DOI: 10.46299/ISG.2025.MONO.TECH.3.3.1

3.1 Purification of aqueous media from Rhodamine B dye using a Fenton-like process

According to the Industry ARC (industry research council) report, the global production of Rhodamine B dyes during the period of 2022-2027 is estimated at $232.5 million [81]. Rhodamine B is a chemically stable, well-soluble in water xanthene dye (its solubility is 50 g/L at 25 °C), which is widely used in the chemical, pulp and paper, paint and textile (for dyeing leather, silk, wool, cotton, etc.) industries. Its long-term effect on the human body may be accompanied by potential carcinogenic and mutagenic effects [82]. The chemical stability of the structure of rhodamine B (Fig. 1) results in its low ability to degradation by biological methods.

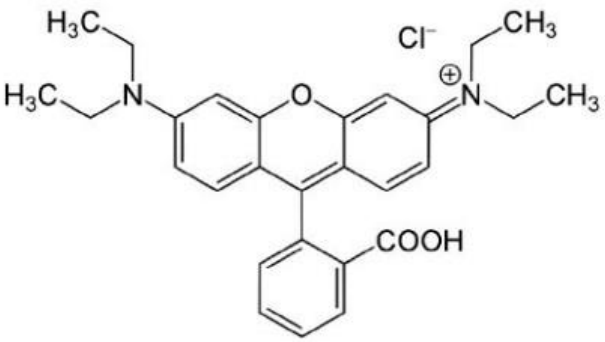

Figure 1. Chemical structure of Rhodamine B [made by the authors]

A feature of the development of modern water purification technologies is the use of advanced oxidation processes for the removal of harmful organic pollutants from aqueous media. Advanced oxidation processes belong to innovative and environmentally friendly methods of water purification from various harmful substances [83], including dyes. The essence of advanced oxidation processes lies in the generation of highly reactive intermediates, known as secondary oxidants (most commonly, reactive oxygen species), as a result of the activation (catalytic or in physical fields) of primary oxidants (hydrogen peroxide, ozone, persulfates, etc.). The

most common reactive oxygen species formed during the realization of advanced oxidation processes are hydroxyl radicals with an oxidation potential of 2.7 eV. It is these hydroxyl radicals that often play a key role in the degradation of organic pollutants in aqueous media.

The most well-known advanced oxidation process today is the Fenton process. For the degradation of Rhodamine B in aqueous media, both the traditional Fenton process and its various modifications, known as Fenton-like processes, are used.

So, the aim of this work was to review the applications of the Fenton process and Fenton-like processes for aqueous media purification from the Rhodamine B xanthene dye, as well as to conduct experimental investigation of the efficiency and intensity of oxidative degradation of this dye using the developed Fenton-like advanced oxidation process "ultrasonic cavitation/$MgMn_2O_4$ (nanoparticles)/$Na_2CO_3 \cdot 1.5H_2O_2$".

The Fenton reaction was discovered by H.J.H. Fenton in 1894. He used hydrogen peroxide activated by Fe^{2+} ions (iron(II) salts) to oxidize tartaric acid [84]. Usually, the mechanism of the Fenton process is described by the following reactions (Eqs. (1)-(9)) [83, 84]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH, \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+, \quad (2)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-, \quad (3)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^-, \quad (4)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+, \quad (5)$$

$$2{}^{\bullet}OH \rightarrow H_2O_2, \quad (6)$$

$${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O, \quad (7)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2, \quad (8)$$

$${}^{\bullet}OH + HO_2^{\bullet} \rightarrow H_2O + O_2. \quad (9)$$

Eq. (1) is considered the core of the Fenton process. According to this equation, hydrogen peroxide decomposes to form hydroxyl radicals ($^{\bullet}OH$) and oxidizes Fe^{2+}

ions to Fe^{3+}. The formed hydroxyl radicals actively attack molecules of organic pollutants, leading to their mineralization into CO_2, H_2O, and inorganic salts. The regeneration of Fe^{2+} ions by a cyclic mechanism is called a Fenton-like reaction (Eq. 2). In this case, Fe^{3+} ions are reduced to Fe^{2+} ions in an excess of hydrogen peroxide. This is accompanied by the formation of hydroperoxyl radicals ($HO_2^{\bullet}$), which are less reactive compared to hydroxyl radicals. Iron (in the form of Fe^{2+} and Fe^{3+} ions) acts as a catalyst for the decomposition of hydrogen peroxide.

