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FERRITE-FILLED POLYMER COMPOSITES AS CATALYSTS FOR FENTON SYSTEM

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Abstract. The effect of fillers: cobalt ferrite ($CoFe_2O_4$) nanoparticle and various types of surfactants on the structure of the obtained ferrite-filled polymer composites and their adsorption and catalytic properties towards organic dyes in the Fenton system was investigated. Ferrite-polymer composites based on triethylene glycol dimethacrylate (TGM-3) and pre-synthesized cobalt ferrite ($CoFe_2O_4$) nanoparticles with notable magnetic properties were obtained *via in situ* photoinitiated free radical polymerization. To evenly distribute $CoFe_2O_4$ nanoparticles in the polymer matrix and increase its porosity during synthesis, various surfactants, both synthetic (sodium dodecyl sulfate) and natural (rhamnolipids), were used. The synthesized ferrite-filled polymer composites are transparent, strong, elastic, and homogeneous in structure. The adsorption and catalytic properties of the obtained films based on a polymer composite TGM-3–$CoFe_2O_4$ in an aqueous solution of the organic dye methylene blue (MB) as a model wastewater pollutant were studied. It was found that the composites obtained with the addition of surfactants show good adsorption and catalytic properties, as evidenced by the high degree of MB extraction from the solution (up to 94 %). The use of natural surfactants (rhamnolipids) makes it possible to increase the adsorption efficiency by 4–5 %, and catalytic oxidation by 20 %. In addition to their adsorption and catalytic properties, these films are magnetically separable, allowing them to be easily removed from the environment and making them promising for water resource recovery processes.

Keywords: ferrite-filled polymer composites, photoinitiated polymerization, triethylene glycol dimethacrylate, cobalt ferrite nanoparticles, Fenton system, adsorption.

1. Introduction

Currently, new production methods and properties of various filled polymer composites are being actively developed. They are very promising for practical use in a wide variety of industries due to their unique properties, such as high strength, lightness, resistance to corrosion and chemicals, and the ability to modify properties. Specifically, metal-filled polymer composites are used to produce various types of heaters, electrodes, sensors, protective coatings against electromagnetic radiation, flame retardant, catalytic, and adsorption materials, *etc.* Metal-filled polymer composites are materials consisting of a polymer matrix (base) and a metal filler (powders, particles, fibers). Such composites combine the properties of polymers (mechanical resistance, lightness, flexibility, and dielectric properties) and metals (strength, electrical conductivity, thermal conductivity, and magnetic properties) by varying the type and amount of metal filler and the polymer matrix. The range of created and promising filled polymer composite materials is extremely diverse due to the ability to vary components, structure, technology, as well as their areas of application, along with reducing the cost of materials and production processes.[1, 2]

Polymer nanocomposites represent a special class of polymer composite materials. As an additive to the polymer matrix, they contain fillers that differ in both chemical composition and morphology of individual elements. The properties of this type of composite can vary with very small changes in the filler concentration due to its large specific surface area and intense intermolecular interaction with the polymer.[3, 4]

A special position among dispersed fillers holds metal powders: iron, copper, aluminum, and other metals and alloys. Their addition to the polymer matrix allows reduction of the friction coefficient, moisture permeability, and electrical resistance, and at the same time increases thermal conductivity, resistance to ionizing radiation, imparts certain magnetic properties to polymer composite materials, *etc.* In addition, metal powders increase the stiffness and strength of composites under compression, reduce the coefficient of thermal expansion and shrinkage during matrix hardening.[5]

Ferrite nanoparticles are promising materials in modern science and technology due to their structural, magnetic, and electrical properties.[6] Furthermore, their magnetic properties can be controlled with practical applications in mind by properly selecting several divalent cations and their ratios in the ferrite structure. Nanosized powders have opened a new direction in physical materials science, and the need for materials with high resistivity has led to the synthesis of various ferrite compositions.

Nanodispersed cobalt ferrite ($CoFe_2O_4$), which we used as a filler in the synthesis of polymer composites, is known as a magnetically hard material with high coercivity, low magnetization, and high physical and chemical stability.[7] Cobalt ferrite $CoFe_2O_4$ has a reverse spinel structure, where Co^{2+} ions have a preference for octahedral sites. It is possible to control the magnetic characteristics of ferrite-based materials to some extent by changing the size, shape, composition, and structure of the ferrite nanoparticles.[8]

TGM-3 oligoether acrylate (triethylene glycol dimethacrylate) is a hydrophobic, low viscosity, nontoxic bifunctional methacrylic monomer that can also be used as a crosslinking agent in a composite. It provides the polymer with adhesion, weather resistance, a high degree of crosslinking, flexibility, improved impact strength, heat resistance, and abrasion resistance. TGM-3 enhances the adhesion strength and viscosity of polymer composites.[9] The curing of these binders occurs *via* a mechanism of radical chain polymerization, which is initiated by heating, irradiation, or free radicals, with the formation of only carbon-carbon bonds without the release of low-molecular compounds, and based on the activation and opening of double bonds and the formation of a network structure of the polymer.[10]

Therefore, ferrite-filled polymer composites, particularly based on dimethacrylate polymers and cobalt ferrite, combine the desirable properties of the polymer matrix (for example, mechanical stability, flexibility, and processability) with the magnetic characteristics of $CoFe_2O_4$ nanoparticles. Good dispersion and adhesion of cobalt ferrite nanoparticles in the polymer matrix are crucial for optimizing the composite properties.

