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Influence of the medium pH on the catalytic activity of the CuO-based catalyst in the Fenton system

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The influence of the medium pH on the activity of the heterogeneous nanostructured magnetically sensitive catalyst $SiO_2/CoFe_2O_4/SiO_2/CuO$ in the Fenton system was investigated and the reaction mechanism was proposed. It was determined that the catalytic centers are Cu^+ and Cu^{2+}. It was established that the rate of destruction of the dye methylene blue (MB) as a model wastewater pollutant in the first 20 min of the process depends on pH, and its value decreases in the pH range (9) > (6) > (3). After 2 h, for all initial pH values, the degree of MB destruction reaches 85-90%, and the pH changes to neutral. The proposed system can be used in the technology of post-treatment of industrial and domestic wastewater.

Keywords: $SiO_2/CoFe_2O_4/SiO_2/CuO$ catalyst, Fenton system, medium pH, oxidation of methylene blue, reaction mechanism.

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Introduction

Water is an important component of the ecosystem, and its security has become a key issue facing society. Effective water treatment and reuse of domestic and industrial wastewater is one of the most priority global problems today. Currently, this issue has become even more urgent in Ukraine in connection with military actions, destruction of infrastructure, and dangerous water pollution. Such waters are heavily polluted not only with inorganic compounds, but are also characterized by a high content of petroleum derivatives, in particular, phenol, benzene, etc., which are toxic and resistant to standard water purification methods [1]. Traditional methods of wastewater treatment, such as the physical adsorption method [2], the electrochemical method [3], the biodegradation method [4] are not able to fully solve this problem.

In recent years, advanced oxidation processes (AOP) have been actively used to treat wastewater with persistent organic pollutants [5]. In these processes, active oxidative radicals formed *in situ* are used to degrade various organic compounds dissolved in water. Among them, the most common is the Fenton process, in which the oxidation of organic compounds occurs by peroxide radicals formed as a result of the catalytic decomposition of H_2O_2. The conducted research showed that the Fenton oxidation process is not only an effective method for removing many dangerous organic pollutants from wastewater, but also the most promising in terms of economic efficiency and ease of operation [6, 7].

The basis of the Fenton process is the redox cycle of metals of variable valence, such as Fe^{2+}/Fe^{3+}, Cu^+/Cu^{2+}, Co^{2+}/Co^{3+}, etc., which is used as a catalyst for obtaining reactive radicals from H_2O_2 [7, 8]. The high reactivity of Cu in relation to H_2O_2, the fast kinetics of the formation of reactive oxygen species compared to Fe, as well as the low cost and environmental friendliness led to the development of a large number of catalytic Fenton systems based on it [9-11].

For the traditional homogeneous Fenton process, in addition to secondary contamination with metal hydroxides, the limitations of the working range of the pH value of the medium should be attributed to the disadvantages. Since the reaction must be carried out under acidic conditions of $pH \leq 3$ [12], this requires acidification of the solution before purification and neutralization afterward. In addition, homogeneous catalysts have low reusability [13].

When using a heterogeneous Fenton system based on copper compounds, the activation of hydrogen peroxide occurs in a wider pH range compared to iron-containing catalysts, and the process of oxidation of organic compounds can be carried out under conditions close to neutral [14]. However, pH control is important not only to ensure complete oxidation of pollutants, but also to minimize leaching of active metals [15].

The present article is devoted to the study of the influence of the medium pH on the activity of a heterogeneous catalyst based on copper (II) oxide.

I. Experimental

1.1. Synthesis of the catalyst.

For the study, a multilayer catalyst based on CuO was synthesized. The synthesis of heterogeneous nanostructured magnetosensitive catalyst $SiO_2/CoFe_2O_4/SiO_2/CuO$ was carried out in three stages. At the first stage, iron and cobalt hydroxides from solutions of their salts (ratio 1:2) were deposited on preformed SiO_2 particles. At the second stage, a porous layer of SiO_2 was formed on the obtained particles by the sol-gel method, on which copper hydroxide was deposited at the third stage of synthesis. Annealing of the obtained composite was carried out after the third stage of synthesis at a temperature of 550°C. Such conditions made it possible to obtain a nanostructured multilayer catalyst with a magnetosensitive $CoFe_2O_4$ core, a porous SiO_2 protective layer, on which catalytically active CuO centers are located [16].

