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Toxicity of water treated with Fenton-like ferrite catalyst

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Recently, there has been a rapid growth in the use of nanoparticles in water treatment processes. However, an important task is to study the toxicity of the materials used and the reaction products formed. The purpose of this study was to evaluate the impact of the proposed water treatment method on the ecosystem. Algae are excellent model organisms for studying the toxic effects of catalyst nanoparticles. This work investigates the toxicity of cobalt ferrite ($CoFe_2O_4$) and hydrogen peroxide (H_2O_2) on the microalgae *Chlorella vulgaris* Beij. (*C. vulgaris*). The growth rate of *C. vulgaris* depends on the residual concentration of H_2O_2, indicating a stressful physiological state of the microalgae. Exposure to sintered cobalt ferrite granules does not affect the growth of freshwater algae. At a residual H_2O_2 concentration of 11.9 mM, algal cells' morphology, membrane integrity, and viability were severely impaired. Hydrogen peroxide is known to cause oxidative stress, as evidenced by a decrease in the growth rate of *C. vulgaris* and an increase in the number of dead cells. The study showed that the high residual concentration of H_2O_2 is the main obstacle to the discharge of treated water into the natural ecosystem.

Keywords: cobalt ferrite; hydrogen peroxide; catalyst; *Chlorella vulgaris*.

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Introduction

In recent years, conventional methods for treating contaminated water have typically involved the use of a variety of chemical, physical, and biological materials. However, traditional water treatment methods are becoming less effectivy each year. The release of persistent pollutants into water, such as pharmaceuticals, pesticides, organochlorine compounds, dyes, heavy metals, and microbial organisms, is increasing every year. Therefore, recent research is aimed at finding effective methods to purify and disinfect water. Due to the rapid development of nanotechnology, nanomaterials play a crucial role in removal of water pollutants. Ferrites are widely used in advanced oxidation processes (AOPs) in various industries [1], including wastewater treatment [2–4].

Cobalt ferrite is an important material in electronic devices because of its high coercivity and saturation magnetization [5]. Magnetic nanoparticles play a fundamental role in the process of magnetic hyperthermia, by providing localized and controlled heating. This makes them highly effective in biomedicine [6]. $CoFe_2O_4$ shows significant antibacterial activity against *Staphylococcus aureus*, *Escherichia coli*, and *Enterococcus faecium* [7,8]. The high activity of ferrite in various fields can be attributed to the structural properties of the nanomaterial, including porosity, grain size, particle morphology, crystallinity, doping of additional metals, and surface charge [2,9]. However, the environmental impact of spinel ferrite and its effects on global ecosystems are not yet well understood. Studies have shown that prolonged use results in the release of Co^{2+} and Fe^{3+} ions. Exposure to nanomaterials can cause to cellular damage, including cytotoxicity, genotoxicity, and oxidative stress [2,10].

Advanced oxidation processes have been shown to be effective in destroying organic contaminants in water. The Fenton reaction is highly oxidizing and can aid in the degradation of organic contaminants by producing reactive oxygen species [11]. Hydroxyl and hydroperoxyl

radicals form through a catalytic reaction between Fe^{2+} or Fe^{3+} and H_2O_2. The Fenton reaction has several advantages, including low cost and the ability to use materials that are not economically expensive. In addition, the catalyst can be easily separated using magnetic methods [12]. Such physicochemical processes are promising and innovative in the treatment of contaminated water [11]. For example, the catalytic activity of the heterogeneous Fenton systems $CuFe_2O_4$ and Cu_2O–$CuFe_2O_4$ for the decomposition of stable phenol was tested in [13]. The study shows that the interaction between monovalent Cu(I) and divalent Cu(II), as well as Fe(II)/Fe(III) redox coupled with H_2O_2, increases the generation of hydroxyl radicals and improves the catalytic ability of ferrites.

In their study [14], the authors evaluated the impact of ferrites structural characteristics MFe_2O_4 (where M = Zn, Mn, Fe, Cu) on heterogeneous Fenton catalytic processes. The series of catalysts was studied for the efficiency of phenol destruction in the presence of hydrogen peroxide. The catalysts were studied for the efficiency of phenol destruction in the presence of H_2O_2. The organic pollutant was most effectively degraded by copper ferrite. The correlation between the number of surface-active sites and the number of surface hydroxyl groups, which is important in catalytic processes, has been established. Using the catalytic Fenton reaction with a concentration of H_2O_2 at 1.0 M, $CoFe_2O_4$ effectively destroyed 96.5% of the dye Remazol Red RR [15].