In recent decades, total industrialization has caused a significant strain on the environment, particularly the planet's water resources. Studies have shown that there are over 700 new pollutants in Europe's aquatic environment, and the number is continuously increasing. Synthetic organic pollutants, including pharmaceuticals, personal care products, pesticides, dyes, and pigments, which are widely used in various economic sectors and everyday life, pose a great threat to the ecosystem. The harmful effects of organic substances, particularly dyes entering water bodies, due to their toxicity and complexity in decolorization and decomposition, are amplified by the cumulative effect (progressive increase of harmful compounds in each subsequent link of the trophic chain). Advanced oxidation processes (AOP), based on the formation of highly reactive radicals (particularly hydroxyl radicals) for the catalytic oxidation of organic substances to carbon dioxide, are effective wastewater treatment methods for such pollutants. The formation of hydroxyl radicals from hydrogen peroxide (H_2O_2) is an environmentally friendly process with green byproducts, H_2O and O_2. This process can be carried out under atmospheric pressure and low temperatures (below 100 °C). The Fenton process is a traditional AOP based on the formation of active hydroxyl radicals (•OH) as a result of the interaction of H_2O_2 with transition metal ions. These radicals (•OH) are powerful oxidizing agents with high electrochemical potential that quickly break down complex organic pollutants, converting them into simpler, non-toxic compounds such as carbon dioxide (CO_2) and water (H_2O). Creating catalytic systems with good adsorption properties, a crucial characteristic of any catalyst, and magnetic properties for easy removal from the reaction medium can help solve the problem of wastewater treatment.[7]

Metal-filled polymer composites are gaining increasing recognition as potential catalysts due to the synergistic effect between metal nanoparticles and the polymer matrix. These composites can show increased catalytic activity, selectivity, and stability compared to their components, making them attractive for various chemical reactions, particularly for the oxidation of organic pollutants in wastewater. This paper presents the study results of the influence of metal oxide particles on the polymer matrix structure and the adsorption and catalytic properties of the resulting ferrite-filled polymer composites. To synthesize the composite, polyfunctional crosslinked dimethacrylate TGM-3 was used with the addition of pre-synthesized cobalt ferrite and synthetic (sodium dodecyl sulfate) or natural (rhamnolipid) surfactants. The introduction of surfactants during the synthesis of ferrite-filled polymer composites prevents agglomeration of $CoFe_2O_4$ nanoparticles and promotes their even distribution in the polymer matrix, increasing its porosity.

2. Experimental

2.1. Materials

The following reagents were used for the research: monomer triethylene glycol dimethacrylate (TGM-3) with the chemical formula $CH_2=C(CH_3)–C(O)–(CH_2CH_2O)_3–O–C(O)–C(CH_3)=CH_2$, of the chemically pure grade, (Aldrich); photoinitiator 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651) with the chemical formula $C_6H_5–C(OCH_3)_2–C(O)–C_6H_5$, of the chemically pure grade, (Fluka); ferric nitrate nonahydrate with the chemical formula $Fe(NO_3)_3 \cdot 9H_2O$ of the pure grade (Sfera sim); cobalt nitrate hexahydrate with the chemical formula $Co(NO_3)_2 \cdot 6H_2O$ of the pure grade (Sfera sim); citric acid monohydrate with the chemical formula $C_6H_8O_7 \cdot H_2O$ of the pure grade (Sfera sim); aqueous ammonia 25 % with the chemical formula NH_4OH of the grade chemically pure, for analysis, (Sfera Sim). The monomer was purified by mixing with pre-activated Al_2O_3 powder and then subsequent centrifugation.

The following surfactants were used: synthetic – sodium dodecyl sulfate (NaDS) with the chemical formula $C_{12}H_{25}SO_4Na$ of the pure grade (Optimum System), and natural ones – rhamnolipids (RL) with the chemical formula $C_{26}H_{48}O_9$. Surfactants were added to the initial photocomposition for further synthesis of the ferrite-polymer composite in dry form.

2.2. Methods

2.2.1. Rhamnolipid synthesis

The rhamnolipids (RL) used in the work were synthesized in the Division of Chemistry and Biotechnology of Fossil Fuels of the Department of PhChFF InPOCC NAS of Ukraine by extraction from the supernatant of the culture fluid of the *Pseudomonas* sp. PS-17 strain. Cultivation of the strain was carried out using the liquid nutrient medium (g/L): $NaNO_3$ – 4.0; $K_2HPO_4 \cdot 3H_2O$ – 2.0; KH_2PO_4 – 1.2; $MgSO_4 \cdot 7H_2O$ – 0.5; sodium citrate – 4.0, distilled water – to 1L. Glycerol was used as a carbon and energy source (4 % weight). 1-day culture of the strain *Pseudomonas* sp. PS-17, grown on the same medium (primary inoculum was added in a quantity of 5 % of the medium's volume), was used as an inoculum. Microorganisms were cultivated in 750 ml Erlenmeyer flasks with 150 ml medium on the rotary shaker (220 rpm) at 28–30 °C for 5 days. The biomass was separated *via* centrifugation of the cultural broth at 6000 rpm for 20 minutes. Rhamnolipids were isolated from the biocomplex obtained *via* acidizing the supernatant using a 10 % solution of HCl to pH 3.0, followed by settling and centrifugation at 8000 rpm for 20 minutes. The complex was extracted with the mixture of solvents chloroform/methanol (2 : 1), and the organic phase was evaporated under vacuum.[11]

Surfactants of biogenic origin (biosurfactants) have the potential to replace synthetic surfactants. Biosurfactants, produced by microbial synthesis using substrates, are environmentally friendly and economically profitable. These substances have a wide range of functional properties and a number of advantages compared to synthetic ones: biodegradability, low toxicity, high activity, and stability of physicochemical properties across a broad range of temperatures, pH values, and salt concentrations. Rhamnolipid biosurfactants, at low concentrations, effectively and significantly decrease the surface and interfacial tension of aqueous solutions, and also form finely dispersed and stable emulsions and are used as solubilizers and emulsifiers.[12]

2.2.2. Synthesis of cobalt ferrite nanoparticles

Cobalt ferrite nanoparticles ($CoFe_2O_4$) with magnetic properties were synthesized *via* the co-precipitation method from a solution of iron and cobalt salts with ammonium hydroxide in the presence of a surfactant. Nitrates of Fe (III) and Co (II) in a ratio of 2 : 1 were used for the synthesis. The reaction was carried out with intensive stirring at a temperature of 80 °C.