Eqs. (2)-(5) are limiting, that is, they determine the overall rate of the Fenton process. Eqs. (6)-(9) correspond to termination reactions.

Both the traditional Fenton process [85-87] and its various modifications, known as Fenton-like processes [88-105], are used for the degradation of Rhodamine B in aqueous media.

Ollo et al. [85] reported that using the Fenton process for oxidative degradation of Rhodamine B (with a concentration of 5 mg/L in an aqueous medium) for 30 min led to achieving a degree of dye degradation of 99.4%. The experimental conditions were as follows: reaction temperature – 25 °C; pH = 2; initial concentration of Fe^{2+} ions – 8.4×10^{-4} mg/L; initial concentration of H_2O_2 – 3×10^{-3} M. It was found that the rate of Rhodamine B degradation decreased with an increase in the concentration of inorganic anions in the following order: $Cl^- < NO_3^- < SO_4^{2-} < PO_4^{3-}$.

Ghribi and Bagane [86] also reported about the high efficiency of Rhodamine B degradation in an acidic medium using the homogeneous Fenton process. Thus, at the reaction temperature of 25 °C, pH = 3, $C_0(Fe^{2+})$ = 1.04 mM, $C_0(H_2O_2)$ = 12.1 mM, during 120 min of purification, it was possible to achieve a degree of Rhodamine B decolorization of 97.6% (the initial dye concentration in the reaction medium was 30 mg/L).

In the case of applying the homogeneous Fenton reaction for the simultaneous degradation of Rhodamine B (initial concentration – 3.6 mg/L) and Acid Red 14 (initial concentration – 25 mg/L) binary solution for 30 min, the degradation degrees of Rhodamine B and Acid Red 14 of 81.6% and 80.2% were achieved, respectively [87].

The conditions of the experimental studies were as follows: temperature of the reaction medium – 25 °C; pH = 3.7; initial concentration of Fe^{2+} ions – 143.9 mg/L; initial concentration of H_2O_2 – 126.9 mg/L.

Gayathri et al. reported that solar Fenton and solar photocatalytic Fenton processes are effective for the complete removal of dye pollutants, and the presence of ZnO as the catalyst enhanced the Fenton-assisted mineralization of Rhodamine B under solar irradiation [88]. The mechanism of the solar photocatalytic Fenton process is shown in Fig. 2.

Figure 2. The proposed mechanism of the solar photocatalytic Fenton process [88] under the terms of the Creative Commons CC BY license.

A perspective technique for the mineralization of organic pollutants is the Fe^0-based Fenton process [89, 90]. Compared to the traditional Fenton process based on Fe^{2+} and H_2O_2, the Fe^0/H_2O_2 process has advantages such as low corrosion of Fe^0 powder, low hydrogen peroxide consumption, and a wide operating range of pH values. Hou et al. [89] reported that complete decolorization of an aqueous solution of Rhodamine B (initial dye concentration – 0.1 mM) and a 69% reduction in total organic

carbon (TOC) were achieved using the Fe^0/H_2O_2 process for 30 min. The experimental conditions were as follows: temperature of the reaction medium – 25 °C; pH = 4.0; initial content of Fe^0 powder – 1.0 g/L; initial H_2O_2 concentration – 2.0 mM. During purification, the total concentration of iron cations did not exceed 0.3 mg/L. Liang et al. [90] proposed two competitive pathways (Fig. 3) to degrade Rhodamine B using the Fe^0/H_2O_2 process: one is an N-de-ethylation process, and the other is cleavage of the chromophore.

