the content of colouring agent active bright orange CS/5K of 10–50  $\text{mg}/\text{dm}^3$  with the Fenton reagent and its modifications was carried out in a photo-Fenton system modified by photocatalytic agents  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{MnO}_2$ , UV-radiations  $\lambda = 254$  nm.

## 3. Results and Discussion

### 3.1. Quantum-Chemical Calculation of Thermodynamic Features Dye

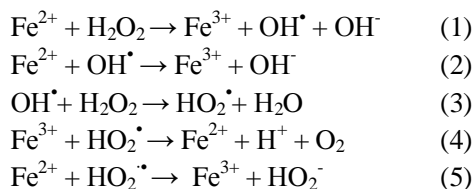
Quantum-chemical calculation of the composition and thermodynamic features of the colouring agent active bright orange CS/5K has been carried out by means of Hypercube Hyperchem Professional v8.01 software (trial) (Fig. 1). Spatial composition, received as a result of the present research, has proven to have different orientations in aqueous medium rather than in vacuum. This is used for calculation of similar frames, and consequently the different heat energy, that affects the reaction between the colouring agent and Fenton reagent (Fig. 2).

Oxidation of the colouring agent was made with the help of Fenton reagent system. Hydrogen peroxide compound in chemical reactions is known to react with substrates as intermediates ( $\text{HO}_2^-$ ,  $\text{HO}_2^\bullet$ ,  $\text{OH}^\bullet$ ) which show different activity [1]. The most active is  $\text{OH}^\bullet$  and the least one –  $\text{HO}_2^-$ . Peroxide in the Fenton system is known as an oxidation agent, and  $\text{Fe}^{2+}$  acts as a catalytic agent. As a result of peroxide decomposition, reactionary-capable  $\text{OH}^\bullet$ , is formed, and  $\text{Fe}^{2+}$  increases the velocity of  $\text{H}_2\text{O}_2$  decomposition.

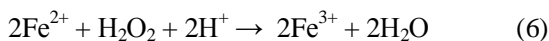


**Fig. 1.** The spatial structure of the colouring agent “active bright orange CS/5K” molecule

On the basis of the data [1, 6, 7] available in the literature, the mechanism of the given process has been analyzed. Currently the behavior of Fenton system is presented by a set of consecutive stages:



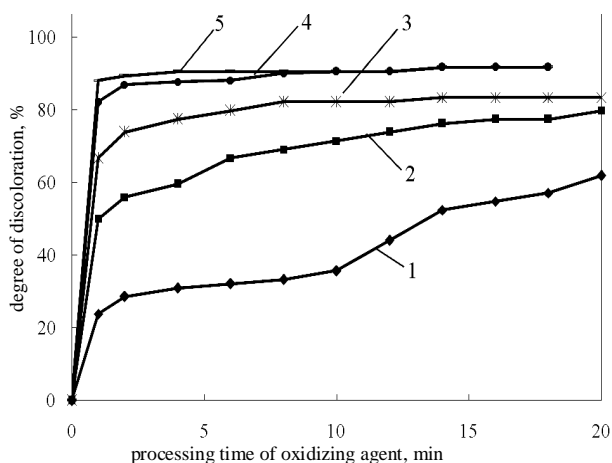
During the process  $[\text{Fe}^{2+}] > [\text{H}_2\text{O}_2]$  the mechanism includes only reactions (1) and (2), *i.e.* actually there is an oxidation of iron aquacomplexes (III), instead of catalytic  $\text{H}_2\text{O}_2$  disproportionation. The equation in this case is represented as follows [1]:



It is known that insofar as the initial rate of oxidation depends on the initial concentration of  $\text{Fe}^{2+}$ , the overall rate of the process and the degree of the substrate removal depends on the ability of intermediates to regenerate the active form of the catalyst  $\text{Fe}^{2+}$ , which is oxidized during the process to  $\text{Fe}^{3+}$ . When restoration  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$  in the reaction system is not implemented, or proceeds slowly for a complete removal of the substrate and subsequent oxidation intermediates requires high concentration of iron salts [1, 4, 8].