After adding a surfactant to the reaction medium (in this case, citric acid $C_6H_8O_7 \cdot H_2O$ was used), iron and cobalt hydroxides dissolve as citrates $(FeCo \cdot C_6H_2O_7) \cdot nH_2O$, which, upon calcination in an oxygen atmosphere, decompose to cobalt ferrite particles with a developed specific surface area and noticeable magnetic properties.[13, 14]

The synthesis reactions can be presented by the following equations:

$$2Fe(NO_3)_3 + Co(NO_3)_2 + 8NH_4OH \rightarrow Co(OH)_2 + 2Fe(OH)_3 + 8NH_4NO_3,$$

$$Co(OH)_2 + 2Fe(OH)_3 \rightarrow CoFe_2O_4 + 4H_2O.$$

2.2.3. Synthesis of ferrite-filled polymer composites

Ferrite-polymer composites based on triethylene glycol dimethacrylate (TGM-3) and cobalt ferrite nanoparticles $CoFe_2O_4$ were obtained *via* photoinitiated *in situ* radical polymerization.

First, a solution of the photoinitiator 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651) in monomer (TGM-3) was made, which subsequently served as a polymer matrix for all systems. The photoinitiator content in all cases was 2 mol. % based on monomer. To obtain ferrite-filled polymer composites, the initial solution (TGM-3 + IR 651) was mixed with a certain amount of the appropriate surfactant and cobalt ferrite. Mixing was carried out at room temperature, and the samples were additionally treated with ultrasound to homogenize the system. The amount of added surfactant and $CoFe_2O_4$ for all studied samples was 5 wt. %. The initial solution of TGM-3, TGM-3+$CoFe_2O_4$ without surfactant, and TGM-3+$CoFe_2O_4$+surfactant were investigated for comparison.

Photopolymerization of ferrite-polymer composite systems TGM-3–$CoFe_2O_4$ was carried out in thin films, sealed from atmospheric oxygen by a cover glass, using a laser interferometer under UV irradiation of a DRT-400 lamp according to method.[15] The determined amount of the liquid photocomposition was subjected to photoinitiated polymerization at room temperature and a constant intensity of UV irradiation of 17 W/m^2 till deep conversions. The synthesized ferrite-filled polymer composites are transparent, strong, elastic, and homogeneous in structure.

2.2.4. Study of the structure of the synthesized composite

The structure of a ferrite-organic composite, synthesized from triethylene glycol dimethacrylate polymer and pre-synthesized cobalt ferrite nanoparticles, was verified by FTIR spectra recorded on a NICOLET 6700 spectrometer (Thermo Fisher Scientific) using the KBr technique (5 % sample in KBr). Measurements were recorded in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}.

2.2.5. Study of the adsorption properties of the synthesized composite

The study of the adsorption properties of the synthesized ferrite-filled polymer composites TGM-3–$CoFe_2O_4$ was conducted using a model solution of methylene blue (MB) dye, with the formula $C_{16}H_{18}ClN_3S$, of the grade pure for analysis as an organic pollutant in wastewater. An aqueous solution of MB was prepared by dissolving a certain amount of dye in distilled water by the method described in.[16] The adsorption process was carried out at room temperature without stirring at an initial MB concentration of $6\cdot10^{-5}$ mol/L. Samples were taken at specified time intervals until equilibrium was established. The change in the concentration of the MB dye in the reaction system was determined spectrophotometrically by the optical density of the solution in a glass cuvette with a layer thickness of 1 cm at a wavelength of 620 nm using a Spekol 11 spectrophotometer.

2.2.6. Study of catalytic properties of the synthesized composite

The study of the catalytic activity of the synthesized ferrite-organic composites in the Fenton system was carried out on a model solution of methylene blue using 35 % hydrogen peroxide with the formula H_2O_2 of the medical grade (Sfera Sim) as an oxidant according to method.[7] The experiment was performed under the following conditions: methylene blue solution with a volume of 5 ml and an initial concentration of $5\cdot10^{-5}$ mol/L, composite ~ 60 mg, and H_2O_2 volume of 0.05 ml. The degree of catalytic destruction (*P*) for methylene blue was calculated from the decrease in optical density of the solution, which correlates with the concentration of dye in the reactor:

$$P=\frac{E_0-E}{E_0}\cdot100\%, \qquad (1)$$

where E_0 is the initial optical density of the solution; E is the current value of the optical density of the solution.

