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*Yuriy Sukhatskiy, Tetiana Dmytrenko, Mariana Shepida, Martyn Sozanskyi, Zenovii Znak***DEGRADATION OF DIAZINE DYE SAFRANIN T USING POTASSIUM PERSULFATE ACTIVATED BY ULTRASONIC TREATMENT AND $MnFe_2O_4$ SPINEL NANOPARTICLES**

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An advanced oxidation process of ultrasound/ $MnFe_2O_4/K_2S_2O_8$ was developed for the degradation of diazine dye safranin T, according to which potassium persulfate was co-activated by ultrasonic (US) cavitation and $MnFe_2O_4$ spinel nanoparticles synthesized via co-precipitation in the ultrasonic field. A synthesis product annealed at a temperature of 400°C, with an average size of $MnFe_2O_4$ crystallites of about 7 nm, was used as a catalyst for the decomposition of potassium persulfate. Based on the results of experimental studies on the influence of various factors on the degree and rate constant of safranin T oxidative degradation, as well as considering energy and resource-saving principles, the rational conditions of oxidative degradation were determined as follows: the reaction medium temperature of 60°C, the molar ratio of safranin T: $K_2S_2O_8$ =1:100, the catalyst loading of 0.1 g/l, and the specific power of the ultrasonic cavitation treatment of 51.0 W/l. It was established that under such conditions the oxidative degradation degree of safranin T was equal to 98.3%, and the rate constant was $1.5 \cdot 10^{-3} \text{ s}^{-1}$. The changes in the UV-Vis spectra of safranin T, namely a decrease in the intensity of absorption bands, both in the visible (at a wavelength of 520 nm) and in the UV (at a wavelength of 275 nm) regions of the spectrum, confirmed the degradation of safranin T. In addition, the absence of the appearance of new peaks in the visible and UV regions of the spectrum indicated mineralization of the dye.

Keywords: diazine dye, safranin T, advanced oxidation process, potassium persulfate, ultrasound, $MnFe_2O_4$ spinel nanoparticles, catalyst, degradation.

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Introduction

Safranin T (Basic red 2) is a cationic diazine fluorescent dye used in the textile, food, pulp-paper, pharmaceutical, and cosmetics industries [1,2]. Among the known applications of safranin T are histological and cytological studies and photopolymerization in visible light [3]. It is harmful to human health, can cause conjunctivitis and dermatitis, and also leads to eutrophication pollution of water bodies [1]. Most often, adsorption methods are used to remove safranin T from water. Their advantages include simplicity of design and ease of operation. For example, Elsherif et al. [4] used activated carbon obtained from orange peels as an adsorbent for safranin T, and Salem et al. [2] used magnetite/Ag nanocomposite, which was

suitable for repeated (5-fold) use. The disadvantage of adsorption methods is the removal of the pollutant (dye) from water without its mineralization and, accordingly, the need to dispose of used sorbents.

Advanced oxidation processes are a potentially effective route for the complete degradation (mineralization) of bioresistant organic pollutants, including dyes [1,3,5–9]. The efficient degradation of safranin T can be achieved using the photocatalysis technique [3,9] or the photo-Fenton process [1,8].

It was found that by using a UV-radiation/ TiO_2/IO_4^- system for 5 min at pH 10, temperature of 298 K, IO_4^- concentration of 0.15 mM, TiO_2 loading of 0.4 g/L, and specific UV radiation power of $15 \text{ mW} \cdot \text{cm}^{-2}$ (with a wavelength of 365 nm), the

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Degradation of diazine dye safranin T using potassium persulfate activated by ultrasonic treatment and $MnFe_2O_4$ spinel nanoparticles

degradation degree of safranin T (with concentration of 10 mg/L) was determined to be 97.8% [3]. Jadhav et al. [9] synthesized the Fe₂O₃-SnO₂ nanocomposite using the wet impregnation method. This nanocomposite was employed for the photocatalytic degradation of safranin T under the influence of natural sunlight.

The heterogeneous photo-Fenton process for the degradation of safranin T is based on iron-containing materials, such as the nanomagnetite/copper oxide/potassium carrageenan nanocomposite (MKCO) [1] and iron-impregnated peanut shell ash [8]. Application of a heterogeneous photo-Fenton process (UV-radiation/MKCO/H₂O₂) for 10 min allowed for the achievement of a degradation degree of 93% for safranin T (at a concentration of 10 mg/L) [1]. The research conditions were as follows: pH 3; the temperature 21°C; the wavelength of UV radiation 254 nm; the H₂O₂ concentration 50 mM; and the catalyst dosage 1 g/L. The main reactive species in the Fenton process and its modifications are hydroxyl radicals, which possess an oxidation potential of 2.8 eV [1,10,11].

Quite powerful oxidizing agents (with a redox potential ranging from -2.5 to 3.1 eV) of non-selective action are sulfate anion radicals (SO₄^{•-}), which can effectively oxidize organic pollutants in aqueous mediums, resulting in the formation of CO₂ and H₂O. Sulfate anion radicals are generated as a result of the activation of persulfates. Various methods of persulfate activation have been discovered [12], including ultraviolet, ultrasonic, thermal or microwave radiation; electrochemical activation; activation with carbon materials such as activated carbon, biochar, carbon nanotubes, graphene, etc.; organic compounds such as glucose, sucrose, ascorbic acid, 1,4-benzoquinone, metal-organic framework structures based on ferrocene, surfactants, etc.; transition metals and their compounds, particularly spinels; and activation in an alkaline medium.