### 3.2. Kinetics Process of Wastewater Treatment from the Dye

When researching the influence of ion density  $\text{Fe}^{2+}$  on the efficiency of removal of the colouring agent (active bright orange CS/5K) concentration of  $10 \text{ mg/dm}^3$ , the experimental data revealed that, the greatest possible extent of decolouration of sewage (90 %) is attained at the content of  $\text{Fe}^{2+}$   $8 \text{ mg/dm}^3$  and concentration of  $\text{H}_2\text{O}_2$  – 3.5 %, for up to 18 min of oxidation process (Fig. 2).



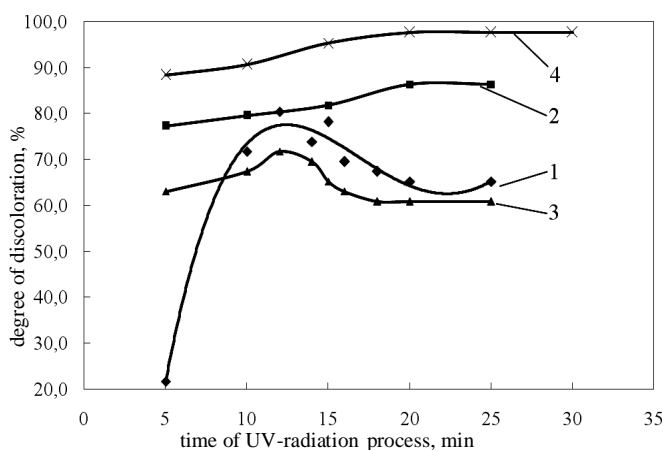
**Fig. 2.** The influence of ion density  $\text{Fe}^{2+}$  on the efficiency of colouring agent removal (active bright orange CS/5K) with the concentration of  $10 \text{ mg/dm}^3$ , concentration of  $\text{Fe}^{2+}$ ,  $\text{mg/dm}^3$ : 1 (1); 2 (2); 3 (3); 5 (4) and 8 (5)

An introduction into the Fenton reagent system of the additional quantity the photocatalytic agent, such as  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{MnO}_2$ , revealed that the efficiency of sewage treatment does not exceed 90 % in case of use  $\text{ZrO}_2$  (Fig. 3, curve 4), and not over 70 % for  $\text{MnO}_2$ , (Fig. 3, curve 3), hence the introduction of additional quantity of the pulverous Photocatalytic agent to an aqueous medium worsens UV-radiation infiltration on  $\text{OH}^\bullet$  formation (Fig. 3).

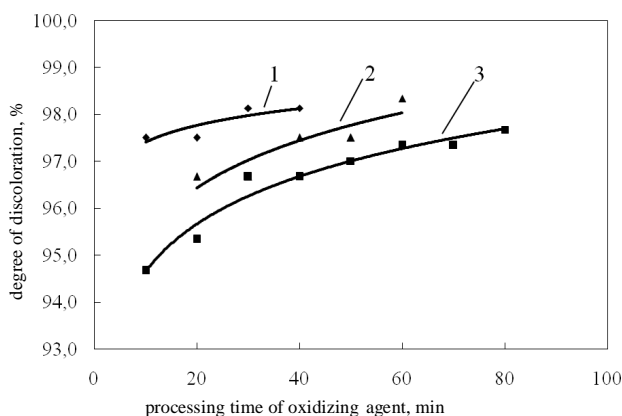
In order to level off the dispersion of UV-radiation, it is necessary to change the procedure of entering the photocatalytic agent or to explore the procedure of drawing the oxides on a film or glass, which immediately contact with an aqueous medium, liable to purification.

The increased time of oxidation sewage with the Fenton system containing  $10 \text{ mg/dm}^3$  colouring agent up to 60 min, results in the efficiency of decolouration IS raising to 96 % (the content of ions  $\text{Fe}^{2+}$   $5 \text{ mg/dm}^3$ ) and concentration of  $\text{H}_2\text{O}_2$  – 3.5 %. The increased concentration of the colouring agent up to  $15 \text{ mg/dm}^3$  with the ions of  $\text{Fe}^{2+}$   $5 \text{ mg/dm}^3$ , results in the level of decolouration reaching 97.5 % for 60 min (Fig. 4, curve 1). The increased content of the colouring agent up to  $20 \text{ mg/dm}^3$  results in 98 %, attained for 30 min (Fig. 4, curve 2). When the content of a contaminant is up to  $50 \text{ mg/dm}^3$ , 97 % of it can be removed by UV-processing for 80 min (Fig. 4, curve 3).