3. Results and Discussion

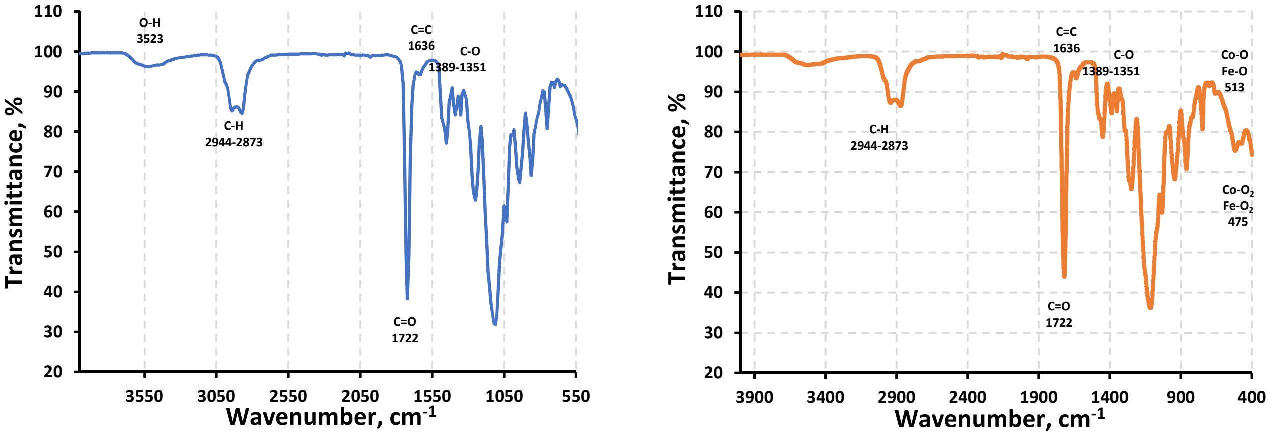
3.1. Characteristics of the TGM-3–$CoFe_2O_4$ composite

Analysis of the composite peaks shown in the IR spectrum confirmed the presence of all the declared phases in the composite (Fig. 1). Fig. 1, *a* shows the absorption bands for O–H vibrations at 3523 cm^{-1}, C–H vibrations in the range 2944–2873 cm^{-1}, C=O double bond vibrations at 1722 cm^{-1} and C=C at 1636 cm^{-1}, C–O vibrations at 1389 cm^{-1} and 1351 cm^{-1}, and also at 1113 cm^{-1} for the C–O–C group. All these absorption peaks are characteristic of the polymer matrix structure of triethylene glycol dimethacrylate (TGM-3).[17]

When pre-synthesized cobalt ferrite ($CoFe_2O_4$) nanoparticles are introduced into the polymer matrix, new peaks are observed in the composite IR spectrum (Fig. 1, *b*). The noticeable peak at 513 cm^{-1} is explained by the valence vibration modes of the Fe–O and Co–O bonds in the magnetic particles[18] and the peak at 475 cm^{-1} is associated with the the metal oxide vibrations in the complexes of Co(II)–O_2 octahedral and Fe(III)–O_2 tetrahedral groups of the cobalt ferrite phase,[19] which confirms the presence of cobalt ferrite particles in the polymer matrix of triethylene glycol dimethacrylate.

3.2. Study of the adsorption properties of the synthesized composites

The adsorption capacity of synthesized ferrite-containing polymer composites and the process kinetic parameters were studied using the example of methylene blue dye adsorption from an aqueous solution. Synthesized samples with different compositions were used for this study: TGM-3/$CoFe_2O_4$/NaDS (1); TGM-3/$CoFe_2O_4$/RL (2); TGM-3/$CoFe_2O_4$ (3); pure TGM-3 (4). Fig. 2 shows the kinetic curves of MB adsorption for the presented compositions of ferrite-polymer composites.



a b

Fig. 1. FTIR spectra: a) pure TGM-3; b) TGM-3/$CoFe_2O_4$

The kinetic curves of MB adsorption for the presented samples of ferrite-polymer composites (Fig. 2) show the adsorption properties of samples 1 and 2, in contrast to the pure polymer matrix of triethylene glycol dimethacrylate (sample 4) and the ferrite-organic composite obtained without the introduction of surfactants (sample 3).

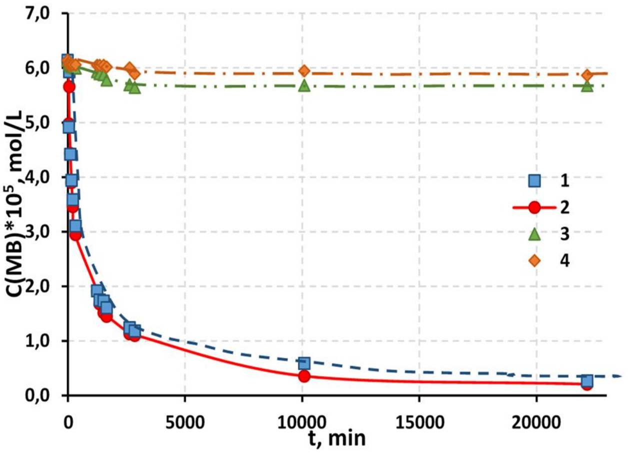


Fig. 2. Kinetic curves of methylene blue adsorption by composites based on a polymer matrix of triethylene glycol dimethacrylate (TGM-3): 1 – TGM-3/$CoFe_2O_4$/NaDS; 2 – TGM-3/$CoFe_2O_4$/RL; 3 – TGM-3/$CoFe_2O_4$; 4 – TGM–3

The adsorption efficiency was calculated by the equation:[7]

$$A_{ef} = \frac{C_0 - C_e}{C_0} \cdot 100\ \%. \qquad (2)$$

The amount of adsorbed dye (adsorption value of a given sorbent) was determined by the formula:

$$q_e = \frac{(C_0 - C_e)M}{m} \cdot V, \qquad (3)$$

where C_0 and C_e are the initial and equilibrium concentrations of the dye MB solution, mol/L; M is the molar mass of the dye MB, g/mol; V is the volume of the solution, L; m is the mass of the sorbent, g.