Chlorella vulgaris is a unicellular model organism commonly used in ecotoxicological studies [16]. Algae are known for their potential as a source of biomass, biologically active compounds, and oxygen [9]. Few scientific papers have conducted comprehensive studies on spinel ferrite nanoparticles. Therefore, the toxicity of the studied materials is often neglected in various industries, despite its important role. Understanding the toxicity mechanism of nanomaterials will allow us to make adjustments during synthesis and improve the safety of ferrites. As the use of spinel materials in water treatment technologies becomes more popular, algae - an essential biomass of aquatic ecosystems - are ideal model organisms to evaluate toxic effects on the environment [17,18].

Zinc oxide (ZnO) and iron oxide (Fe_2O_3) nanoparticles were found to be significantly toxic to *Chlorella vulgaris* cells, with inhibitory concentration IC_{50} values of 0.258 $mg \cdot L^{-1}$ and 12.99 $mg \cdot L^{-1}$, respectively [17]. The effect of nanoparticles on algae resulted in a decrease in chlorophyll content, an increase in proline, and a change in catalase activity. This indicates a stressful state of the algae and a decrease in the organism's overall functioning [17]. At a concentration of only 2 μM, $ZnFe_2O_4$ reduced algal growth by 47%. The negative effect on *Chlorella pyrenoidosa* was accompanied by a reduction in both the chlorophyll content and algal cell number. The study results indicate a correlation between the concentration of zinc ferrite and the inhibition of model organism growth. It was observed that higher concentrations of zinc ferrite led to stronger inhibition [19]. The impact of cobalt ferrite on the viability of *Chlorella* algae was studied for 72 hours [9]. The authors observed changes in cell morphology, ROS formation, catalase, and protein oxidation processes. The work resulted in minor damage to the integrity of the membranes caused by the adsorption of nanoparticles on the surface of green algae and the subsequent release of Fe^{3+} and Co^{2+} cations.

H_2O_2 is a widely available and low-cost reagent in Fenton catalytic processes, which is important for large-scale applications. The use of hydrogen peroxide is necessary, but excessive amounts can be toxic [20]. For example, [21] found that the lipid biosynthesis of *Chlorella pyrenoidosa* can be promoted by low concentrations of hydrogen peroxide (7 mM). The presence of 2 mM H_2O_2 resulted in the reproduction of algal cells. In their study, [22] investigated the effect of different hydrogen peroxide concentrations on the lipid content and biomass productivity of *C. vulgaris*. The study found that lipid biosynthesis increased at H_2O_2 concentrations of 2 and 4 mM. However, at 6 mM, the growth of unicellular alga was significantly inhibited. H_2O_2 toxicity was also been reported in [23]. In this case, the viability of chlorella was negatively affected by hydrogen peroxide. Toxicological studies of spinel nanomaterials are crucial for the development of eco-friendly water treatment technologies.

I. Experimental

1.1. Reactor parameters

The effect of electromagnetic heating (EMH) on the decomposition of H_2O_2 has been studied in a fixed bed flow reactor (60 cm). The reactor contains 445 g of $CoFe_2O_4$ granules. The process for synthesizing $CoFe_2O_4$ nanoparticles is described in [8]. The reactor was placed inside a coil equipped with a water cooling system to control the temperature while under the influence of an electromagnetic field. The six-turn coil has an outer diameter of 5 cm and a depth of 6 cm. The solution in the reactor was heated to 40°C under the influence of an electromagnetic field. The experiments were conducted in parallel without EMH at a temperature of 25°C.

1.2. Analysis of H_2O_2 concentration

The concentration of hydrogen peroxide at the reactor outlet was determined using the metavanadate method and a ULAB 102-UV spectrophotometer. 1 cm^3 of the sample was taken and placed in a 5 cm^3 volumetric flask. Then, 1.5 cm^3 of 2 M H_2SO_4 solution and 1.5 cm^3 of 0.1 M NH_4VO_3 solution were added. The flask was filled to the mark with water. The absorbance at 470 nm was measured in a 10-mm cuvette after 10 minutes (reference solution – blank solution).