The examination of the impact of  $\text{H}_2\text{O}_2$  strength on the efficiency of sewage treatment has revealed that the diminution of  $\text{H}_2\text{O}_2$  concentration from 3.5 to 0.35 % has a limited impact on the efficiency of oxidation and made up 98 % at the content of ions  $\text{Fe}^{2+}$   $3 \text{ mg/dm}^3$ .



**Fig. 3.** The influence of the introduction of various photocatalytic agents on the efficiency of sewage discoloration:  $\text{TiO}_2$  (1);  $\text{TiO}_2$  (Degussa) (2);  $\text{MnO}_2$  (3) and  $\text{ZrO}_2$  (4)



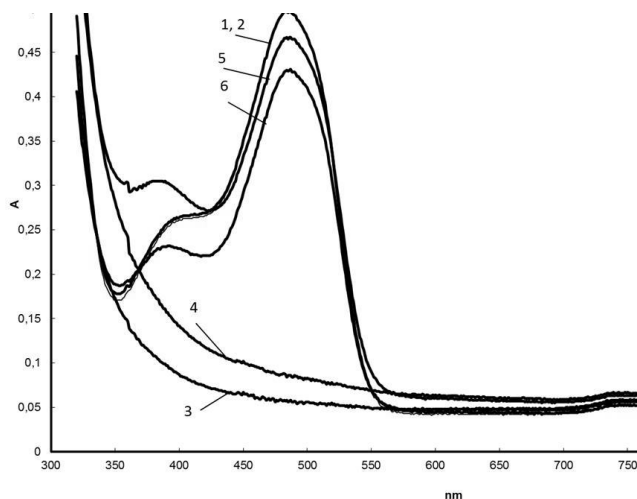
**Fig. 4.** The dependence of the degree of wastewater discoloration containing different concentration of the active bright orange CS/5K, the duration of oxidation. The concentration of active bright orange CS/5K, mg/dm<sup>3</sup>: 15 (1); 20 (2) and 50 (3)

The expediency of diminution of the quantity of reagents does not have any impact on the efficiency of the colouring agent removal from sewage, with the time of oxidative processing incrementing. So, the content of Fe<sup>2+</sup> ions of 3 mg/dm<sup>3</sup> and the concentration of H<sub>2</sub>O<sub>2</sub> – 0.35 % , maximum attained decolouration is 98 % for 60 min of oxidation (initial dye strength of 50 mg/dm<sup>3</sup>).

The calculations of Hypercube Hyperchem Professional v8.01 software (trial) show that the combination heat of the colouring agent makes up 144.71 kJ/mol. The electronic spectrum of the dye and compounds with it received from the Spectrophotometer-VIS Portlab 501 (Fig. 5, curve 1).

Having analyzed the electronic spectrum of the system colouring agent – TiO<sub>2</sub> , it is possible to draw the following conclusion: in the system the colouring agent remains the same, therefore, the titanium(IV) oxide does not acidify an organic component. The change of an electronic spectrum of the system colouring agent – H<sub>2</sub>O<sub>2</sub> + Fe<sup>2+</sup>+TiO<sub>2</sub> (Fig. 5, curve 4) and the colouring agent – H<sub>2</sub>O<sub>2</sub>+Fe<sup>2+</sup> (Fig. 5, curve 3) testifies the decomposition of the colouring agent in the system Fenton reagent and its modification, which proves that there is oxidation of the colouring agent into the simpler compound.

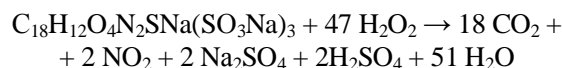
The bias of the peak of the systems electronic spectrum: the colouring agent – H<sub>2</sub>O<sub>2</sub> testifies the limited decomposition of the colouring agent (Fig. 5, curve 5). The curve 6 and diminution of intensity of peaks in the system colouring agent – Fe<sup>2+</sup> (Fig. 5, curve 6) specifies the emersion of iron-organic complex, formed at the first stage of oxidation decomposition of the colouring agent by the Fenton reagent .