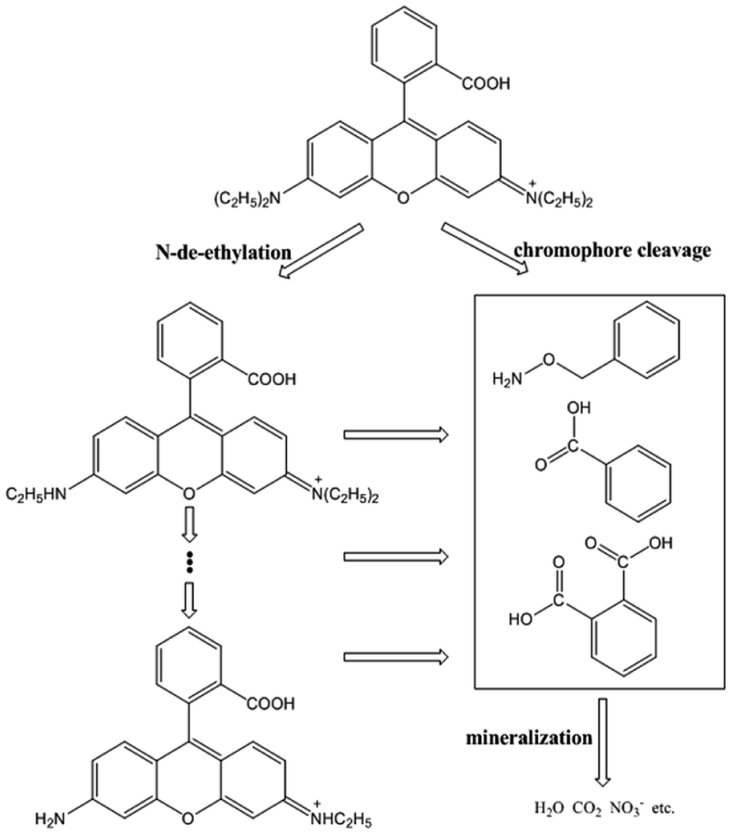

Figure 3. Degradation pathway of Rhodamine B by Fenton-like system [90] under the terms of the Creative Commons CC BY license.

In Fenton-like processes, the following are used as catalysts for hydrogen peroxide decomposition: Co-N co-doped carbon nanotubes [91], zeolite-supported Co and Cu oxides (Co/Cu/zeolite) [92], Zn-Cr layered double hydroxide catalysts [93], natural minerals (iron-bearing attapulgite granular catalyst [94], thermally activated natural chalcopyrite [95]), Fe-based metal-organic frameworks (for example, MIL-88B-Fe as Fe_3O $[C_6H_4(CO_2)_2]_3X{\cdot}nH_2O$, where X = Cl^- or OH^-), photocatalytically active materials (Fe-Mo-O doping g-C_3N_4 exfoliated composite [97], iron molybdate

$Fe_2(MoO_4)_3$ nanopowders [98], iron(II) doped copper ferrite $Cu^{II}_{(x)}Fe^{II}_{(1-x)}Fe^{III}_2O_4$ nanoparticles [99], quasicrystals $Al_{65}Cu_{20}Fe_{15}$ [100]).

Based on studies of the influence of anions (CH_3COO^-, SO_4^{2-}, Cl^-, CO_3^{2-}, and HCO_3^-) in the reaction medium on the oxidative capacity of the heterogeneous Fenton process, Zhang et al. found that HCO_3^- (Fig. 4) had the best promotion effect, which could degrade Rhodamine B, achieving a 7 times increase in the degradation efficiency of Rhodamine B compared with the traditional heterogeneous Fenton system (from 13.7% to 95.3%) [92].