The obtained values (Table 1) confirm that the adsorption capacity of the ferrite-polymer composite depends on the introduction of surfactants during synthesis. Adding 5 % by weight surfactant during the synthesis of ferrite-organic composites not only improves the even distribution of cobalt ferrite particles in the polymer matrix but also leads to a sharp increase in its porosity,[20–23] which has a positive effect on the materialєs adsorption properties (an increase in adsorption efficiency of more than an order of magnitude). The degree of MB extraction for these samples reaches 90–94 %, which indicates a high affinity of the adsorbent for the methylene blue dye. At the same time, the adsorption process efficiency and MB adsorption value are higher for sample 2, synthesized with a natural surfactant (rhamnolipid), which indicates the influence on the material porosity not only of the surfactantsє presence, but also of their type.

Table 1. Main parameters of the MB adsorption process on the surface of ferrite-polymer composites

No.	Samples	$C_0 \times 10^5$, mol/L	$C_e \times 10^5$, mol/L	A_{ef}, %	q_e, mg/g
1	TGM-3/$CoFe_2O_4$/NaDS	6.1	0.59	90.37	1.36
2	TGM-3/$CoFe_2O_4$/RL	6.1	0.36	94.18	1.51
3	TGM-3/$CoFe_2O_4$	6.1	5.68	7.42	0.11
4	TGM–3+IR 651	6.1	5.95	3.10	0.05

The main kinetic parameters of the adsorption process for samples 1 (TGM-3/$CoFe_2O_4$/NaDS) and 2

(TGM-3/$CoFe_2O_4$/RL) were determined according to the theory, considering the adsorption process from a solution as a pseudo-chemical equilibrium reaction of displacement of solvent molecules from adsorption centers on the adsorbent surface by adsorbate molecules.[16]

To determine the fraction of adsorption centers occupied by dye molecules, we introduce the constant (A, L/mol) $A = \frac{V}{q_0 S}$ = const for the given process, where V is the solution volume, L; q_0S is a number of adsorption centers determined by the adsorption capacity (q_0, mol/m^2) and the surface (S, m^2) of the adsorbent, which are determined values for a separate experiment. This allows us to take into account the number of occupied adsorption centers when calculating the kinetics of heterogeneous adsorption from the solution.[7, 16]

The calculation was made according to the equation of heterogeneous adsorption from a solution:

$$\ln\frac{C}{a+C} + \ln\frac{a+C_0}{C_0} = a \cdot k \cdot t, \qquad (4)$$

where C is the current concentration of the dye in the solution, mol/L; C_0 is the initial concentration of the dye in the solution, mol/L; a is the constant for a given value C_0, which takes into account the part of adsorption centers occupied by MB molecules; k is the reaction rate constant; t is the reaction time, min.

Linear dependences $\ln\frac{C}{a+C} = f(t)$ for determining the main kinetic parameters of the process for the two composites (Fig. 3, Table 2) were obtained by selecting the coefficient a for a given initial concentration of MB in Eq. (4).

The obtained straight lines for each sample (Fig. 3, Table 2) have high correlation coefficients (R^2), indicating a good fit of the proposed equation for describing the adsorption isotherm of MB by ferrite-organic composites TGM-3/$CoFe_2O_4$/NaDS and TGM-3/$CoFe_2O_4$/RL. The adsorption kinetic parameters correspond to the proposed pseudo-first-order model, where the reaction rate is proportional to the residual dye concentration in the solution and the number of adsorption centers occupied by the solvent, if the diffusion stage controls adsorption.[13]

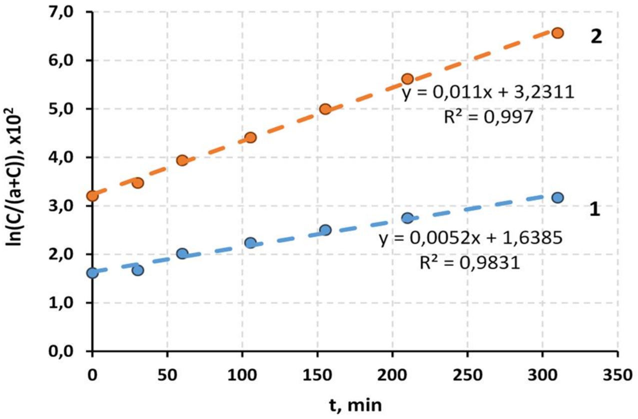


Fig. 3. Adsorption isotherms of MB for ferrite-polymer composites (initial C_{MB} =6.1·10^{-5} mol/L):
1 – TGM-3/$CoFe_2O_4$/NaDS; 2 – TGM-3/$CoFe_2O_4$/RL

The research results indicate that ferrite-filled polymer composites TGM-3/$CoFe_2O_4$/NaDS and TGM-3/$CoFe_2O_4$/RL demonstrate good adsorption properties, regardless of the surfactant nature. However, the use of natural surfactant improves adsorption efficiency by 4–5 %.

Table 2. Kinetic parameters of MB adsorption on the surface of ferrite-filled polymer composites TGM-3/$CoFe_2O_4$/surfactant

No.	Surfactant	C_0×10^5, mol/L	k, min^{-1}	$\ln\frac{a+C_0}{C_0}$	a×10^2, mol/L	A×10^{-4}, L/mol	R^2
1	NaDS	6.1	50	0.85	1.62	1.60	0.9831
2	RL	6.1	50	0.81	3.21	1.58	0.997

3.3. Study of the catalytic properties of the synthesized composites

The catalytic activity of composites based on TGM-3–$CoFe_2O_4$ was studied in the oxidation of methylene blue using hydrogen peroxide. According to experimental data (Fig. 4), ferrite-polymer composites demonstrate catalytic properties regardless of the surfactant nature. The introduction of surfactants allows the formation of a porous polymer network with evenly distributed cobalt ferrite nanoparticles in the volume. The pores and high adsorption properties of the composites facilitate the diffusion of dye and hydrogen peroxide molecules from the solution to the $CoFe_2O_4$ catalytic centers located in the volume of the polymer matrix, where the oxidation of the organic compound occurs.