This work was aimed at studying the efficiency and intensity of degradation of the diazine dye safranin T using potassium persulfate co-activated by ultrasound (US) and MnFe₂O₄ spinel nanoparticles.

Experimental

The synthesis of MnFe₂O₄ spinel nanoparticles was carried out using the co-precipitation method in an ultrasonic field. Manganese (II) chloride tetrahydrate (MnCl₂·4H₂O) and iron (III) chloride hexahydrate (FeCl₃·6H₂O) were used as precursors for the synthesis. MnCl₂·4H₂O and FeCl₃·6H₂O, at a molar ratio of 1:2, were dissolved in 300 ml of distilled water with constant stirring. The formed solution was heated to a temperature of 70°C in a water bath. Then, the US vibration generator was synchronously turned on, and

the precipitating agent (a NaOH aqueous solution with a molar concentration of 2 M) was slowly added dropwise to the solution with constant stirring until pH 11 was reached. To control the pH of the medium, an ADWA AD1200 ATC pH-meter with a combined AD1131B glass electrode and an AD7662 temperature compensator were used. The action of acoustic vibrations in the US range and the addition of NaOH drops were stopped when pH 11 was reached. Mixing of the resulting suspension with dispersed brown particles was carried out for 2 h at a temperature of 60°C. This ensured complete crystallization and growth of nano-sized particles.

To efficiently remove impurities from the synthesized materials, they were washed three times with deionized water and ethanol until a neutral pH was reached. Centrifugation (duration of 5 min and frequency of 5000 rpm) was used to separate the solid phase from the liquid. The separated solid phase was dried at a temperature of 100°C for 12 h, and then annealed in an air atmosphere at a temperature of 200–800°C for 5 h. In this case, the heating rate of the material was 5°C/min. During the synthesis of MnFe₂O₄ spinel nanoparticles, the generator of US vibrations with a frequency of 20 kHz and a specific power of US treatment of the reaction medium of 200 W/l was a magnetostrictive emitter (Bandelin Sonopuls HD 2200.2).

The phase composition of the synthesized materials, the average crystallite size, and the crystal lattice parameters of the synthesis products were determined based on the results obtained by X-ray diffraction using an AERIS Research diffractometer (Malvern PANalytical) with CuK_α-radiation. To calculate the average crystallite size (*D*, nm), the Debye-Scherrer equation was used [13]:

$$D = \frac{k\lambda}{\beta \cos\theta}, \quad (1)$$

where *k* is the Scherrer constant, which is equal to 0.9 for spherical particles; λ is the wavelength of X-ray radiation ($\lambda=1.5406 \text{ \AA}$) [14]; β is the full width at half maximum of reflection peaks, rad; and θ is the diffraction angle, rad.

The morphology (shape and size) of the synthesized particles was studied by scanning electron microscopy (SEM; ZEISS EVO 40XVP microscope).

To degrade the diazine dye safranin T (C₂₀H₁₉ClN₄), an advanced oxidation process of US/MnFe₂O₄/K₂S₂O₈ was developed, according to which potassium persulfate was co-activated by US cavitation and MnFe₂O₄ spinel nanoparticles. The study of safranin T degradation was performed in a

thermostated glass reactor with a volume of 300 ml. The filling factor of the reactor with an aqueous dye solution was 66.7%. The concentration of safranin T in an aqueous solution was 20 mg/L or 57.06 μ M. The oxidation process was initiated by adding potassium persulfate and MnFe_2O_4 spinel nanoparticles to the dye solution. The MnFe_2O_4 spinel nanoparticles acted as the catalyst for the decomposition of persulfates. At the same time as adding the oxidizing agent and spinel to the dye solution, a magnetostrictive type US emitter (US frequency of 22 kHz), «Ultrasonic Disintegrator UD-20», was turned on. This device is equipped with a panel for adjusting the specific power of the reaction medium treatment. Adjustment of the pH of the reaction medium (up to pH 3) was provided by an aqueous solution of HCl ($C_M=0.1$ M). During the studies, the influence of the following parameters on the efficiency and intensity of oxidative degradation of safranin T was studied: temperature, molar ratio of safranin T to potassium persulfate, catalyst loading, and the specific power of US treatment. The following ranges of parameter changes were considered during the study: temperature of 20–60°C, molar ratio of safranin T to potassium persulfate of (1:25)–(1:100), catalyst loading of 0.1–1 g/L, and the specific power of US cavitation treatment of 40.0–62.5 W/l.

The degradation efficiency of safranin T (using the advanced US/ MnFe_2O_4 / $\text{K}_2\text{S}_2\text{O}_8$ oxidation process) was evaluated by the oxidative degradation degree. The process intensity was assessed by the oxidative degradation rate constant. The oxidative degradation degree of safranin T (x , %) was calculated according to formula (2):

$$x = \frac{C_0 - C}{C_0}, \quad (2)$$

where C_0 is the initial concentration of safranin T in its aqueous solution, mol/l; C is the concentration of safranin T in its aqueous solution at the moment of time τ , mol/l.