The concentration of hydrogen peroxide (H_2O_2) was calculated using the following equation:

$$H_2O_2 \text{concentration} = \frac{A_x}{0{,}29917} \cdot 5 \quad [\text{mM}] \qquad (1)$$

1.3. Cultivation of *Chlorella vulgaris* Beij.

The study focused on a pure culture of the green freshwater algae *Chlorella vulgaris* Beij. (*C. vulgaris*). The algae were cultivated on Tamiya medium [24] at a

concentration of 1:10 in a 60 L aquarium with specific operating parameters (25±1 °C, 2000 lux, pH = 7.4 and 16/8 h light/dark). To achieve optimal growth of *C. vulgaris*, we utilized an aerator that provided a constant supply of oxygen. The culture medium was supplemented with salt solutions, specifically potassium nitrate (KNO_3) and $ZnSO_4 \cdot 7H_2O$ (Zn^{2+}), to enhance growth. The maximum culture density in the developed bioreactor is achieved on the 30-th day of cultivation, with a cell content of 5×10^3 cells/cm^3. The concentration of growth stimulants can alter the level of *C. vulgaris*. The density of *C. vulgaris* cells was regularly monitored using a UV-Vis spectrophotometer at 692 nm for light absorption. Figure 1a-b shows UV-Vis spectra of solutions containing different concentrations of *C. vulgaris*, along with the calibration curve used to determine *C. vulgaris* concentration. The quantity of cells was determined simultaneously using a Goryaev grid. The corresponding concentrations of H_2O_2 at the reactor outlet were added to the microalgae culture during the exponential growth phase. The culture was then incubated for 24, 48, 72, 96, 120, and 144 hours. Samples of algal biomass were taken immediately before the experiment. Every 7 days, the nutrient medium (1 dm^3) was added with appropriate concentrations of salt solutions [24].

The concentration of *Chlorella vulgaris* was determined using the following equation:

$$C = \frac{A_x}{2.24667*10^{-4}} \quad [\text{cell/mL}] \qquad (2)$$

The biomass level of *Chlorella vulgaris* algal cells was calculated using the following equation:

$$Biomass\ concentration = \frac{Chlorella\ vulgaris\ in\ test}{Chlorella\ vulgaris\ in\ control} * 100 \quad [\%] \qquad (3)$$

The experiments were conducted using 200 mL containers with a working volume of 100 mL. The reactors were filled with solutions of *C. vulgaris* that were grown in the main reactor to achieve an initial cell density of approximately 1.5-2.5 $\times10^3$ cells/mL. The reactors were placed in a growth chamber with a 16:8 light/dark ratio and maintained at a temperature of 25±1 °C for a period of 7 days. Before sampling, gently stirred the culture contents to suspend the biomass attached to the walls of the jars. Samples were taken at various intervals (primarily on 1, 2, 3, 4, 5, 6, and 7 day) to monitor cell density and were then returned to the reactors. The experiments were conducted in six replicates, and the average values were recorded.

II. Results and discussion

The mechanism of the Fenton reaction is based on the formation of hydroxyl ($^{\bullet}OH$) and other radicals, which partially or completely decompose organic compounds and gram-negative bacteria [25]. The main problem with these reactions is the short lifetime of the radicals, which is a crucial factor in the Fenton reaction. For example, the $^{\bullet}OH$ radical has the longest lifetime, about 2.7 μs, compared to superoxide anions ($O_2^{\bullet-}$) which have a lifetime of 1.3 μs [26]. However, the lifetime of singlet oxygen ($^1O_2$) is 2.80 s and the diffusion distance is 0.998 cm at a pressure of 1.0 atm and a temperature of 23°C [27]. The distance over which free radicals diffuse is particularly important in catalytic reactions. Most reactive oxygen species (ROS), due to their instability and high reactivity, cannot diffuse far from the site of their generation due to their instability and high reactivity. The catalytic reaction is positively influenced by the stronger electrostatic affinity between the catalyst and pollutant in the presence of H_2O_2. It is well-established that the high adsorption properties of the catalyst significantly reduce the distance that ROS, must travel formed by the decomposition of H_2O_2, must travel, thereby enhancing the catalytic properties. The size and surface area of the catalyst are important factors affecting catalytic activity. It is obvious that nanometer-sized materials have a larger surface area than larger materials. The strong electrostatic attraction of the contaminant and the large surface area