1.2. Research methods.

The cationic dye methylene blue (MB, $C_{16}H_{18}N_3SCl$) was used as a model organic pollutant of wastewater. The oxidation process of the methylene blue dye in the Fenton system was carried out under constant conditions (5 ml of a model solution of MB ($5\cdot10^{-5}$ mol/L), 10 mg of catalyst and $4.5\cdot10^{-3}$ mol of H_2O_2 (35%)) at room temperature without forced stirring at initial solution pH values of 3, 6 and 9. The pH value was adjusted with hydrochloric acid and sodium hydroxide solutions without buffering. The change in dye concentration in the reaction system was determined by the value of the optical density of the solution in a glass cuvette with a layer thickness of 1 cm at a wavelength of 620 nm [17] using a Spekol 11 spectrophotometer. Sampling was carried out after magnetic separation of the catalyst at certain time intervals [18].

The investigation of the surface morphology of the obtained particles was carried out using a REMMA 102-02 scanning electron microscope (SEM) with an X-ray microanalyzer system (ESD).

The composition of the synthesized nanostructured particles was investigated by the method of Fourier transform infrared spectroscopy (FTIR). For the preliminary preparation of the samples, the method of pressing the sample into a tablet with KBr was used (tablets: 5% of the sample in KBr). FTIR spectra of the $SiO_2/CoFe_2O_4/SiO_2/CuO$ composite were recorded using spectrometer NICOLET 6700 (Thermo Fisher Scientific). The measurements were carried out in the wave numbers range of 400 – 4000 cm^{-1} with a resolution of 4 cm^{-1} [19].

II. Results and Discussion

2.1. Characteristics of the catalyst.

In Fig. 1 presents SEM-photography of the surface of the synthesized catalyst $SiO_2/CoFe_2O_4/SiO_2/CuO$, which clearly shows CuO catalytic centers.

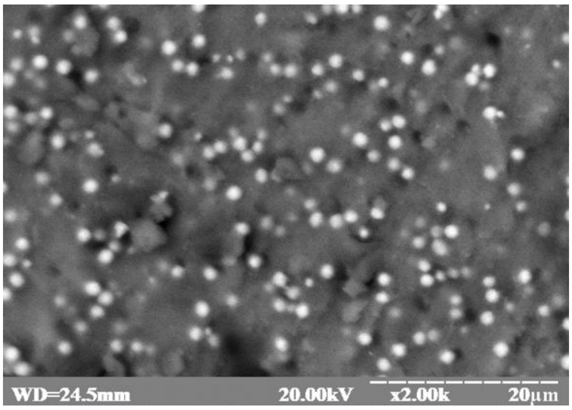


Fig. 1. FESEM-image of particles $SiO_2/CoFe_2O_4/SiO_2/CuO$ obtained by means of a scanning electron microscope REMMA 102-02.

The analysis of the obtained peaks on the IR spectrum of the $SiO_2/CoFe_2O_4/SiO_2/CuO$ composite (Fig. 2) confirmed the presence in the structure of the catalyst core of ferrite cobalt of a spinel structure – the presence of a characteristic plateau at 590 – 560 cm^{-1} and a valence oscillation, which is observed about 465 cm^{-1} [21, 22]. The characteristic asymmetric oscillation of the Si–O–Si, observed at 1100 cm^{-1}, indicates the formed silicate shell [22], and the width of the shoulder is probably related to the contribution of the Si–O–Fe (Co) vibration. This indicates the interaction of $Fe^{3+}(Co^{2+})$ with silica network [20]. Infrared absorption peaks at 590 and 470 cm^{-1} were attributed to the valence vibrations of Cu–O in CuO, and the absorption peaks at 1040 and 670 cm^{-1} indicate the presence of Si–O–Cu bonds [23]. The band at 800 cm^{-1} can be attributed to the valence vibration of Cu–O in Cu_2O, which indicates the existence of copper (I) oxide in the structure of the catalyst [24]. Thus, the obtained results of the composition of the synthesized catalyst $SiO_2/CoFe_2O_4/SiO_2/CuO$ showed that the catalytic centers are Cu^+ and Cu^{2+}.