Periodically, samples of the reaction medium were taken and centrifuged (at 5000 rpm for 5 minutes) to separate spinel particles. The dye content of the samples was then analyzed using a UV-Vis spectrophotometer (UV-3100PC, Shanghai Mapada Instruments Co., Ltd.) in the wavelength range of 190 to 1100 nm (the maximum absorption for safranin T was observed at a wavelength of 520 nm). The calculation of the safranin T concentration in the aqueous solution was based on calibration curves that were previously constructed.

Results and discussion

Diffraction patterns of the materials prepared at different calcination temperatures of the product synthesized through co-precipitation in a US field are shown in Fig. 1. The Bragg diffraction peaks at calcination temperatures of 200 and 400°C are in good agreement with the MnFe_2O_4 spinel model with space group Fd-3m (reference JCPDS No. 00-022-1086) [13]. The absence of peaks characteristic of impurities indicates the purity of the MnFe_2O_4 spinel crystals. As the calcination temperature increased to 600°C, peaks of Fe_2O_3 and Mn_2O_3 appeared on the diffractogram, and peaks of Fe_2O_3 and Mn_3O_4 ($\text{Mn}_2\text{O}_3 \cdot \text{MnO}$) emerged at 800°C. This was caused by the thermal decomposition of the MnFe_2O_4 spinel into individual oxides. This effect of calcination temperature on the phase composition of the synthesized products does not contradict with the research results obtained by Junlabhut et al. [15].

The qualitative and quantitative compositions of the phases, the crystal lattice parameters, and the average crystallite sizes of the samples prepared at different calcination temperatures of the product synthesized by co-precipitation in a US field are provided in Table 1.

As the calcination temperature increased from 200 to 400°C, the average size of MnFe_2O_4 crystallites decreased from 11 to 7 nm (Table 1). The enlargement of particles, when the calcination temperature of the synthesized product exceeds 400°C, is attributed to the magnetic properties of the compounds (Fe_2O_3 , Mn_2O_3 , and Mn_3O_4) resulting from the thermal decomposition of the MnFe_2O_4 spinel.

Considering the above, a product with an average crystallite size of MnFe_2O_4 of about 7 nm was used as a catalyst in the studies on the oxidative degradation of safranin T. The objective was to increase the specific surface area of the catalyst and, consequently, enhance the efficiency of the heterogeneous activation of potassium persulfate during the decomposition of persulfates.

Based on the analysis of SEM images (Fig. 2), it was observed that MnFe_2O_4 forms agglomerates of quasi-spherical particles ranging in size from 5 to 20 nm. This observation is consistent with the results of calculations of the average crystallite size using the Debye-Scherrer equation. The agglomeration is a consequence of the interaction between magnetic particles and the occurrence of van der Waals forces between nanoparticles.

The main reactive species that are formed as a result of the co-activation of aqueous persulfates

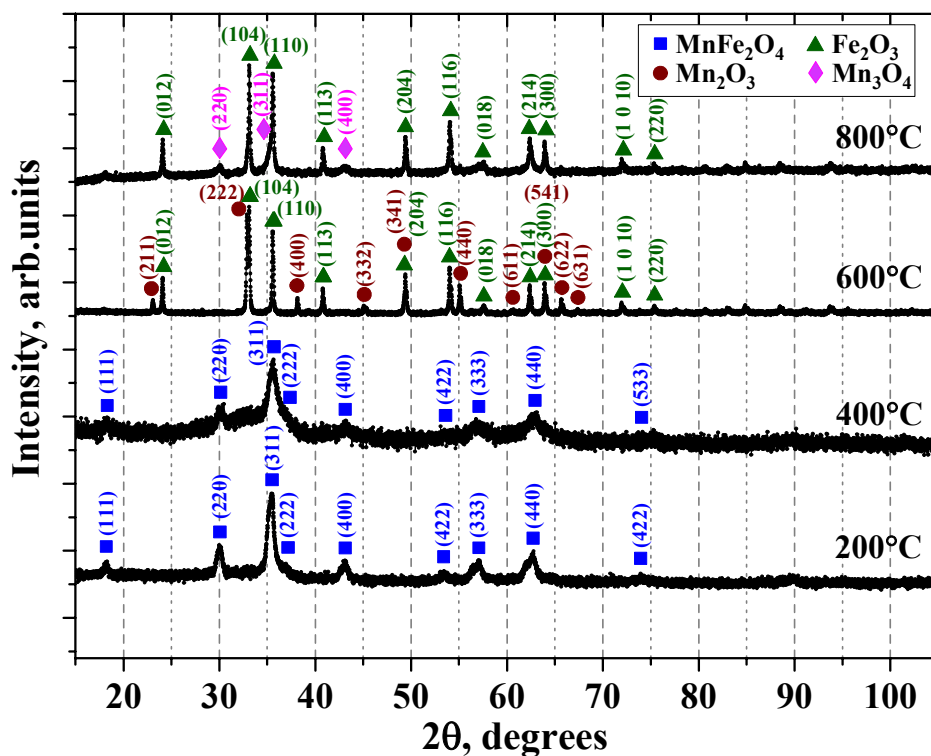


Fig. 1. Diffraction patterns of materials obtained at different calcination temperatures of the product synthesized by co-precipitation in a US field