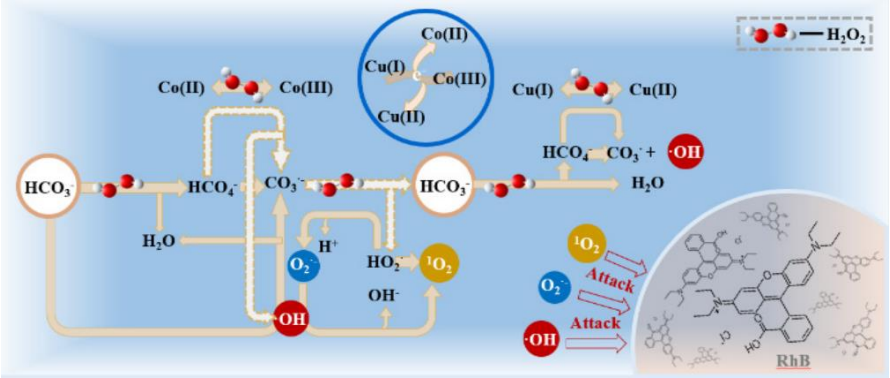

Figure 4. The proposed reaction mechanisms of bicarbonate ions enhanced Co/Cu/zeolite catalyzed heterogeneous Fenton process [92] under the terms of the Creative Commons CC BY license

The rate constant for the oxidative degradation of Rhodamine B using the HCO_3^- enhanced Co/Cu/zeolite/H_2O_2 process (3.181 h^{-1}) was approximately 20 times higher than that of the Co/Cu/zeolite/H_2O_2 process (0.158 h^{-1}). The radical quenching and EPR experiment results (Fig. 4) indicated that singlet oxygen ($^1O_2$) was the main oxidative species, followed by superoxide anion radicals ($O_2^{\bullet-}$) and hydroxyl radicals ($^{\bullet}OH$).

The catalyst based on Zn-Cr layered double hydroxide [93] demonstrated good activity during the decomposition of hydrogen peroxide to generate hydroxyl radicals, which participated in the oxidation of Rhodamine B. Over a period of 90 min a degree of Rhodamine B decolorization of 99.8% was achieved under the following conditions:

an initial Rhodamine B concentration in its aqueous solution of 20 mg/L, a volume of the solution of 100 mL, a molar ratio of Zn:Cr = 2:1 in the layered double hydroxide, a catalyst content in the reaction medium of 3.0 g/L, an H_2O_2 concentration of 9 g/L, and a pH=6.5.

Yang et al. [95] used thermally activated natural chalcopyrite ($CuFeS_2$) for the Fenton-like degradation of Rhodamine B. It was found that the use of the thermally activated chalcopyrite/H_2O_2 system for 50 min under optimal conditions (the reaction temperature – 25 °C; the initial pH 5.1; the initial concentration of Rhodamine B in the aqueous solution – 10 mg/L; the catalyst dosage – 0.75 g/L; the initial H_2O_2 concentration – 43.0 mM) resulted in a degree of Rhodamine B degradation of 96.7%. The calculated activation energy value of the Rhodamine B degradation was 9 kJ/mol. The dominant reactive oxygen species in the thermally activated chalcopyrite/H_2O_2 system were hydroxyl radicals (Fig. 5).

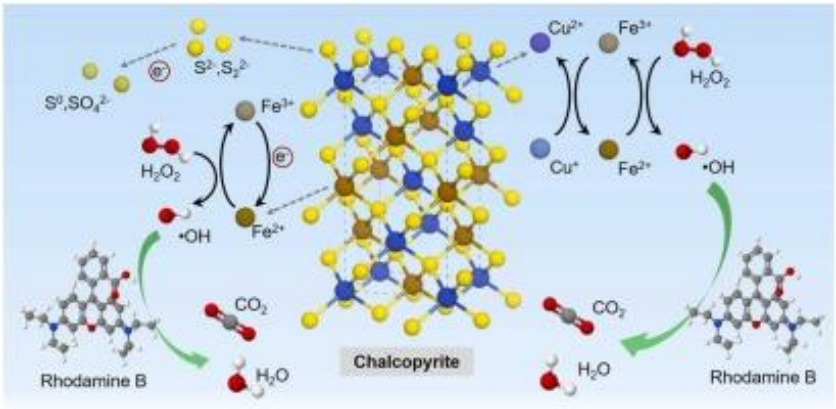

Figure 5. The proposed mechanism of Rhodamine B degradation in thermally activated chalcopyrite/H_2O_2 system [95] under the terms of the Creative Commons CC BY license