2.2. The effect of medium pH on the activity of the MB oxidation process.

As the research results showed (Figs. 3a and 3b, Table 1), the synthesized catalyst exhibits high activity in the entire investigated pH range. The degree of MB destruction after 2 hours of the process reaches 85-90 % at all pH values. However, the influence of the medium pH on the rate of oxidation is noticeable at the initial stages of the process. The highest efficiency of MB destruction in

20 minutes of the process was observed at pH = 9, and the efficiency of the process decreased in the order of pH (9) > pH (6) > pH (3) (Fig. 3a, Table 1).

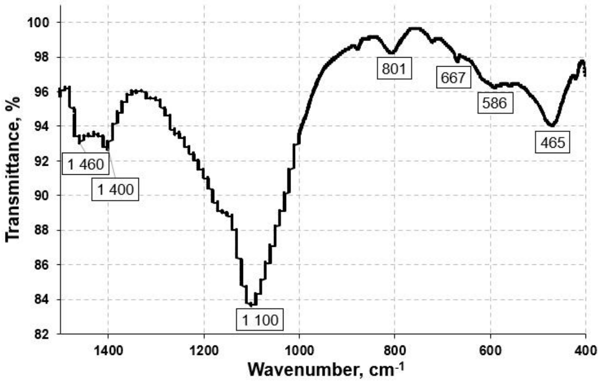


Fig. 2. FTIR spectrum of $SiO_2/CoFe_2O_4/SiO_2/CuO$ sample.

Based on the experimental results, the following possible mechanism of the heterogeneous Fenton reaction on the $SiO_2/CoFe_2O_4/SiO_2/CuO$ catalyst is proposed:

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + HO\cdot + OH^{-} \tag{1}$$

$$Cu^{2+} + H_2O_2 \rightarrow Cu^{+} + HO_2\cdot + H^{+} \tag{2}$$

$$HO_2\cdot + H_2O_2 \rightarrow O_2 + H_2O + OH\cdot \tag{3}$$

When using the Cu^{+}/Cu^{2+} redox cycle, it is the reaction of Cu^{+} with hydrogen peroxide that is responsible for the formation of hydroxyl radicals and Cu^{2+} (1). At the same time, the reduction of Cu^{2+} to Cu^{+} by reaction (2) proceeds more slowly [25].

The formed hydroxyl radical reacts with organic impurities, the destruction of which can occur incompletely – to the formation of shorter and simpler organic compounds, or to complete mineralization with the formation of carbon dioxide, water and mineral salts:

$$RH + HO\cdot \rightarrow R\cdot + H_2O \tag{4}$$

$$R\cdot + Cu^{2+} \rightarrow R^{+} + Cu^{+} \tag{5}$$

$$R^{+} + O_2 \rightarrow ROO^{+} \rightarrow CO_2 + H_2O \tag{6}$$

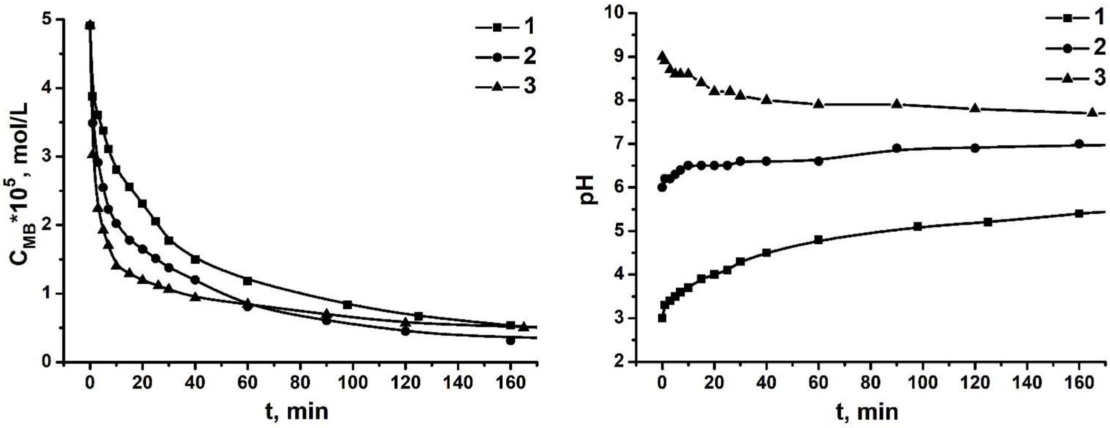
In the presence of copper (I) oxide on the surface (Fig. 2), the formation reaction of hydroxyl radicals (1) occurs from the first seconds of the destruction process at all pH values. According to Le Chatelier's principle, reaction (1) occurs rapidly in an acidic medium at the initial stages of the process, and reaction (2) slows down at the same time. Thus, the amount of Cu^{+} decreases, which will affect the concentration of formed hydroxyl radicals •OH, and, accordingly, the rate of the oxidation reaction of organic compounds (4). That is, at pH = 3, the catalytic activity of the $SiO_2/CoFe_2O_4/SiO_2/CuO$ composite at the initial stage of the process is weaker (Fig. 3a). When the process occurs in an alkaline medium, reaction (2) is activated, the amount of Cu^{+} increases, as a result of which an increase in the rate of MB oxidation is observed.

The simultaneous occurrence of reactions (1) and (2),

Table 1.

Degree and rate of MB destruction in the Fenton process at different initial pH values

N s/o	Time t, min	pH = 3		pH = 6		pH = 9	
		Degree of destruction P, %	Rate process $W\cdot10^8$, mol/L·s	Degree of destruction P, %	Rate process $W\cdot10^8$, mol/L·s	Degree of destruction P, %	Rate process $W\cdot10^8$, mol/L·s
1	10	43	3.5	56	4.8	71	5.8
2	20	53	2.1	66	2.7	76	3.1
3	60	76	1.0	83	1.1	83	1.1
4	120	86	0.6	90	0.6	88	0.6



a) b)

Fig. 3. Kinetic curves of the oxidation of methylene blue (a) and the change in the pH value during its destruction (b) by the $SiO_2/CoFe_2O_4/SiO_2/CuO$ catalyst at the dye concentration $C_{MB} = 5\cdot10^{-5}$ mol/L at different initial pH values: 1 – 3; 2 – 6; 3 – 9.

the rates of which depend on the medium conditions, lead to its partial neutralization (Fig. 3b). At the initial stage, the formation of OH^- or H^+ ions by reactions (1) and (2) significantly affects the medium pH, the value of which changes by an order of magnitude towards neutral. During the "equalization" of pH values, the rate of MB destruction for all three processes approaches. After 120 minutes of the process, the degree of oxidation for all investigated systems is practically the same and reaches 85-90 %.

Conclusions

The heterogeneous nanostructured magnetosensitive catalyst $SiO_2/CoFe_2O_4/SiO_2/CuO$ synthesized by us can be successfully used in a wide range of pH values without losing its activity. The influence of the medium pH is observed only at the initial stage of the process and does not affect the final result of the oxidation of organic matter. The advantage of this catalyst is the ease of its extraction from the reaction medium using a magnet, as well as the neutralization of pH as a result of the oxidation process. Such a Fenton system based on the proposed multilayer catalyst $SiO_2/CoFe_2O_4/SiO_2/CuO$ can significantly simplify the technology of post-treatment of industrial and domestic wastewater, which is characterized by a variable pH value.

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Conflicts of Interest: *The authors declare no conflict of interest.*

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[1] X. Zhang, Y. Ding, H. Tang, et al., *Degradation of bisphenol A by hydrogen peroxide activated with $CuFeO_2$ microparticles as a heterogeneous Fenton-like catalyst: Efficiency, stability and mechanism*, Chemical Engineering Journal, 236, 251 (2014); https://doi.org/10.1016/j.cej.2013.09.051.

[2] Q. Zhou, W. Gong, C. Xie, et al., *Removal of Neutral Red from aqueous solution by adsorption on spent cottonseed hull substrate*, Journal of Hazardous Materials, 185(1), 502 (2011); https://doi.org/10.1016/j.jhazmat.2010.09.029.