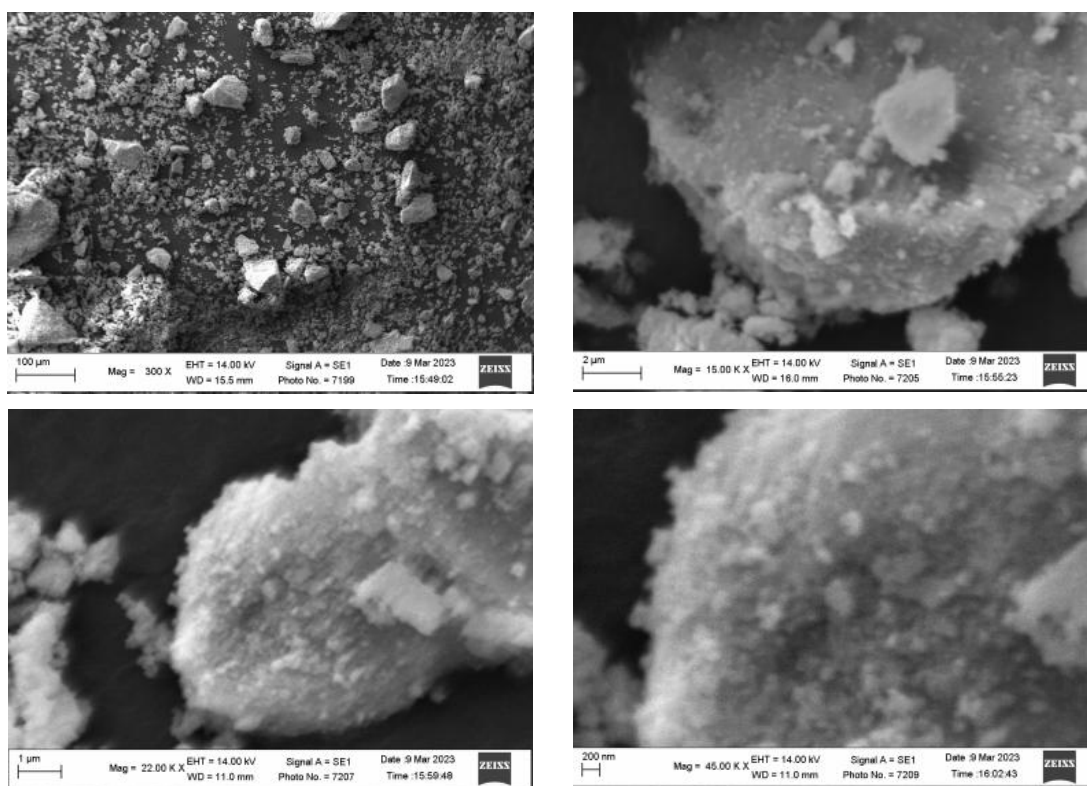


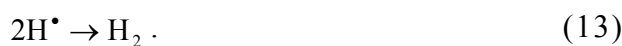
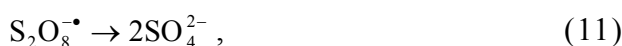
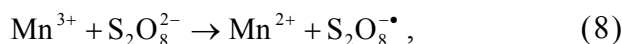
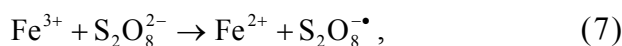
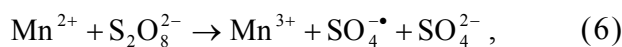
Fig. 2. SEM images of MnFe₂O₄ spinel nanoparticles (calcination temperature 400°C)

Table 1

Structural and phase characteristics of samples obtained at different calcination temperatures of the product synthesized by co-precipitation in a US field

Calcination temperature, °C	Phase	Mole fraction of the phase, %	Lattice parameters, Å	2θ, degrees	cosθ	β, rad	D, nm
200	MnFe ₂ O ₄	100.00	a=8.391(1)	35.453	0.95258	0.013430	11
400	MnFe ₂ O ₄	100.00	a=8.347(3)	35.643	0.95207	0.020504	7
600	Fe ₂ O ₃	64.08	a=5.0348(1); c=13.7275(3)	33.194	0.95839	0.003070	47
	Mn ₂ O ₃	35.92	a=9.4086(2)	32.952	0.95898	0.003327	44
800	Fe ₂ O ₃	77.63	a=5.0342(1); c=13.7266(4)	33.197	0.95836	0.003208	45
	Mn ₃ O ₄	22.37	a=8.390(3)	35.458	0.95256	0.018653	8

solutions by US and MnFe₂O₄ spinel nanoparticles are sulfate anion radicals (SO₄^{•-}) and hydroxyl radicals (•OH). The proposed mechanism of the co-activation of aqueous persulfates solutions by US and MnFe₂O₄ spinel nanoparticles is described by the following reaction equations [12]:



Under the US action, persulfate ions (S₂O₈²⁻) decompose, forming sulfate anion radicals (Eq. (3)), and water decomposes, forming hydrogen radicals and hydroxyl radicals (Eq. (4)). Water dissociation also occurs (Eq. (5)). Mn²⁺ (Eq. (6)) and Fe²⁺ (Eq. (9)) ions catalyze the decomposition of persulfate ions, which results in the formation of sulfate anion radicals. In this case, Mn²⁺ ions are oxidized to Mn³⁺, and Fe²⁺ ions are oxidized to Fe³⁺. Sulfate anion radicals

react with hydroxyl groups (Eq. (10)), resulting in the formation of hydroxyl radicals and sulfate ions. The regeneration of Mn²⁺ and Fe²⁺ is described by equations (7) and (8), respectively. Thermodynamically unstable persulfate anion radicals [12] formed during regeneration decompose, leading to the formation of sulfate ions (Eq. (11)). Hydroxyl radicals (Eq. (12)) and hydrogen radicals (Eq. (13)) recombine, resulting in the formation of hydrogen peroxide and hydrogen, respectively.

The effect of the temperature of the reaction medium on the degradation of the diazine dye safranin T using potassium persulfate co-activated with US and MnFe₂O₄ spinel nanoparticles (advanced oxidation process of US/MnFe₂O₄/K₂S₂O₈) is shown in Fig. 3.

The achieved degradation degree of safranin T in the US/MnFe₂O₄/K₂S₂O₈ developed advanced oxidation process for a duration of 3600 s is 64.2%, 74.0% and 92.7% at a temperature of 20°C, 40°C and 60°C, respectively (Fig. 3a). Increasing the treatment duration to 7200 s resulted in an increase in the oxidative degradation degree as follows: by 13.5% (from 64.2% to 77.7%), by 12.6% (from 74.0% to 86.6%) and by 5.6% (from 92.7% to 98.3%) at a temperature of 20°C, 40°C and 60°C, respectively. Thus, thermal energy was another (the third) activator of persulfates [12], along with US and MnFe₂O₄ spinel nanoparticles.

The results presented in Fig. 3b indicate that the oxidative degradation of the diazine dye safranin T when using the US/MnFe₂O₄/K₂S₂O₈ process proceeds as a pseudo-first-order reaction. It was found that with an increase in the temperature of the reaction medium from 20 to 60°C, the oxidative degradation rate constant of safranin T was increased by 2.5 times, from 0.6·10⁻³ s⁻¹ to 1.5·10⁻³ s⁻¹.

Based on the dependence in the Arrhenius coordinates shown in Fig. 4, the values of the effective activation energy (E_a) for the oxidative degradation of safranin T when using the US/MnFe₂O₄/K₂S₂O₈

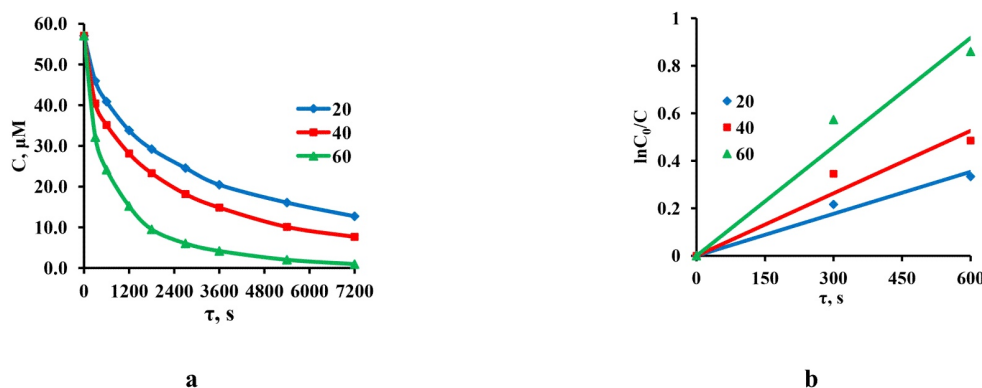


Fig. 3. Effect of temperature (in °C) of the reaction medium on (a) – degradation of diazine dye safranin T and (b) – pseudo-first-order kinetic plots of safranin T dye degradation ($V=200\pm 1$ ml; $C_0(\text{safranin T})=57.06$ μM ; pH 3; the molar ratio of safranin T: $\text{K}_2\text{S}_2\text{O}_8=1:100$; the catalyst loading (MnFe_2O_4 nanoparticles) 0.1 g/L; and the specific power of US cavitation treatment 51.0 W/l)

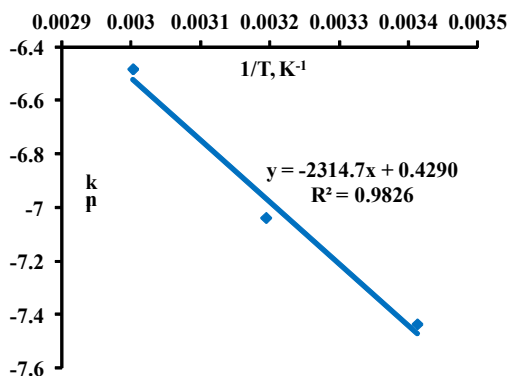


Fig. 4. Arrhenius plots for oxidative degradation of safranin T when using the US/ $\text{MnFe}_2\text{O}_4/\text{K}_2\text{S}_2\text{O}_8$ process

process were calculated as follows:

$$E_a = -Rt\text{g}\alpha = -8.314 \cdot (-2314.7) \approx 19244 \text{ J/mol}, \quad (14)$$

where R is the universal gas constant (8.314 J/(mol·K)); $\text{tg}\alpha$ is the slope of the straight line plotted in the coordinates $\ln k$ vs. $1/T$.

