

# Abstract

Article I focuses on the degradation of dyes, which are synthetic organic compounds commonly used in the textile and food industries. Particular attention was paid to Rhodamine B. The article aims to analyze the degradation of Rhodamine B and other dyes, such as Sudan I and Methyl Blue, using  $\text{Fe}_3\text{O}_4$  nanoparticles.

Magnetite nanoparticles with a non-spherical shape (octahedral and cubic) were synthesized by co-precipitation in a high-pH solution, without the use of organic modifiers.

To determine the chemical composition, The structure and morphology of  $\text{Fe}_3\text{O}_4$  nanoparticles were analyzed using transmission microscopy (TEM) and X-ray diffraction (XRD). The research confirmed that the nanoparticles have a well-formed crystal structure, and most of them take octahedral or cubic shapes.

Degradation tests were carried out on three dyes: Sudan I, Rhodamine B and Methyl Blue. For this purpose, dye solutions were prepared and exposed to UV radiation in the presence of  $\text{Fe}_3\text{O}_4$  and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) nanoparticles. The degradation processes were monitored using a UV-Vis spectrophotometer.

Microscopic examinations showed that  $\text{Fe}_3\text{O}_4$  nanoparticles tend to agglomerate due to their high surface energy. The crystal structure of magnetite was confirmed by X-ray diffraction analysis and electron diffraction patterns.

The degradation of dyes took place under various conditions, with varying degrees of adsorption on the surface of the nanoparticles. Research has shown

that Rhodamine B degrades according to a zero-order kinetics model, while Methyl Blue follows a first-order kinetics model.

The degradation of Sudan I occurs in two stages: hydroxylation and decomposition of intermediate products.

This process is different from the degradation of Rhodamine B and Methyl Blue and does not follow a simple kinetic model. The proposed mechanism is based on the photo-Fenton reaction, in which hydroxyl radicals attack Sudan I molecules, leading to the formation of intermediates such as 4' OH Sudan I and 6 OH Sudan I.

$\text{Fe}_3\text{O}_4$  nanoparticles with a non-spherical shape, synthesized by co-precipitation, can be effectively used to degrade dyes such as Rhodamine B, Methyl Blue and Sudan I. The dye degradation process varies depending on the adsorption capacity on the surface of the nanoparticles, and the degradation mechanism of Sudan I requires a two-step approach.

Article II also focuses on research on the use of magnetite nanoparticles in catalytic processes, especially in the photo-Fenton reaction, which is used to degrade organic pollutants in an aqueous environment.

Magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles are gaining popularity due to their unique properties, such as superparamagnetism, low synthesis costs and wide possibilities of structure modification. Functionalization of their surface can prevent agglomeration and increase their stability. Malonic acid acts as a stabilizer,

which forms strong chemical bonds with iron ions, preventing further oxidation of the nanoparticle surface.

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized by co-precipitation in deionized water with the addition of iron chloride and iron sulfate. For functionalization, the nanoparticles were treated with malonic acid,

which was intended to stabilize the surfaces and reduce their agglomeration.

X-ray diffraction (XRD) and transmission microscopy (TEM) were used to analyze the structure and morphology of nanoparticles. Mössbauer spectroscopy was also used to analyze the magnetic and dielectric properties. The efficiency of the decolorization process was measured using a UV-Vis spectrophotometer.

Studies on the degradation of the Rhodamine B dye in the Fenton and photo-Fenton reactions showed that the nanoparticles after functionalization had reduced catalytic activity. The degradation efficiency decreased from 86% to 35% in the Fenton reaction and in the photo-Fenton process from 93% to 85.5%

Functionalization with malonic acid limited the ability to catalyze by binding Fe<sup>2+</sup> ions on the surface of the nanoparticles. At the same time, these nanoparticles showed better magnetic stability and higher saturation magnetization (68 emu/g compared to 64 emu/g for unmodified nanoparticles).

Surface modification with malonic acid improved the electrical conductivity of the nanoparticles by reducing the oxidation layer, which facilitated the flow of charge carriers in the boundary layers.

Magnetite nanoparticles stabilized with malonic acid have smaller agglomerates, better electrical conductivity and higher magnetic stability. However,

their catalytic activity in Fenton and photo-Fenton reactions deteriorated due to surface functionalization.

Article III focuses on the comparison of the mechanical, structural and catalytic properties of two high entropy alloys (HEA) - AlCoFeNiTi and AlCoFeNiTiSi.

The aim of the article was to investigate the effect of silicon addition on the microstructure, component phases and catalytic ability of alloys in the degradation processes of organic dyes. Particular attention was paid to the analysis of phase composition, hardness, corrosion resistance and catalytic activity in the heterogeneous photo-Fenton reaction.

High entropy alloys (HEA) are characterized by a unique combination of properties such as high mechanical strength, thermal stability and corrosion resistance. The literature often emphasizes the importance of these materials in difficult environmental conditions, which makes them ideal candidates for industrial applications, such as catalysts in chemical processes. The article analyzes in detail the influence of silicon as an alloy addition on the structure and properties of AlCoFeNiTi to better understand how it affects the catalytic and mechanical capabilities of this alloy.