For the photo-Fenton-like degradation of Rhodamine B under visible light irradiation, Fe-Mo-O doping g-C_3N_4 exfoliated composite [97], iron molybdate $Fe_2(MoO_4)_3$ nanopowders [98], and iron(II) doped copper ferrite $Cu^{II}_{(x)}Fe^{II}_{(1-x)}Fe^{III}_2O_4$ nanoparticles [99] were used, and under UV irradiation – $Al_{65}Cu_{20}Fe_{15}$ quasicrystals [100] were used.

As a result of applying a new photocatalytic process (UV/quasicrystals $Al_{65}Cu_{20}Fe_{15}$/$Na_2CO_3 \cdot 1.5H_2O_2$), in which sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$; SPC) was an alternative source of H_2O_2, a 95% degree of Rhodamine B degradation (the initial dye concentration in the aqueous solution – 5 mg/L) was possible to achieve over 60 min of purification [100]. At the same time, the rate constant of Rhodamine B degradation was 0.048 s^{-1}. The experimental conditions were as follows: the UV irradiation power – 36 W; the UV irradiation wavelength – 365 nm; the initial SPC concentration in the reaction medium – 33.3 g/L; the quasicrystal concentration – 8.3 g/L.

Wang et al. [101] proposed a new system (Ce(IV)/H_2O_2/hydroxylamine) to accelerate the formation of aminoxyl radical ($NH_2O^{\bullet}$) by the addition of cerium Ce(IV) to induce the continuous production of hydroxyl radicals (Fig. 6) through reaction with hydrogen peroxide.

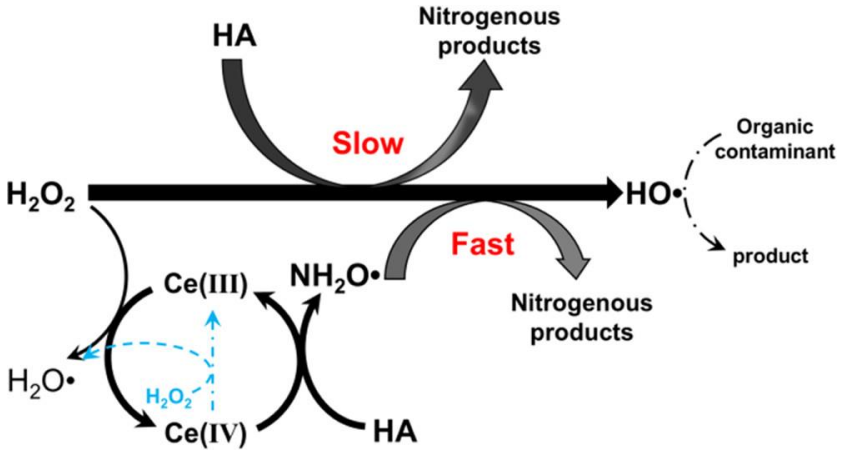

Figure 6. The proposed mechanism of organic contaminant degradation in Ce(IV)/H_2O_2/hydroxylamine system [101] under the terms of the Creative Commons CC BY license

The usage of such a triple system for 12 h to mineralize Rhodamine B made it possible to reduce the total organic carbon content (which is used to assess the degree of mineralization) by 85.6%. The experimental conditions were as follows: the initial concentration of Rhodamine B in its aqueous solution – 10 mg/L; the volume of

solution – 100 mL; the pH of the initial solution – 4.0; $[H_2O_2]_0$ – 2 mM; $[\text{hydroxylamine}]_0$ – 2 mM; $[Ce^{4+}]_0$ – 0.1 mM.