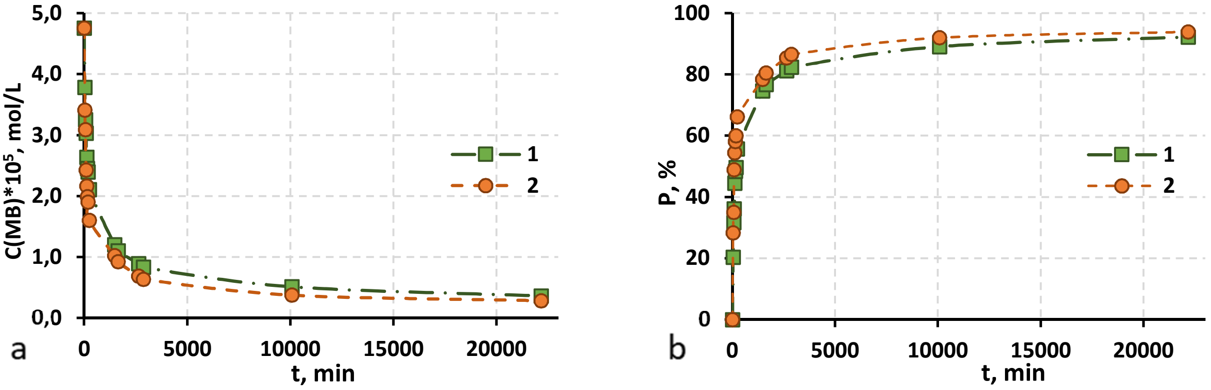


Fig. 4. Kinetic curves of MB oxidation ($5\cdot10^{-5}$ mol/L) on composites 1 – TGM-3/$CoFe_2O_4$/NaDS and 2 –TGM-3/$CoFe_2O_4$/RL: dependence of the change in the concentration of MB dye (a) and the degree of MB extraction (b) from an aqueous solution on time in the Fenton system

To distinct the oxidation and adsorption processes, the catalytic properties of the synthesized $CoFe_2O_4$ introduced into a polymer matrix were studied within a Fenton system under identical research conditions. Experimental results showed that the degree of MB oxidation in the Fenton system using pure $CoFe_2O_4$ particles as a catalyst does not exceed 25 % (Fig. 5, curve 5). That is, the study's findings on ferrite-organic composites can be explained by the simultaneous occurrence of two processes: oxidation of the MB dye within a Fenton system, in which the catalyst is $CoFe_2O_4$ nanoparticles embedded in the polymer network, and adsorption of the dye on the surface of the polymer matrix. The total degree of MB extraction from the aqueous solution for this process reaches 92–94 %.

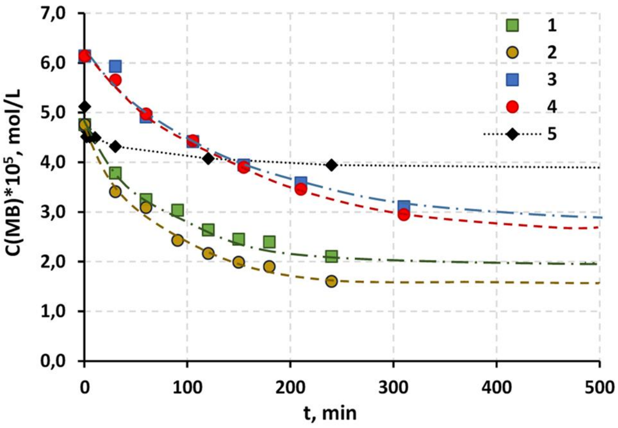


Fig. 5. Kinetic curves of MB extraction: within a Fenton system – 1 – TGM-3/ $CoFe_2O_4$/NaDS; 2 – TGM-3/$CoFe_2O_4$/RL; 5 – TGM-3/ $CoFe_2O_4$; adsorption – 3 – TGM-3/ $CoFe_2O_4$/NaDS; 4 – TGM-3/$CoFe_2O_4$/RL

The influence of the oxidation process on the extraction rate of MB dye from the solution is noticeable at the initial stage of the process (up to 3 h, Fig. 5), where it is 1.3–1.5 times higher than the MB adsorption process carried out under the same conditions. At this stage, the influence of the nature of the surfactant introduced during the synthesis of the ferrite-polymer composite is also clearly visible. Thus, for the TGM-3/$CoFe_2O_4$/RL sample, the oxidation process rate is 20 % higher than for TGM-3/$CoFe_2O_4$/NaDS. It can be concluded (Fig. 5) that increasing the porosity of the polymer matrix through the introduction of natural origin surfactants (rhamnolipids)[20–23] enhances the diffusion of dye molecules to catalytic centers, thereby increasing the oxidation rate.

As the process continues, the rate of dye extraction within a Fenton system slows down and equals the rate of pure adsorption. This slowdown may be related to the probable blocking of the catalytic centers by the products of incomplete MB oxidation, and after blocking most catalytic centers, the extraction of dye from the solution occurs only due to its adsorption on the composite surface.

It should also be noted that the introduction of $CoFe_2O_4$ nanoparticles into a polymer matrix of triethylene glycol dimethacrylate (TGM-3) allows obtaining a material with good magnetic properties.[8, 14] Such films can be easily removed from the reaction medium to regenerate and simplify the water purification process from organic pollutants, as they do not require an additional filtration stage, typical of classical homogeneous and heterogeneous Fenton systems. All this, together with simplicity, environmental friendliness, and the ability to easily create materials in desired shapes, makes this technology promising for water resource restoration.