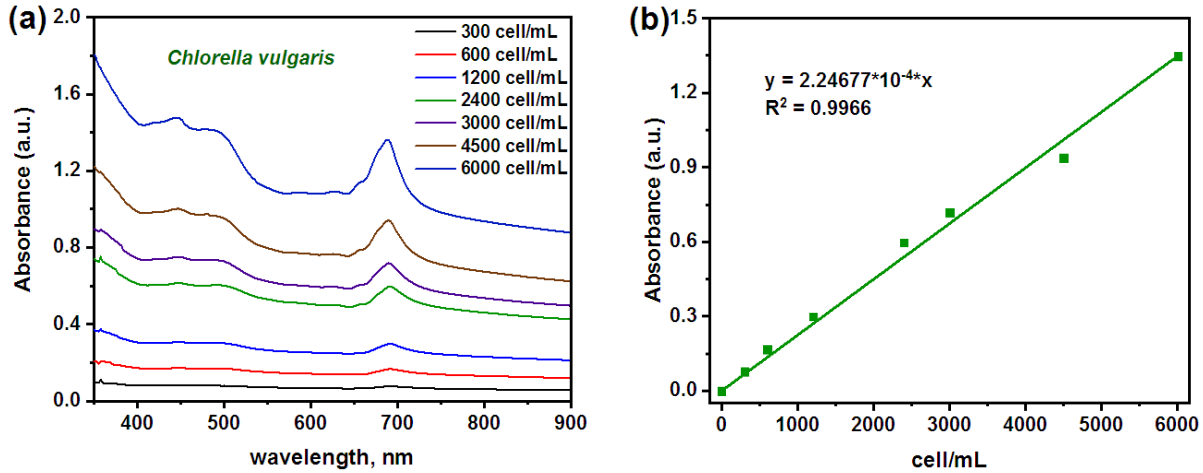

Fig. 1. (a) The cultivated microalgae were measured for growth using a UV-Vis spectrophotometer at a wavelength of 692 nm; (b) relationship between *C. vulgaris* cell density and absorbance (692 nm).

allow for higher adsorption and catalytic reaction efficiency. An effective catalyst is a material that is less than 10 nm in size, has an controllable surface charge, and is soluble/dispersible in water.

2.1. Decomposition of H_2O_2 in a fixed bed reactor

The concentration of hydrogen peroxide (H_2O_2) was varied from 0.5 to 25 mM. The solution flows through the reactor at a rate of 2.5 mL/min, with a residence time of 52.5 min. Figure 2a shows the efficiency curves of H_2O_2 decomposition in a flow-through reactor under the influence of electromagnetic heating. The decomposition efficiency decomposition decreases as the concentration of H_2O_2 increases. At a concentration of 0.5 mM, the decomposition efficiency is 96.7%, while at 25 mM, it is 92.8%. Figure 2b shows the efficiency curves of H_2O_2 decomposition in a flow-through reactor without the influence of electromagnetic heating. The efficiency of decomposition ranges from 100% at a hydrogen peroxide concentration of 0.5 mM to 51.4% at a concentration of 25 mM.

Figure 3 shows the relationship between the residual H_2O_2 concentration and the H_2O_2 concentration at the reactor inlet, as well as the impact of electromagnetic heating. The residual H_2O_2 concentration is a critical factor in determining water toxicity and its suitability for consumption.

2.2. Toxicity study of reactor outlet water without electromagnetic heating

C. vulgaris organisms were used to study the effect of residual H_2O_2 concentration on water toxicity. Conclusions were drawn based on the changes in the kinetics of algal growth over a period of 7-day period compared to the control solution. The control solution consisted of settled water with 10% Tamiya medium, which was identical to the algae growth solution. In experiments conducted without electromagnetic heating, the degree of degradation of H_2O_2 was significantly lower, resulting in higher water toxicity at the outlet of the ferrite reactor. The toxicity is directly proportional dependent to the concentration of H_2O_2. Higher concentrations increase the likelihood that H_2O_2 molecules will interact with the surface of the algae cells. When algae are first exposed to H_2O_2, there is increased algal cell death. At the highest concentration (25 mM), the degradation of H_2O_2 was only observed to be only at 11.9 mM. In this case, the cells of *C. vulgaris* are rapidly destroyed within 48 hours, followed by an adaptation and a slowing down of the death of the algae. The biomass is reduced by 59.2% when the