With an increase in the molar ratio of safranin T: $\text{K}_2\text{S}_2\text{O}_8$ from 1:25 to 1:100 using the advanced oxidation process of US/ $\text{MnFe}_2\text{O}_4/\text{K}_2\text{S}_2\text{O}_8$ for 3600 s, the oxidative degradation degree of safranin T increased by 19.7% (from 73.0% to 92.7%) (Fig. 5a). This was due to a higher amount of sulfate and hydroxyl radicals formed as a result of activating a higher dose of potassium persulfate in the aqueous medium. Increasing the treatment duration to 7200 s resulted in an increase of the degradation degree by 15.0% (from 73.0% to 88.0%) and by 5.6% (from 92.7% to 98.3%) for the molar ratio of safranin T: $\text{K}_2\text{S}_2\text{O}_8=1:25$ and for the molar ratio of safranin

T: $\text{K}_2\text{S}_2\text{O}_8=1:100$, respectively.

In this case, the rate constant of safranin T oxidative degradation, similar to the effect of temperature (Fig. 3b), also increased by 2.5 times (Fig. 5b): from $0.6 \cdot 10^{-3} \text{ s}^{-1}$ (for the safranin T: $\text{K}_2\text{S}_2\text{O}_8$ molar ratio=1:25) to $1.5 \cdot 10^{-3} \text{ s}^{-1}$ (for the safranin T: $\text{K}_2\text{S}_2\text{O}_8$ molar ratio=1:100).

Increasing the catalyst loading (MnFe_2O_4 nanoparticles) from 0.1 to 1.0 g/l had practically no effect on the oxidative degradation degree of safranin T when using the US/ $\text{MnFe}_2\text{O}_4/\text{K}_2\text{S}_2\text{O}_8$ process for 7200 s (Table 2).

Table 2
Effect of catalyst loading (MnFe_2O_4 nanoparticles) on the degree (x) and rate constant (k) of safranin T oxidative degradation

Catalyst loading, g/l	x, %	k, s^{-1}
0.1	98.3	$1.5 \cdot 10^{-3}$
0.5	98.5	$1.9 \cdot 10^{-3}$
1.0	98.6	$2.1 \cdot 10^{-3}$

However, in this case, the oxidative degradation rate constant of safranin T increased by 40%: from $1.5 \cdot 10^{-3} \text{ s}^{-1}$ to $2.1 \cdot 10^{-3} \text{ s}^{-1}$. Considering the above, it is advisable to fix the catalyst content at 0.1 g/l in order to reduce the cost of water treatment from safranin T.

With an increase in the specific power of US treatment from 40.0 to 51.0 W/l, the oxidative degradation degree of safranin T when using the US/ $\text{MnFe}_2\text{O}_4/\text{K}_2\text{S}_2\text{O}_8$ process increased by 8.1% (from 90.2% to 98.3%) during the 7200 s duration (Table 3). It was related to the enhanced radical generation due to the collapse of a larger number of cavitation bubbles. A further increase in the specific

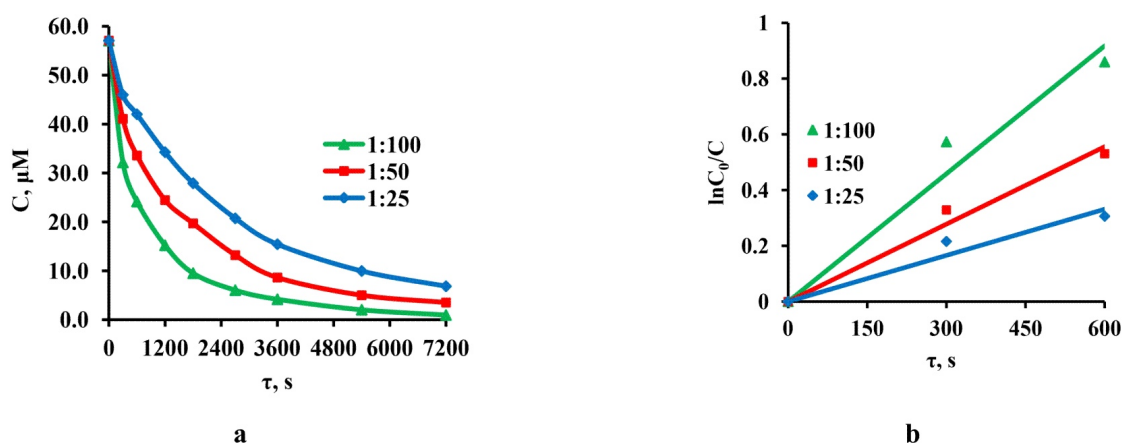


Fig. 5. Effect of the molar ratio of safranin T: $\text{K}_2\text{S}_2\text{O}_8$ on (a) – the degradation of the safranin T diazine dye and (b) – pseudo-first-order kinetic plots of safranin T dye degradation ($V=200\pm 1$ ml, $C_0(\text{safranin T})=57.06$ μM , pH 3, temperature 60°C , the catalyst loading (MnFe_2O_4 nanoparticles) 0.1 g/L, and the specific power of US cavitation treatment 51.0 W/l)