4. Conclusions

Experimental studies have shown that the introduction of 5 wt. % surfactant into the photoinitiated polymerization process of ferrite-filled polymer composites based on triethylene glycol dimethacrylate (TGM-3) and cobalt ferrite nanoparticles ($CoFe_2O_4$) allows the production of a porous material with nanoparticles evenly distributed within the polymer matrix volume. The composites TGM-3–$CoFe_2O_4$ produced with the addition of surfactants are characterized by good adsorption and catalytic properties, as evidenced by the high degree of MB extraction from the solution (up to 94 %) and the introduction of natural surfactants improves the adsorption efficiency by 4–5 % and accelerates the rate of MB oxidation, especially at the initial stage of the process. The resulting films based on a ferrite-polymer composite with magnetic properties that can be easily removed from the reaction medium for regeneration are characterized by a simple and uncomplicated technological process for manufacturing materials in a given shape, which makes them promising for water resource restoration processes.

References

[1] Ilyas, R. A.; Sapuan, S. M.; Asyraf, M. R. M.; Dayana D. A. Z. N.; Amelia, J. J. N.; Rani, M. S. A.; Norrrahim, M. N. F.; Nurazzi, N. M.; Aisyah, H. A.; Sharma, S.; *et al.* Polymer Composites Filled with Metal Derivatives: A Review of Flame Retardants. *Polymers.* **2021**, *13*, 1701. https://doi.org/10.3390/polym13111701

[2] Skorokhoda, V.; Semenyuk, N.; Dudok, G.; Kysil, H. Silver-Containing Osteoplastic Nanocomposites Based on Polyvinylpyrrolidone Copolymers. *Voprosy Khimii i Khimicheskoi Tekhnologii* **2022**, *3*, 67–73. https://doi.org/10.32434/0321-4095-2022-142-3-67-73

[3] Dantas de Oliveira, A., Augusto Gonçalves Beatrice, C. Polymer Nanocomposites with Different Types of Nanofiller. In *Nanocomposites – Recent Evolutions*; Sivasankaran S, Ed.; IntechOpen, 2019. Available from: http://dx.doi.org/10.5772/intechopen.81329

[4] Dudok, G.; Semenyuk, N.; Kysil, K.; Ilkiv, I.; Skorokhoda, V. Regularities of Obtaining Silver Nanoparticles in the Presence of Polyvinylpyrrolidone. Proceedings of the 2021 IEEE 11th International Conference "Nanomaterials: Applications and Properties", Odesa, Ukraine, September 05–11, **2021**, NAP 2021, 1–4. https://doi.org/10.1109/NAP51885.2021.9568511

[5] Mamunya, Ye. P.; Davydenko, V.; Pissis. P.; Lebedev, E. V. Electrical and Thermal Conductivity of Polymers Filled with Metal Powders. *Eur. Polym. J.* **2002**, *38*, 1887–1897. http://doi.org/10.1016/S0014-3057(02)00064-2

[6] Hou, Y. H.; Zhao, Y. J.; Liu, Z. W.; Yu, H. Y.; Zhong, X. C.; Qiu, W. Q.; Zeng, D. C.; Wen, L. S. Structural, Electronic and Magnetic Properties of Partially Inverse Spinel $CoFe_2O_4$: A First-Principles Study. *J. Phys. D: Applied Physics.* **2010**, *43*, 445003. http://doi.org/10.1088/0022-3727/43/44/445003

[7] Medvedevskikh, Yu.; Makido, O.; Khovanets', G.; Karpenko, O.; Pokynbroda, T.; Yevchuk, I. Investigation of the Adsorption Properties of a New Composite Catalyst for the Fenton System. *Chem. Chem. Technol.* **2024**, *18*, 474–484. https://doi.org/10.23939/chcht18.04.474

[8] Makido, O.; Khovanets', G.; Kochubei, V.; Yevchuk, I. Nanostructured Magnetically Sensitive Catalysts for the Fenton System: Obtaining, Research, Application. *Chem. Chem. Technol.* **2022,** *16*, 227–236. https://doi.org/10.23939/chcht16.02.227

[9] Andrzejewska, E. Photopolymerization Kinetics of Multifunctional Monomers. *Progr. Polym. Sci.* **2001**, *26*, 605–665. https://doi.org/10.1016/S0079-6700(01)00004-1

[10] Wang, Z.; Cui, F.; Sui, Y.; Yan, J. Radical Chemistry in Polymer Science: An Overview and Recent Advances. *Beilstein J. Org. Chem.* **2023**, *19*, 1580–1603. https://doi.org/10.3762/bjoc.19.116

[11] Semeniuk, I.; Kochubei, V.; Skorokhoda, V.; Midyana, H.; Karpenko, E.; Pokynbroda, T.; Melnyk, V. Biosynthesis Products of Pseudomonas sp. PS-17 Strain Metabolites. 1. Obtaining and Thermal Characteristics. *Chem. Chem. Technol.* **2020**, *14*, 26–31. https://doi.org/10.23939/chcht14.01.026

[12] Prokopalo, A. M.; Maziar, I. V.; Zayarnyuk, N. Z.; Krychkovska, A. M.; Karpenko, O. V.; Lubenets, V. I. Combined Solutions Using Biosurfactants Based on Water-Insolute Biologically Active Compounds. *Chem. Techn. Appl. Subst.* **2022**, *5*, 96–101. https://doi.org/10.23939/ctas2022.01.096

[13] Makido, O.; Khovanets', G.; Khavunko, O. Synthesis of Catalysts Based on Magnetic Particles $CoFe_2O_4$. *Proc. Shevchenko Sci. Soc. Chem. Sci.* **2021**, *LXVI*, 90–97. http://doi.org/10.37827/ntsh.chem.2021.66.090