**Fig. 5.** The electronic spectrums of the colouring agent active bright orange CS/5K and compounds with it: colouring agent (1); colouring agent – TiO<sub>2</sub> (2); colouring agent – H<sub>2</sub>O<sub>2</sub>+Fe<sup>2+</sup> (3); colouring agent – H<sub>2</sub>O<sub>2</sub>+Fe<sup>2+</sup>+TiO<sub>2</sub> (4); colouring agent – H<sub>2</sub>O<sub>2</sub> (5) and colouring agent – Fe<sup>2+</sup> (6)

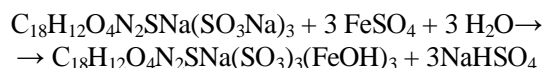
### 3.3. Mechanism of Wastewater Treatment from Active Bright Orange CS/5K

The reaction of colouring agents with oxidation agents can be represented as follows:

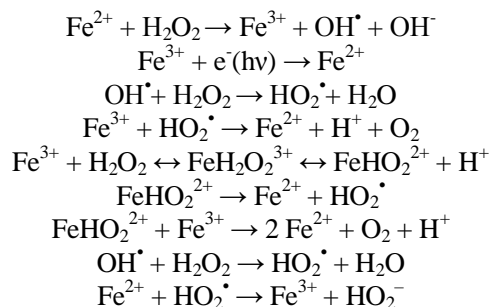


Stages of the colouring agent active bright orange CS/5K oxidation in the system [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>]/UV

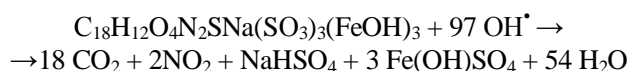
1 stage – the formation of iron-organic complex:



2 stage – the formation of oxidative agents in the system:



3 stage – the decomposition of organic complex into the simple matter:



## 4. Conclusions

It is suggested to treat sewage, polluted by organic dye, with photooxidative methods, namely Fenton reagent, the following conditions are required: time of UV-radiation – 60 min, the content of ions  $\text{Fe}^{2+}$  5 mg/dm<sup>3</sup>, with the concentration of  $\text{H}_2\text{O}_2$  – 0.35 %. It has been proven that it is not efficient to utilize various photocatalytic systems ( $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{MnO}_2$ ). In order to decolourate sewage with 15 mg/dm<sup>3</sup> of colouring agent active bright orange CS/5K, the effective method is to apply the Fenton reagent, reaching up to 98 %, removal with the application of catalytic system  $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]/\text{UV}$  for 60 min and the concentration of  $\text{H}_2\text{O}_2$  0.35 % and  $\text{Fe}^{2+}$  5 mg/dm<sup>3</sup>.

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## References

- [1] Slozhenko E., Soboleva N. and Honcharuk V.: *Khim. i Techn. Vody*, 2004, **26**, 219.
- [2] Vysotskaya N.: *Uspekhi Khimii*, 1973, **42**, 1843.
- [3] Dresviannikov A. *et al.*: *Vesnik Kazan. Techn. Univ.*, 2007, **3-4**, 172.
- [4] Garcia J. *et al.*: *J. Hazardous Mat.*, 2007, **147**, 105.
- [5] Tryba B.: *Appl. Catalysis B*, 2006, **63**, 215.
- [6] Chamarro E. *et al.*: *Water Research*, 2001, **35**, 1047.
- [7] Legrini O. *et al.*: *Chem. Rev.*, 1993, **93**, 671.
- [8] Sychev A. and Isak V.: *Uspekhi Khimii*, 1995, **64**, 1183.

### ЗАКОНОМІРНОСТІ ПРОЦЕСУ ОЧИЩЕННЯ СТІЧНИХ ВОД ВІД БАРВНИКА ФОТООКИСНИМИ МЕТОДАМИ

*Анотація.* Встановлено, що для вилучення зі стічних виробничих вод барвника активний яскраво-помаранчевий КХ доцільно використовувати реактив Фентона. За допомогою програми Hypercube Hyperchem Professional v8.01 (trial) проведено квантово-хімічний розрахунок будови та теплоутворення барвника активний яскраво-помаранчевий КХ. На основі інформації з джерел літератури та отриманих експериментальних даних запропоновано механізм окиснення барвника активного яскраво-помаранчевого КХ системою фото-Фентон.

*Ключові слова:* барвник, фотоокиснення, кінетичні закономірності, квантово-хімічний розрахунок, механізм.