power of US treatment to 62.5 W/l had almost no effect on the degradation degree of safranin T, which increased only by 0.2% (reaching 98.5%). This was caused by the rapid generation of a large number of closely spaced cavitation bubbles, resulting in the merging of most of them. At the same time, the size of the bubbles increased while the probability of their collapse decreased. This phenomenon is called «choked cavitation». Similar results were obtained in studies on the effect of the specific power of cavitation treatment on the degradation degree of benzene [6]. However, it should be noted that with an increase in the specific power of US treatment, the oxidative degradation rate constant of safranin T also increased (Table 3). Thus, it is advisable to limit the specific power of US treatment to 51.0 W/l in order to reduce the energy consumption of the treatment process.

Table 3

Effect of specific power of US treatment on the degree (x) and rate constant (k) of oxidative degradation of safranin T

Specific power of US treatment, W/l	x , %	k , s^{-1}
40.0	90.2	$0.6 \cdot 10^{-3}$
51.0	98.3	$1.5 \cdot 10^{-3}$
62.5	98.5	$1.9 \cdot 10^{-3}$

Therefore, the rational conditions for the oxidative degradation of safranin T when using the US/ $\text{MnFe}_2\text{O}_4/\text{K}_2\text{S}_2\text{O}_8$ process, determined based on the results of experimental studies and in accordance with the principles of energy and resource efficiency, are as follows: the reaction medium temperature 60°C , the molar ratio of safranin T: $\text{K}_2\text{S}_2\text{O}_8=1:100$, the catalyst loading 0.1 g/l, and the specific power of US

cavitation treatment 51.0 W/l. Under these conditions, the oxidative degradation degree of safranin T was 98.3%, and the oxidative degradation rate constant was $1.5 \cdot 10^{-3} \text{ s}^{-1}$.

Figure 6 shows the UV-Vis spectra of the oxidative degradation of safranin T when using the US/ $\text{MnFe}_2\text{O}_4/\text{K}_2\text{S}_2\text{O}_8$ process. The initial aqueous solution of safranin T is characterized by two distinct bands. The first band belongs to the chromophoric group and is located in the visible region with maximum absorption at a wavelength of 520 nm. The second band corresponds to the aromatic (benzene) rings and is located in the UV region, with a maximum absorption at a wavelength of 275 nm.

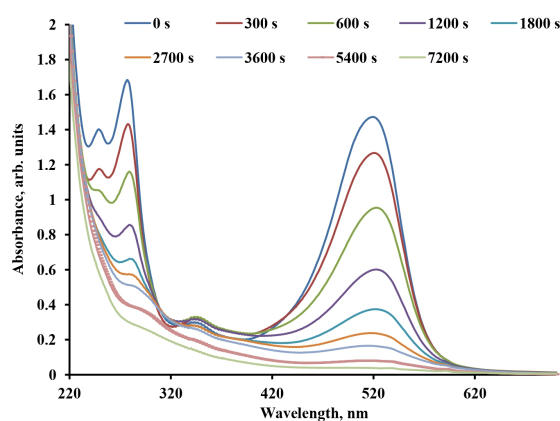


Fig. 6. UV-Vis spectra of safranin T oxidative degradation when using the US/ $\text{MnFe}_2\text{O}_4/\text{K}_2\text{S}_2\text{O}_8$ process ($V=200\pm 1$ ml, $C_0(\text{safranin T})=57.06$ μM , pH 3, the molar ratio of safranin T: $\text{K}_2\text{S}_2\text{O}_8=1:100$, temperature 60°C , the catalyst loading (MnFe_2O_4 nanoparticles) 0.1 g/L, and the specific power of US cavitation treatment 51.0 W/l)

The hypochromic effect (a decrease in absorption intensity both in the visible and UV regions) confirms the degradation of safranin T under the action of highly reactive intermediates with high oxidative potential, sulfate and hydroxyl radicals, which are formed as a result of the co-activation of potassium persulfate in the aqueous medium by US and MnFe₂O₄ spinel nanoparticles. The absence of the appearance of new peaks in the visible and UV regions indicates the mineralization of the dye into molecular compounds (water and carbon dioxide) and inorganic ions (for example, NO₃⁻ and Cl⁻).

Conclusions

For the degradation of the diazo dye safranin T, an advanced oxidation process of US/MnFe₂O₄/K₂S₂O₈ was developed, according to which potassium persulfate was co-activated by US cavitation and MnFe₂O₄ spinel nanoparticles synthesized via co-precipitation method in a US field. The synthesized product, annealed at a temperature of 400°C, with an average size of MnFe₂O₄ crystallites of about 7 nm, was used as a catalyst for the decomposition of potassium persulfate.