[3] Y.-H. Huang, Y.-F. Huang, P.-S. Chang, C.-Y. Chen, *Comparative study of oxidation of dye-Reactive Black B by different advanced oxidation processes: Fenton, electro-Fenton and photo-Fenton*, Journal of Hazardous Materials, 154(1-3), 655 (2008); https://doi.org/10.1016/j.jhazmat.2007.10.077.

[4] M. M. Haque, W. T. Smith, D. K. Y. Wong, *Conducting polypyrrole films as a potential tool for electrochemical treatment of azo dyes in textile wastewaters*, Journal of Hazardous Materials, 283, 164 (2015); https://doi.org/10.1016/j.jhazmat.2014.07.038.

[5] S. Hussain, E. Aneggi, D. Goi, *Catalytic activity of metals in heterogeneous Fenton-like oxidation of wastewater contaminants: a review*, Environmental Chemistry Letters, 19(3), 2405 (2021); https://doi.org/10.1007/s10311-021-01185-z.

[6] E. Neyens, J. Baeyens, *A review of classic Fenton's peroxidation as an advanced oxidation technique*, Journal of Hazardous Materials, 98 (1-3), 33 (2003); https://doi.org/ 10.1016/s0304-3894(02)00282-0.

[7] M. Xu, C. Wu, Y. Zhou, Advancements in the Fenton Process for Wastewater Treatment, In book: Advanced Oxidation Processes - Applications, Trends, and Prospects, Ed. by C. Bustillo-Lecompte, Ch. 4, 1 (IntechOpen Ltd, 2020); https://doi.org/10.5772/intechopen.90256.

[8] M. Cheng, C. Lai, Y. Liu, et al., *Metal-organic frameworks for highly efficient heterogeneous Fenton-like catalysis,* Coordination Chemistry Reviews, 368 (1), 80 (2018); https://doi.org/10.1016/j.ccr.2018.04.012.

[9] C. Wang, Y. Cao, H. Wang, *Copper-based catalyst from waste printed circuit boards for effective Fenton-like discoloration of Rhodamine B at neutral pH*, Chemosphere, 230, 278 (2019); https://doi.org/10.1016/j.chemosphere.2019.05.068.

[10] Y. Wang, H. Zhao, G. Zhao, *Iron-copper bimetallic nanoparticles embedded within ordered mesoporous carbon as effective and stable heterogeneous Fenton catalyst for the degradation of organic contaminants*, Applied Catalysis B: Environmental, 164, 396 (2015); http://dx.doi.org/10.1016/j.apcatb.2014.09.047.

[11] S. Zaman, A. Zainelabdin, G. Amin, et al., *Efficient catalytic effect of CuO nanostructures on the degradation of organic dyes*, Journal of Physics and Chemistry of Solids, 73(11), 1320 (2012); http://dx.doi.org/10.1016/j.jpcs.2012.07.005.

[12] N. Thomas, D. D. Dionysiou, S. C. Pillai, *Heterogeneous Fenton Catalysts: A Review of Recent Advances*, Journal of Hazardous Materials, 404 (Pt. B), 124082 (2020); https://doi.org/10.1016/j.jhazmat.2020.124082.

[13] X. Zhang, Q. Zhang, T. Yang, et al., *Research progress of heterogeneous Fenton catalyst for organic wastewater treatment: Thesis*, IOP Conference Series Earth and Environmental Science, 651(4), 042025 (2021); https://doi.org/10.1088/1755-1315/651/4/042025.

[14] A. D. Bokare, W. Choi, *Review of iron-free Fenton-like systems for activating H_2O_2 in advanced oxidation processes*, Journal of Hazardous Materials, 275, 121 (2014); https://doi.org/10.1016/j.jhazmat.2014.04.054.

[15] M. Silva, J. Baltrus, C. Williams, et al., *Mesoporous Fe-doped MgO nanoparticles as a heterogeneous photo-Fenton-like catalyst for degradation of salicylic acid in wastewater*, Journal of Environmental Chemical Engineering, 9(4), 105589 (2021); https://doi.org/10.1016/j.jece.2021.105589.