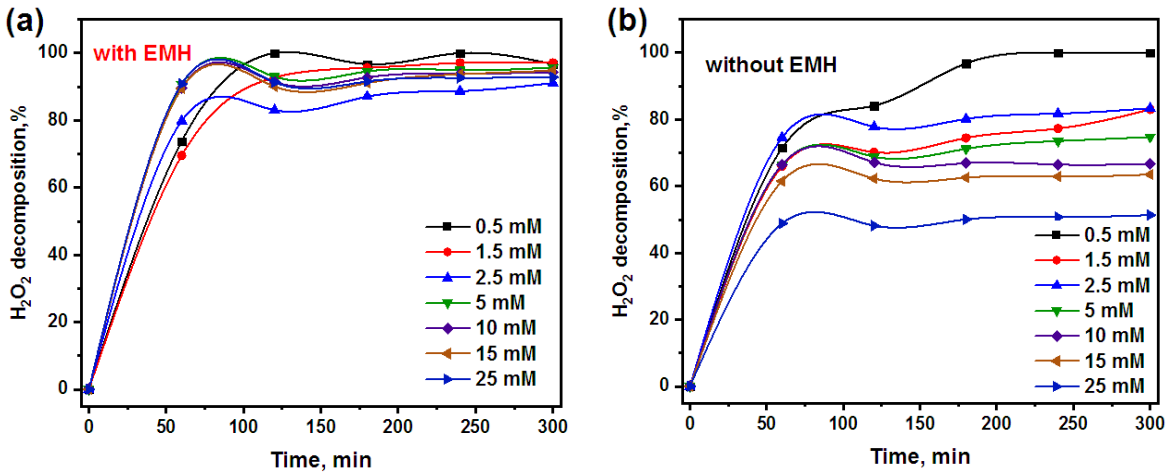

Fig. 2. Efficiency of H_2O_2 decomposition: (a) with EMH; (b) without EMH.

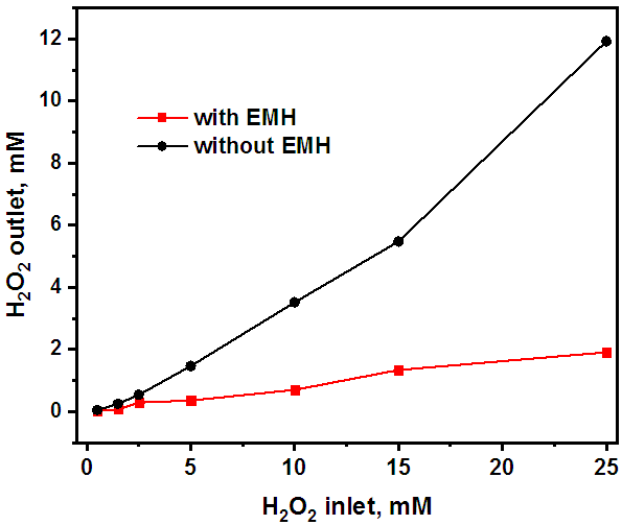

Fig. 3. The relationship between the residual concentration of H_2O_2 and its initial concentration at the inlet of the ferrite reactor, along with the impact of electromagnetic heating.