The aim of the article was to compare the microstructure, phase composition and mechanical and catalytic properties of AlCoFeNiTi and AlCoFeNiTiSi alloys. The research aimed to determine how the addition of silicon affects the phase stability, hardness and corrosion resistance of these alloys, as well as their effectiveness as catalysts in the degradation process of organic dyes.

The alloy samples were prepared by induction casting and then analyzed using techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and Vickers hardness measurement.

The microstructure and phase composition of the alloys were studied in detail to identify the influence of silicon on the phase formation process and the microstructure of the materials. Moreover, the catalytic tests included the photo-Fenton reaction in the presence of the Rhodamine B dye, which enabled the assessment of the catalytic efficiency of the alloys.

SEM analysis showed that the addition of silicon significantly changed the microstructure of the AlCoFeNiTi alloy. The introduction of silicon led to the formation of finer grains, which resulted in better uniformity of the microstructure. XRD studies showed the presence of new phases in the AlCoFeNiTiSi alloy, such as the AlNiSi intermetallic phase, which was not present in the silicon-free alloy. The presence of this phase contributed to stabilizing the alloy structure and increasing its corrosion resistance and mechanical strength.

Vickers hardness measurement showed that the AlCoFeNiTiSi alloy was characterized by higher hardness compared to the AlCoFeNiTi alloy.

The reduction in grain size and the presence of stable intermetallic phases contributed to an increase in hardness, suggesting that the addition of silicon improves the mechanical properties of the alloys. Tensile strength tests have shown that the alloy with the addition of silicon is more resistant to plastic deformation, making it more suitable for applications where high mechanical strength is required.

Corrosion resistance tests were carried out in acidic and alkaline solutions simulating aggressive environmental conditions. The results showed that the addition of silicon significantly improved the corrosion resistance of the AlCoFeNiTi alloy.

The formation of the AlNiSi phase created a protective barrier on the alloy surface, which reduced the corrosion rate. The AlCoFeNiTiSi alloy showed significantly higher resistance to acids and alkalis than its non-silicon counterpart. Catalytic studies were performed in the photo-Fenton reaction using Rhodamine B as a model dye. The results showed that the AlCoFeNiTiSi alloy has higher catalytic activity compared to the AlCoFeNiTi alloy. The addition of silicon increased the number of active catalytic sites on the alloy surface, which contributed to faster degradation of the dye. At pH 4 and a catalyst concentration of 0.4 g/l, 89.2% degradation of Rhodamine B was achieved after 60 minutes of reaction, which was a better result than the silicon-free alloy.

The test results confirmed that the addition of silicon to the AlCoFeNiTi alloy leads to a significant improvement in its mechanical and catalytic properties. The microstructure of the silicon alloy was more uniform, and the presence of intermetallic phases contributed to the increase in hardness and corrosion resistance. The increased catalytic activity of the AlCoFeNiTiSi alloy suggests that it is a material with great potential for applications in wastewater treatment processes.

Research has shown that the introduction of silicon into the AlCoFeNiTi alloy significantly improves its mechanical properties, such as hardness and strength, as well as corrosion resistance. Additionally, the AlCoFeNiTiSi alloy showed higher catalytic activity in the photo-Fenton reaction, which makes it more effective in the degradation processes of organic dyes. These results suggest that the AlCoFeNiTiSi alloy has great potential for applications in industry where high mechanical strength and resistance to difficult environmental conditions are required.

Article IV presents research on the use of magnetic nanomaterials as catalysts in heterogeneous oxidation processes, used for the degradation of organic dyes in an aromatic solution. Particular attention was paid to examining the stability of nanomaterials, their ability to be reused and resistance to loss of catalytic activity. The effectiveness of various

nanomaterials in the degradation of Rhodamine B and Sudan I was also analyzed, and the results indicate their great potential in industrial wastewater treatment.

Advanced oxidation processes (AOPs), such as photo-Fenton reactions, are widely used to remove organic pollutants from water and wastewater. Catalysts play a key role in these processes, which can significantly accelerate the rate of degradation of harmful substances. Magnetic nanomaterials, such as Fe<sub>3</sub>O<sub>4</sub> (magnetite), exhibit high catalytic activity and easy recovery from reactions using a magnetic field. The article presents research on the optimization of the structure of nanomaterials, so as to improve their efficiency and durability in the degradation processes of organic dyes.

The main aim of the research was to determine the stability of magnetic nanomaterials in repeated use and to assess their effectiveness in heterogeneous photo-Fenton reactions. The article also examined the influence of various reaction parameters, such as catalyst concentration and reaction time, on the efficiency of Rhodamine B degradation. It was assumed that magnetic nanomaterials, due to their magnetic and catalytic properties, can be an effective tool for industrial wastewater treatment.