[16] O. Makido, G. Khovanets', V. Kochubei, I. Yevchuk, *Nanostructured Magnetically Sensitive Catalysts for the Fenton System: Obtaining, Research, Application*, Chemistry and Chemical Technology, 16(2), 227 (2022); https://doi.org/10.23939/chcht16.02.227.

[17] D. Melgoza, A. Hernández-Ramírez, J. M. Peralta-Hernández, *Comparative efficiencies of the decolourisation of Methylene Blue using Fenton's and photo-Fenton's reactions*, Photochemical & Photobiological Sciences, 8(5), 596 (2009); https://doi.org/10.1039/b817287k.

[18] O. Yu. Makido, Yu. G. Medvedevskikh, G. I. Khovanets', *Investigation into the adsorption of methylene blue on the surface of a «core–shell» type catalyst for the Fenton system*, Voprosy khimii i khimicheskoi tekhnologii, 6(133), 91 (2020); http://dx.doi.org/10.32434/0321-4095-2020-133-6-91-98.

[19] K. Maresz, A. Ciemięga, P. Bezkosty, et al., *Insight into Structural and Physicochemical Properties of ZrO_2-SiO_2 Monolithic Catalysts with Hierarchical Pore Structure: Effect of Zirconium Precursor*, Catalysts, 13(12), 1516 (2023); https://doi.org/10.3390/catal13121516.

[20] H. Wang, J. Huang, L. Ding, et al., *A facile synthesis of monodisperse $CoFe_2O_4/SiO_2$ nanoparticles*, Applied Surface Science, 257(16), 7107 (2011); https://doi.org/10.1016/j.apsusc.2011.03.063.

[21] R. Asokarajan, K. Neyvasagam, A. Milton Franklin Benial, *Simple Synthesis and Characterization Studies of $CoFe_2O_4$ Nanocrystalline by Co-precipitation process*, International Journal of Current Research, 5(2), 113 (2013).

[22] P. Arévalo-Cid, J. Isasi, F. Martín-Hernández, *Comparative study of core-shell nanostructures based on amino-functionalized Fe_3O_4@SiO_2 and $CoFe_2O_4$@SiO_2 nanocomposites*, Journal of Alloys and Compounds, 766, 609 (2018); https://doi.org/10.1016/j.jallcom.2018.06.246.

[23] H. Li, L. Ban, Z. Wang, et al., *Regulation of Cu Species in CuO/SiO_2 and Its Structural Evolution in Ethynylation Reaction*, Nanomaterials, 9 (6), 842 (2019); https://doi.org/10.3390/nano9060842.

[24] W. Ho, Q. Tay, H. Qi, et al., *Photocatalytic and Adsorption Performances of Faceted Cuprous Oxide (Cu_2O) Particles for the Removal of Methyl Orange (MO) from Aqueous Media*, Molecules, 22(4), 677 (2017); https://doi.org/10.3390/molecules22040677.

[25] M. Silva, J. P. Baltrus, C. Williams, et al., *Heterogeneous Photo-Fenton-like Degradation of Emerging Pharmaceutical Contaminants in Wastewater using Cu-doped MgO Nanoparticles*, Applied Catalysis A: General, 630, 118468 (2022); https://doi.org/10.1016/j.apcata.2021.118468.

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Вплив pH середовища на каталітичну активність каталізатора на основі CuO у системі Фентона

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Досліджено вплив pH середовища на активність гетерогенного наноструктурованого магніточутливого каталізатора $SiO_2/CoFe_2O_4/SiO_2/CuO$ у системі Фентона та запропоновано механізм реакції. Визначено, що каталітичними центрами є Cu^+ та Cu^{2+}. Встановлено, що швидкість деструкції барвника метиленового синього (МС) як модельного забруднювача стічних вод за перші 20 хв процесу залежить від pH, а її значення зменшується в ряді pH (9)>(6)>(3). Після 2 год для всіх початкових значень pH ступінь деструкції МС досягає 85-90%, а pH змінюється до нейтрального. Запропонована система може використовуватися у технології доочищення стічних вод промислового та побутового характеру.

Ключові слова: каталізатор $SiO_2/CoFe_2O_4/SiO_2/CuO$, система Фентона, pH середовища, окиснення метиленового синього, механізм реакції.