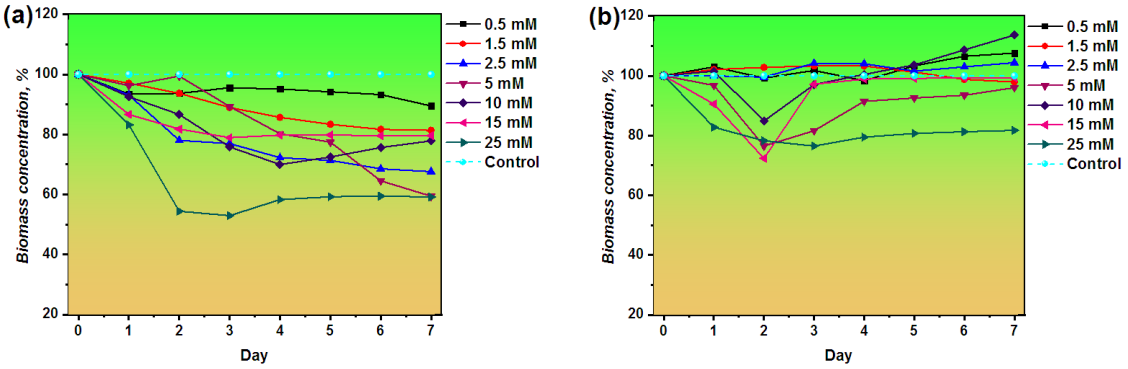

Fig. 4. Variation of *C. vulgaris* cell biomass during 7 days of cultivation: (a) 1/2 dilution; (b) 1/3 dilution.

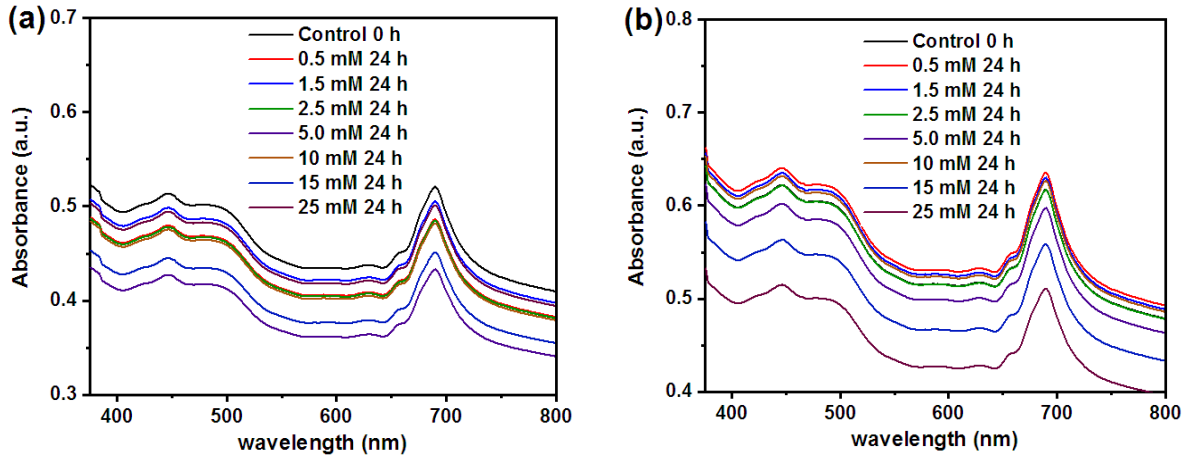

Fig. 5. UV-vis spectra of *C. vulgaris* solutions after 24 h of cultivation: (a) 1/2 dilution; (b) 1/3 dilution.

water at the outlet of the reactor is diluted by half. At a concentration of 15 mM of H_2O_2, the biomass level of *C. vulgaris* was found to be 79.6% when diluted twofold and 99.3% when diluted threefold (Fig. 4). At the lowest input concentration of H_2O_2 (0.5 mM), the biomass level is 89.5% at twofold dilution. When diluted three times, a slight increase to 1086% is observed with respect to the control solution (Fig. 4). Similar effects on biomass levels were observed a concentration of 10 mM H_2O_2. Two- and three-times dilution of the water at the reactor outlet resulted in biomass levels of 77.8% and 113%, respectively. Low concentrations of H_2O_2 can be used to sterilize chlorella cultures from bacteria and fungi. This may have improved the conditions for chlorella growth, as the removal of competing microorganisms increases growth and reduces contamination of cultures. Figure 5 shows the UV-vis spectra obtained after 24 hours of cultivation of the samples. Various biochemical analyses and algal growth kinetics confirmed that reactive oxygen species caused oxidative stress in *C. vulgaris* cells [28]. Free radicals are generated on the surface of cobalt ferrite granules in the presence of H_2O_2. The Fenton process can be used to disinfect water from gram-negative bacteria by efficiently producing hydroxyl, hydroperoxide, superoxide radicals, and other reactive oxygen species efficiently [8].