The efficiency and intensity of Fenton-like processes can be significantly increased by inducing cavitation (acoustic or hydrodynamic) in aqueous media [102-105]. Combinations of ultrasound or cavitation impinging stream (CIS) with the Fenton process provide enhanced generation of hydroxyl radicals, resulting in increased degradation rates of organic pollutants.

For the degradation of Rhodamine B, we developed a Fenton-like advanced oxidation process "ultrasonic cavitation/$MgMn_2O_4$(nanoparticles)/$Na_2CO_3 \cdot 1.5H_2O_2$". This process involves the combined activation (in an ultrasonic field and with spinel nanoparticles) of the oxidizing agent (sodium percarbonate), which was as the "source of solid hydrogen peroxide". Spinel nanoparticles of $MgMn_2O_4$ were synthesized using the co-precipitation method in an ultrasonic field (the specific power of ultrasonic treatment of the reaction medium – 200 W/L; frequency of ultrasonic oscillations – 20 kHz). The precursors were magnesium nitrate hexahydrate and manganese(II) nitrate hexahydrate in a molar ratio of 1:2, and the precipitating agent was a water solution of sodium hydroxide with a molar concentration of 2 M. As a result of the synthesis, a suspension containing dispersed particles of light brown color was obtained. The removal of impurities was carried out by sequentially washing the synthesized product three times with deionized water and ethanol, respectively. Solid particles were separated from the liquid phase by centrifugation (frequency – 5000 rpm). The solid phase was dried at a temperature of 60 °C for 12 h, and then calcined in an air atmosphere at a temperature of 200 °C for 5 h. X-ray phase studies of the synthesis product was performed using an XRD diffractometer AERIS Research with Cu*K*α-radiation. The average crystallite size was calculated using the Debye-Scherrer equation. The shape of $MgMn_2O_4$ spinel particles and their size assessment were determined based on the results of scanning electron microscopy.

During the experimental studies of the oxidative degradation of Rhodamine B ($C_{28}H_{31}ClN_2O_3$) xanthene dye in an ultrasonic field, the temperature of the reaction medium in the glass reactor maintained at a constant value of 25 °C. The initial

concentration of Rhodamine B in the solution obtained by mixing two aqueous solutions (Rhodamine B and sodium percarbonate) was equal to 100 mg/L (209 μM). The concentration of the aqueous solution of the primary oxidant ($Na_2CO_3 \cdot 1.5H_2O_2$) was varied from 1 to 5 mM, and the constant pH value of the reaction medium (which was equal to 3) was adjusted by adding an aqueous solution of HCl. The catalytic decomposition of $Na_2CO_3 \cdot 1.5H_2O_2$ was initiated by introducing nanoscale $MgMn_2O_4$ spinel particles into the reaction medium (catalyst content – 1.0 g/L). Acoustic vibrations in the ultrasonic range with a frequency of 22 kHz were generated by a magnetostrictive emitter "Ultrasonic Disintegrator UD-20".

The peaks on the diffractogram (Fig. 7) of the synthesized product matched well with the standard model of $MgMn_2O_4$ spinel (JCPDS No. 01–072-1336) with a tetragonal structure [106]. Using the Debye-Scherrer equation, the average crystallite size of $MgMn_2O_4$ was calculated to be equal to 24 nm based on the diffraction maximum at $2\theta = 36.13°$ (plane (211)).