Magnetic nanomaterials were prepared using the co-precipitation method, and their structure was examined using scanning electron microscopy (SEM) and X-ray diffraction (XRD). To evaluate the catalytic efficiency, photo-Fenton reactions were performed in the presence of Rhodamine B dye, measuring the degradation rate of the dyes under various conditions such as pH and catalyst concentration.

The stability of the catalysts was also tested by performing multiple reaction cycles and then assessing their activity.

Photo-Fenton reactions were performed in the presence of magnetic nanomaterials, and the efficiency of the catalyst was assessed based on the degradation rate of Rhodamine B. The results showed that the magnetic nanomaterials were extremely effective in degrading Rhodamine B, achieving over 90% degradation after 45 minutes of reaction. Almost identical results were achieved for each of the pH tested (3-6.5). This means that magnetic nanomaterials are catalysts capable of degrading dyes.

The lack of significant differences in the degradation process for the entire pH tested is the result of using sodium percarbonate instead of classic hydrogen peroxide.

The stability of magnetic nanomaterials was investigated by performing multiple cycles of photo-Fenton reactions.

After five reaction cycles, the nanomaterials retained over 90% of their original catalytic activity, which confirms their high durability and reusability. SEM analysis after multiple cycles showed minimal changes in the structure of the nanoparticles, suggesting that they are resistant to degradation under difficult reaction conditions.

Studies have shown that the catalyst concentration has a significant impact on the efficiency of the dye degradation process. Increasing the catalyst concentration accelerated the rate of dye degradation, but reaching its optimum at 0.6 mg/dm<sup>3</sup>, further increasing the catalyst concentration did not result in an improvement in efficiency and even a decrease.

The research results confirmed that magnetic nanomaterials are efficient and stable catalysts for applications in heterogeneous oxidation processes. Their ability to be reused, high catalytic activity and resistance to degradation make them ideal candidates for applications in the chemical industry, especially in decolorization processes caused by dyes. Optimal reaction



conditions, such as pH and catalyst and oxidant concentration, have been carefully studied, which allowed for maximizing the efficiency of the process.

Research has shown that magnetic nanomaterials are effective catalysts in photo-Fenton processes, capable of quickly and effectively degrading organic dyes, such as Rhodamine B. Their stability and reusability make them an attractive solution for industrial water and wastewater treatment processes.

Further research could focus on optimizing the structure of nanomaterials and examining their effectiveness in degrading other organic pollutants.

Article V describes innovative research on the use of quasicrystals as catalysts in the photo-Fenton process aimed at decolorizing the organic dye Rhodamine B.

The article presents a modified version of the photo-Fenton reaction, in which quasicrystals (Al<sub>65</sub>Cu<sub>20</sub>Fe<sub>15</sub>) serve as a source of iron ions, and sodium percarbonate (SP) as an alternative source of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The research results showed the high efficiency of quasicrystals in the dye decolorization process and their potential for repeated use.

The aim of the research was to investigate the possibility of using quasicrystals as effective catalysts in the photo-Fenton process and to assess their effectiveness in the degradation of Rhodamine B. The influence of various reaction parameters, such as the concentration of quasicrystals and sodium percarbonate, on the efficiency of dye degradation was analyzed. It was assumed that quasicrystals will be an efficient source of iron ions, which will increase the efficiency of the process compared to the reference method.

Al<sub>65</sub>Cu<sub>20</sub>Fe<sub>15</sub> quasicrystals were prepared by casting an alloy of aluminum, copper and iron.

Their structure and icosahedral phase were confirmed by X-ray diffraction (XRD) and electron microscopy (SEM). Catalytic studies were performed in the photo-Fenton reaction, using Rhodamine B as a model dye. The reactions were carried out in various concentrations of quasicrystals and sodium peroxide, and their effectiveness was assessed based on the dye decolorization rate.

SEM and XRD analyzes confirmed the presence of an icosahedral phase in Al<sub>65</sub>Cu<sub>20</sub>Fe<sub>15</sub> quasicrystals, which makes them stable materials with high mechanical strength. The structure of quasicrystals allowed for the effective release of iron ions into the reaction solution, which was crucial for initiating the photo-Fenton process. The high thermal and chemical stability of quasicrystals makes them ideal for applications in aggressive reaction conditions.

Photo-Fenton reactions in the presence of quasicrystals and sodium peroxide showed high efficiency in the decolorization of Rhodamine B. Optimal results were obtained at a quasicrystal concentration of 8.3 g/l and sodium peroxide of 33.3 g/l, which allowed for the degradation of 95% of the dye after 60 minutes of reaction. Compared to the traditional photo-Fenton process (UV/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>), the reaction with quasicrystals showed higher efficiency and faster degradation rate.

Research has shown that increasing the concentration of quasicrystals above 8.3 g/l did not bring any further improvement in degradation efficiency, suggesting that this amount of quasicrystals was sufficient to achieve maximum process efficiency.

The test results confirmed that Al<sub>65</sub>Cu<sub>20</sub>Fe<sub>15</sub> quasicrystals are effective catalysts in the modified photo-Fenton reaction.

Their unique icosahedral structure and the ability to release iron ions make them an efficient catalyst.