2.3. Toxicity study of water at the reactor outlet with electromagnetic heating

In the experiments conducted with electromagnetic heating, the degree of decomposition of H_2O_2 was significantly higher. Analysis showed that the concentration of H_2O_2 was 25 mM at the reactor inlet and 1.91 mM at the reactor outlet. This indicated the highest toxicity (Fig. 6 a-b). The degree of dilution affects the toxicity the water from the reactor. After twofold dilution of the solution at the outlet of the reactor containing 1.91 mM H_2O_2 twice, the level of algal biomass is 53.3% (Fig. 6a). When diluted three times, the level of algal biomass increased by 76.0% (Fig. 6b). A H_2O_2 concentration of 0.07 mM at the reactor outlet did not affect the growth of *C. vulgaris*. At three times dilution, the level of algal biomass was similar to the control solution (Fig. 6b). High toxicity levels were observed at a H_2O_2 concentration of 15 mM at the reactor inlet and 1.34 mM at the outlet. The algal biomass increased from 62.10% to 96.6% when the solution containing 1.34 mM H_2O_2 was diluted two and three times, respectively (Fig. 6 a-b). After 48 hours, a significant decrease in the number of cells was observed when the H_2O_2concentration was 10 mM at the reactor inlet and 0.70 mM at the outlet (biomass level of 74.8%). After 48 hours of cultivation, the biomass of *C. vulgaris* increased by 85.8% due to adaptation and growth. The UV-vis spectra obtained after 24 hours of cultivation for the studied are shown in Figure 7. The number of algal cells was calculated on the basis of the obtained spectra. The exact values of the H_2O_2 concentration at the reactor outlet were determined using the metavanadate method and are shown in Figure 4. Figure 6b shows that a 3-fold dilution is sufficient to achieve algal cell growth similar to that of the control solution, except for a 25 mM H_2O_2

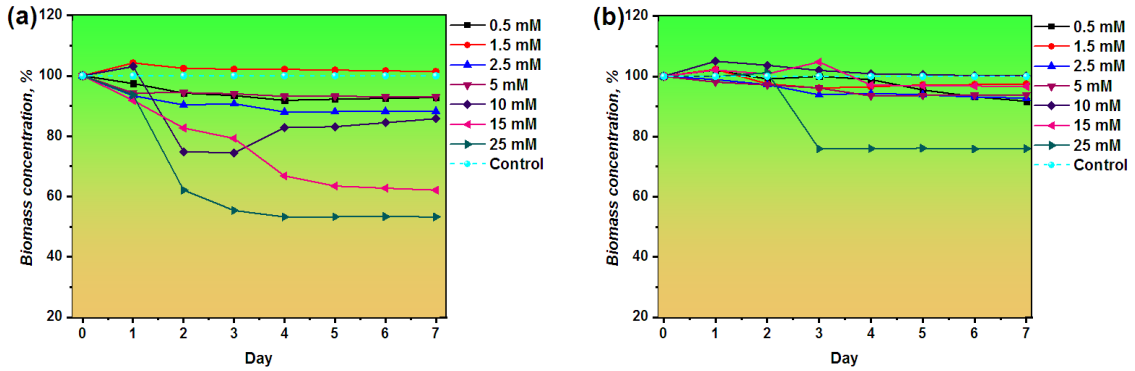

Fig. 6. Variation of *C. vulgaris* cell biomass during 7 days of cultivation: (a) 1/2 dilution; (b) 1/3 dilution.