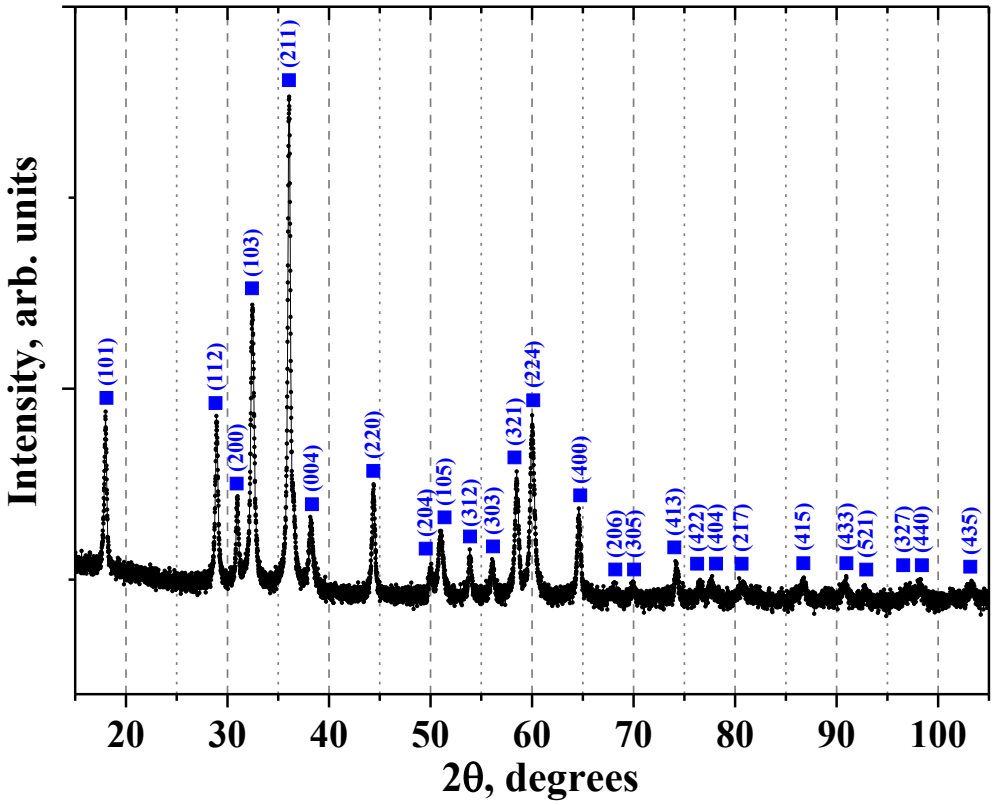

Figure 7. XRD pattern of $MgMn_2O_4$ spinel particles synthesized by co-precipitation in an ultrasonic field [made by the authors]

The formation of agglomerates from nanosized (size – 20...50 nm) quasi-spherical particles of $MgMn_2O_4$ spinel was confirmed by scanning electron microscopy (Fig. 8). The phenomenon of agglomeration was caused by the paramagnetic properties of the spinel particles.

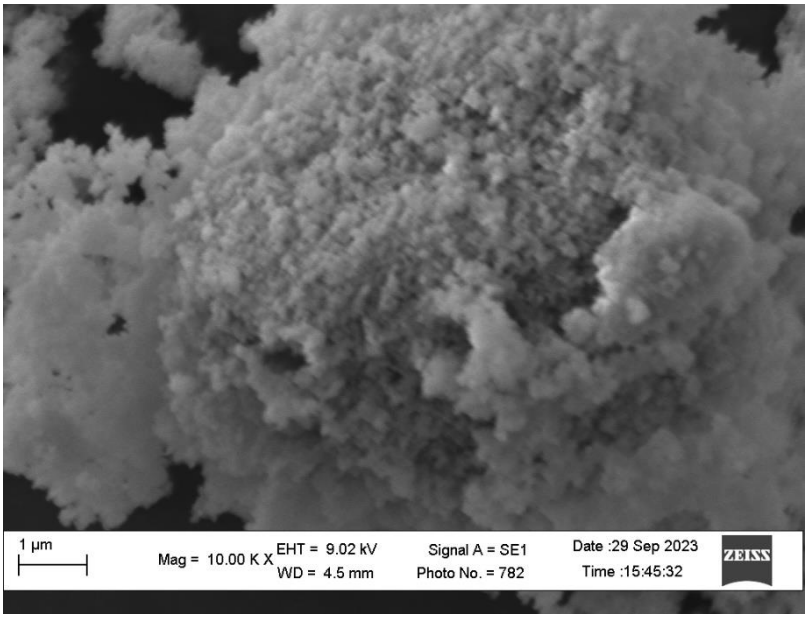

Figure 8. SEM image of $MgMn_2O_4$ spinel particles [made by the authors]