Based on experimental studies of the effect of various factors (reaction medium temperature, safranin T:potassium persulfate molar ratio, catalyst loading, and ultrasound power density) on the degree and the rate constant of safranin T oxidative degradation, and also taking into account energy and resource efficiency principles, the following rational conditions for oxidative degradation have been determined: the reaction medium temperature 60°C, the molar ratio of safranin T:K₂S₂O₈=1:100, the catalyst loading 0.1 g/l, and the specific power of the US cavitation treatment 51.0 W/l. Under these conditions, the oxidative degradation degree of safranin T was 98.3%, and the oxidative degradation rate constant was 1.5·10⁻³ s⁻¹.

The changes in the UV-Vis spectra of safranin T, specifically the decrease in the intensity of absorption bands both in the visible region (at a wavelength of 520 nm) and in the UV region (at a wavelength of 275 nm), confirmed the degradation of safranin T under the action of highly reactive intermediates with high oxidative potential, sulfate and hydroxyl radicals, which are formed as a result of the co-activation of potassium persulfate in the aqueous medium by US and MnFe₂O₄ spinel nanoparticles. At the same time, the absence of the appearance of new peaks in the visible and UV regions indicated the mineralization of the dye into molecular compounds (water and carbon dioxide) and inorganic ions (for example, NO₃⁻ and Cl⁻).

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ДЕГРАДАЦІЯ ДІАЗИНОВОГО БАРВНИКА САФРАНІНУ Т З ВИКОРИСТАННЯМ КАЛІЮ ПЕРСУЛЬФАТУ, АКТИВОВАНОГО УЛЬТРАЗВУКОМ І НАНОЧАСТИНКАМИ ШПІНЕЛІ MnFe₂O₄

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Для деградації діазинового барвника сафраніну Т було розроблено передовий процес окиснення ультразвук/MnFe₂O₄/K₂S₂O₈, відповідно до якого калію персульфат був сумісно активований ультразвуковою (УЗ) кавітацією і наночастинками шпінелі MnFe₂O₄, синтезованими методом співосадження в УЗ полі. Як каталізатор розкладу калію персульфату було використано продукт синтезу, відпалений за температури 400°C, із середнім розміром кристалітів MnFe₂O₄ приблизно 7 нм. На основі результатів експериментальних досліджень впливу низки факторів на ступінь і константу швидкості окиснювальної деградації сафраніну Т, а також з урахуванням принципів енерго- та ресурсоощадності, визначено раціональні умови окиснювальної деградації: температура реакційного середовища 60°C, мольне співвідношення сафранін Т:K₂S₂O₈=1:100, вміст каталізатора 0,1 г/дм³, питома потужність УЗ оброблення 51,0 Вт/дм³. Встановлено, що за таких умов ступінь окиснювальної деградації сафраніну Т дорівнював 98,3%, а константа швидкості 1,5·10⁻³ с⁻¹. За змінами UV-Vis спектрів сафраніну Т, а саме за зменшенням інтенсивності смуг поглинання, як у видимій (за довжини хвилі 520 нм), так і в УФ (за довжини хвилі 275 нм) ділянках спектра, підтверджено деградацію сафраніну Т. При цьому відсутність появи нових піків у видимій та УФ ділянках спектра вказує на мінералізацію барвника.

Ключові слова: діазиновий барвник, сафранін Т, передовий процес окиснення, калій персульфат, ультразвук, наночастинки шпінелі MnFe₂O₄, каталізатор, деградація.

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DEGRADATION OF DIAZINE DYE SAFRANIN T USING POTASSIUM PERSULFATE ACTIVATED BY ULTRASONIC TREATMENT AND $MnFe_2O_4$ SPINEL NANOPARTICLES

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An advanced oxidation process of ultrasound/ $MnFe_2O_4/K_2S_2O_8$ was developed for the degradation of diazine dye safranin T, according to which potassium persulfate was co-activated by ultrasonic (US) cavitation and $MnFe_2O_4$ spinel nanoparticles synthesized via co-precipitation in the ultrasonic field. A synthesis product annealed at a temperature of 400°C, with an average size of $MnFe_2O_4$ crystallites of about 7 nm, was used as a catalyst for the decomposition of potassium persulfate. Based on the results of experimental studies on the influence of various factors on the degree and rate constant of safranin T oxidative degradation, as well as considering energy and resource-saving principles, the rational conditions of oxidative degradation were determined as follows: the reaction medium temperature of 60°C, the molar ratio of safranin T: $K_2S_2O_8$ =1:100, the catalyst loading of 0.1 g/l, and the specific power of the ultrasonic cavitation treatment of 51.0 W/l. It was established that under such conditions the oxidative degradation degree of safranin T was equal to 98.3%, and the rate constant was $1.5 \cdot 10^{-3} s^{-1}$. The changes in the UV-Vis spectra of safranin T, namely a decrease in the intensity of absorption bands, both in the visible (at a wavelength of 520 nm) and in the UV (at a wavelength of 275 nm) regions of the spectrum, confirmed the degradation of safranin T. In addition, the absence of the appearance of new peaks in the visible and UV regions of the spectrum indicated mineralization of the dye.

Keywords: diazine dye; safranin T; advanced oxidation process; potassium persulfate; ultrasound; $MnFe_2O_4$ spinel nanoparticles; catalyst; degradation.

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