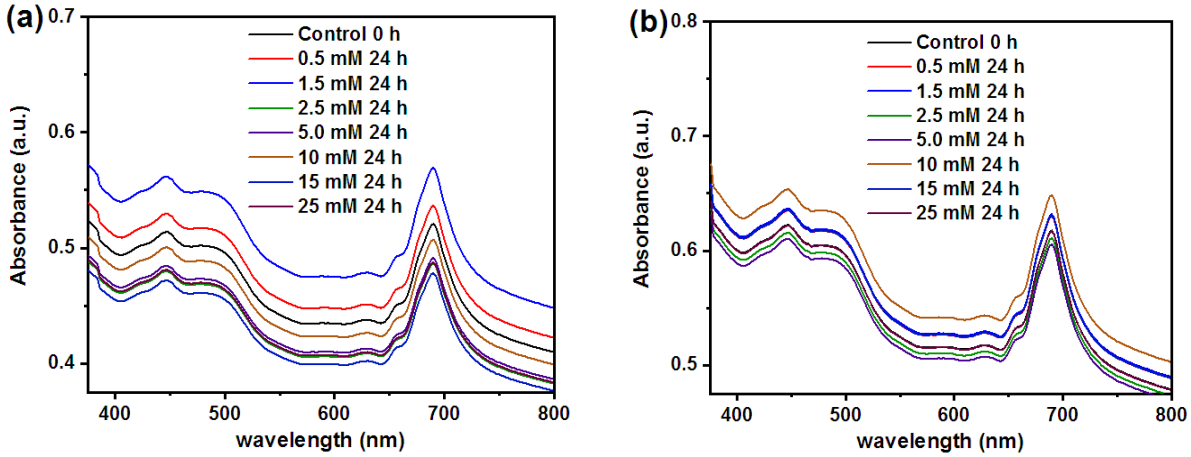

Fig. 7. UV-vis spectra of *C. vulgaris* solutions after 24 h of cultivation: (a) 1/2 dilution; (b) 1/3 dilution.

concentration at the reactor inlet.

Conclusions

This paper investigates the effect of residual H_2O_2 concentration at the outlet of a flow-through reactor intended for water disinfection reactor. Toxicological studies were performed on the freshwater alga *C. vulgaris*. Membrane damage and oxidative stress are the primary causes of H_2O_2 toxicity to algal cells. At high concentrations of residual H_2O_2, the biochemical defense mechanism of the cells is unable to cope with the stress, resulting in cell death. The results showed no risk of using $CoFe_2O_4$ in flow-through reactors for water disinfection. Sintered granules $CoFe_2O_4$ granules can serve as efficient and environmentally friendly catalysts for the purification of water containing dyes, bacteria, and other organic pollutants. The results indicate that $CoFe_2O_4$ granules can serve as catalysts for activating H_2O_2 in the Fenton reaction, which can be used to inactivate bacteria in water. $CoFe_2O_4$ granules act as heterogeneous catalysts due to their ability to accept and donate electrons during oxidation reactions. This ability can be enhanced by using electromagnetic heating. The efficiency of H_2O_2 decomposition can be increased by applying electromagnetic heating during the passage of H_2O_2 through the reactor. The growth rate of *C. vulgaris* cells increased when electromagnetic heating was applied during the decomposition of 25 mM H_2O_2, resulting in residual H_2O_2 concentrations of 1.91 mM and 11.9 mM with and without electromagnetic heating, respectively. However, a high residual concentration of hydrogen peroxide indicates increased oxidative stress and necessitates an increase in the number of dilutions. Therefore, it is important to select the optimal conditions to ensure proper catalytic efficiency and minimize potential toxicity from residual H_2O_2 concentrations when discharged treated water to the environment.

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Токсичність води, очищеної фентоноподібним феритовим каталізатором

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Останнім часом використання наночастинок у процесах очищення води стрімко зростає. Проте важливим завданням є вивчення токсичності використаних матеріалів та утворених продуктів реакції. Тому в цій роботі перевірено вплив запропонованого методу очищення води на екосистему. Водорості є ідеальними модельними організмами для вивчення токсичності води. Це дослідження присвячено вивченню токсичності наночастинок кобальтового фериту ($CoFe_2O_4$) і пероксиду водню (H_2O_2) щодо мікроводоростей *Chlorella vulgaris* Beij. *(C. vulgaris)*. В залежності від концентрації H_2O_2, спостерігається уповільнення росту *C. vulgaris*, що може вказувати на стресовий фізіологічний стан мікроводоростей. Вплив спечених гранул кобальтового фериту не викликає негативних змін в рості прісноводних водоростей. Морфологія клітин водоростей, цілісність і життєздатність мембран були серйозно порушені при залишковій концентрації H_2O_2 (11.9 мМ). Зменшення швидкості росту хлорели, а також збільшення кількості загиблих клітин вказують на розвиток оксидативного стресу в присутності пероксиду водню. Це дослідження показало, що саме висока залишкова концентрація H_2O_2, є основною проблемою під час скиду очищеної води до природньої екосистеми.

Ключові слова: кобальтовий ферит; пероксид водню; каталізатор; *Chlorella vulgaris*.