It was found that as a result of using the developed Fenton-like advanced oxidation process "ultrasonic cavitation/$MgMn_2O_4$(nanoparticles)/$Na_2CO_3 \cdot 1.5H_2O_2$" for the degradation of Rhodamine B for 3600 s, the change in dye concentration in the reaction medium depended on the initial dose of oxidant ($Na_2CO_3 \cdot 1.5H_2O_2$). Thus, at the initial dose of $Na_2CO_3 \cdot 1.5H_2O_2$ in the reaction medium of 1 mM, the concentration of Rhodamine B decreased from 209 to 38 µM for 3600 s, 3 mM – from 209 to 18 µM, 5 mM – from 209 to 4 µM (Fig. 9). Accordingly, the degree of oxidative degradation of Rhodamine B at the initial dose of $Na_2CO_3 \cdot 1.5H_2O_2$ in the reaction medium of 1 mM was 81.9%, 3 mM – 91.5%, 5 mM – 98.0%. The rate constant of oxidative degradation of Rhodamine B increased by 3 times with the increase in the initial dose of $Na_2CO_3 \cdot 1.5H_2O_2$ in the reaction medium from 1 to 5 mM, rising from 1.35×10^{-3} to 4.13×10^{-3} s^{-1}.

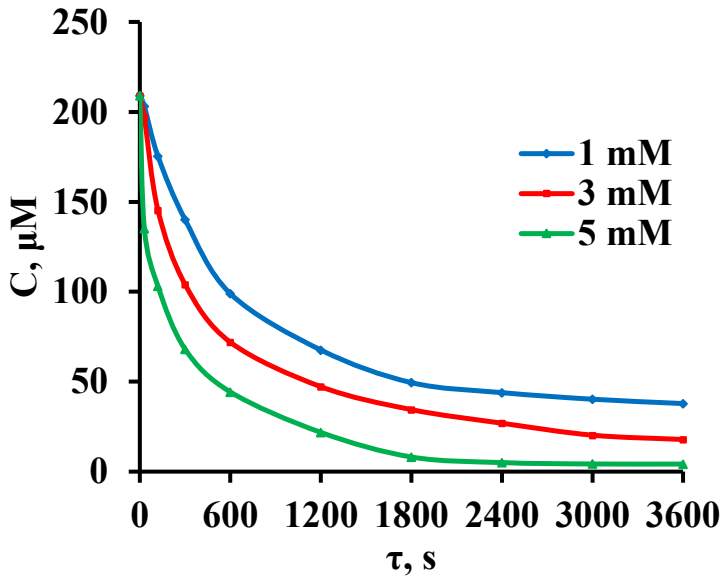

Figure 9. Influence of the initial dose of sodium percarbonate (in mM) in the reaction medium on the kinetics of oxidative degradation of Rhodamine B (conditions: V = 200 mL; $C_0(C_{28}H_{31}ClN_2O_3)$ = 209 μM; catalyst content ($MgMn_2O_4$ spinel nanoparticles) – 1.0 g/L; pH = 3; T = 298 K; specific power of ultrasonic treatment – 51 W/L) [made by the authors]

Acknowledgements

The authors acknowledge the funding of the Ministry of Education and Science of Ukraine for the scientific research project of young scientists “Advanced oxidation processes, including nanocatalytic, based on cavitation technologies for purification of aqueous media from resistant N-substituted organic compounds” (state registration number 0122U000790).