[14] Thakur, P.; Thakur, P.; Kishore, K.; Singh, M.; Sharma, S.; Sharma, P.; Sharma, P.; Lal, M. Structural, Morphological, and Magnetic Properties of $CoFe_2O_4$ Nano-Ferrites Synthesized *via* Co-Precipitation Route. *Mat. Today: Proc.* **2023**. https://doi.org/10.1016/j.matpr.2022.12.233

[15] Khovanets', G. I.; Medvedevskikh, Yu. G.; Yevchuk, I. Yu. Kinetics of Photoinitiated Copolymerization of Bifunctional (meth) Acrylates Till High Conversion and Kinetic Model of the Processes. *Proc. Shevchenko Sci. Soc. Chem. Biochem.* **2010**, *25*, 172–182.

[16] Makido, O. Yu.; Medvedevskikh, Yu. G.; Khovanets′, G. I. 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.* **2020**, *6*, 91–98. http://doi.org/10.32434/0321-4095-2020-133-6-91-98

[17] Ouyang, X.; Huang, X.; Pan, Q.; Zuo, C.; Huang, C.; Yang, X.; Zhao, Y. Synthesis and Characterization of Triethylene Glycol Dimethacrylate Nanocapsules Used in a Self-Healing Bonding Resin. *J. Dent.* **2011**, *39*, 825–833. https://doi.org/10.1016/j.jdent.2011.09.001

[18] Wang, H.; Huang, J.; Ding, L.; Li, D. A Facile Synthesis of Monodisperse $CoFe_2O_4/SiO_2$ Nanoparticles. *Appl. Sur. Sci.* **2011**, *257*, 7107–7112. https://doi.org/10.1016/j.apsusc.2011.03.063

[19] Habibi, M. H.; Parhizkar, H. Ja. FTIR and UV–Vis Diffuse Reflectance Spectroscopy Studies of the Wet Chemical (WC) Route Synthesized Nano-Structure $CoFe_2O_4$ from $CoCl_2$ and $FeCl_3$. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **2014**, *127*, 102–106. https://doi.org/10.1016/j.saa.2014.02.090

[20] Klima, K. M.; Koh, C. H.; Brouwers, H. J. H.; Yu, Qingliang. Synergistic Effect of Surfactants in Porous Geopolymer: Tailoring Pore Size and Pore Connectivity. *Cem. Concr. Compos.* **2022**, *134*, 104774. https://doi.org/10.1016/j.cemconcomp.2022.104774

[21] Qian, G.; Lei, D.; Tong, W.; Guan, X.; Jian K.; Ming, X. Effect of Surfactant on Morphology and Pore Size of Polysulfone Membrane. J. *Polym. Res.* **2018**, *25*, 21. https://doi.org/10.1007/s10965-017-1410-5

[22] Kong, X.; Shu, G.; Lu, X.; Wu, Ch.; Gai, Y. Manipulating Membrane Surface Porosity *via* Deep Insight into Surfactants During Nonsolvent Induced Phase Separation. *J. Membr. Sci.* **2020**, *611*, 118358. https://doi.org/10.1016/j.memsci.2020.118358

[23] Polak, D.; Sułkowska, J.; Szwast M. The Influence of Surfactant Pluronic P123 Addition on the Mixed Matrix Membrane PEBAX® 2533 – ZIF-8 Separation Properties. *Desalin. Water Treat.* **2021**, *214*, 64–73. https://doi.org/10.5004/dwt.2021.26647

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ФЕРИТ-НАПОВНЕНІ ПОЛІМЕРНІ КОМПОЗИТИ ЯК КАТАЛІЗАТОРИ ДЛЯ СИСТЕМИ ФЕНТОНА

Анотація. *Досліджено вплив наповнювачів: наночастинок фериту кобальту ($CoFe_2O_4$) та різної природи ПАР на структуру одержаних ферит-наповнених полімерних композитів і їхні адсорбційні та каталітичні властивості щодо органічних барвників у системі Фентона. Методом фотоініційованої вільнорадикальної полімеризації in situ отримано ферит-полімерні композити на основі полімерної матриці триетиленглікольдиметакрилату (ТГМ-3) та попередньо синтезованих наночастинок фериту кобальту ($CoFe_2O_4$), які мають виражені магнітні властивості. Для рівномірного розподілу наночастинок $CoFe_2O_4$ у полімерній матриці та збільшення її пористості під час синтезу використовували ПАР різної природи – синтетичний (додецилсульфат натрію) та натуральний (рамноліпіди). Синтезовані ферит-наповнені полімерні композити прозорі, міцні, еластичні, однорідні за структурою. Досліджено адсорбційні й каталітичні властивості одержаних плівок на основі полімерного композиту ТГМ-3–$CoFe_2O_4$ у водному розчині органічного барвника метиленового синього (МС) як модельного забруднювача стічних вод. Визначено, що композити, отримані із додаванням ПАР, характеризуються хорошими адсорбційними та каталітичними властивостями, про що свідчить високий ступінь вилучення МС із розчину (до 94 %). Використання ПАР природного походження (рамноліпіди) дає змогу підвищити ефективність адсорбції на 4–5 %, а каталітичного окиснення – на 20 %. Крім адсорбційних і каталітичних властивостей, ці плівки магнітосепарабельні, що дає змогу легко вилучати їх із середовища та робить перспективними для процесів відновлення водних ресурсів.*

Ключові слова: *ферит-наповнені полімерні композити, фотоініційована полімеризація, триетиленглікольдиметакрилат, наночастинки фериту кобальту, система Фентона, адсорбція.*