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RESEARCH ARTICLE

Investigation of the usability of zinc ferrite nanoparticles synthesized by microwave assisted combustion method as photocatalyst for removal of organic dyes from wastewaters

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ABSTRACT

In this study, zinc ferrite nanoparticles, which has an important place among the spinel ferrite structured nanomaterials due to its unique properties, were synthesized by microwave-assisted combustion method and later were used as photocatalysts in the removal of dyestuffs by photocatalytic degradation method from wastewaters of textile industry. In the synthesis studies, it was determined that the microwave effect alone was not sufficient to complete the transformation. Heat treatment application is envisaged to solve this problem and in order to determine the optimum heat treatment temperature, the sample produced by microwave effect were subjected to heat treatment at 300°C, 400°C, 500°C, 600°C, 700°C, 800°C and 900°C, respectively. It has been observed that the heat treatment has a significant effect on the crystal structure of the particles and 700°C has been determined as the optimum heat treatment temperature. The data obtained showed that, under these conditions, the zinc ferrite nanoparticles were successfully synthesized and the powder produced completely consisted of nano-sized particles. Moreover, results showed that the synthesized zinc ferrite nanoparticles has a saturation magnetization value sufficient to separate them from the aqueous medium. Finally, zinc ferrite nanoparticles produced under optimum conditions were used as photocatalysts in the removal of textile dye known as Procion Yellow HE-3G from wastewater by photocatalytic oxidation. In photocatalysis experiments, it was observed that synthesized zinc ferrite nanoparticles provided very high removal efficiencies as photocatalysts and almost all of the dye content in the solution could be removed.

Keywords: Microwave-assisted combustion method, photocatalysis, Procion Yellow HE-3G, zinc ferrite

1. INTRODUCTION

The increase in human population brings about an increase in consumption. As a way of coping with this increase, industrial production has been increasing and diversifying day by day in the modern age. Many different dyestuffs of a wide variety of types are used for various purposes in many industries. When these used dyes are transported to the nature with wastewaters, they can create big environmental problems. It is known that organic dyes can have many negative effects in water. These negative effects have the potential to pose serious threats to human health. In order to prevent against these threats, existing traditional water treatment methods may be insufficient. Therefore, it is highly important to improve the performance of traditional methods or to develop new alternative methods for the treatment of wastewaters. It is expected that nanotechnology, which produces revolutionary innovations and solutions to solve problems in many different fields, will cause a great change in the field of water treatment technologies. By adapting nanotechnological methods to traditional processes, more innovative, more efficient and more environmentally friendly treatment alternatives can be developed for water treatment [1-3]. Today, scientific studies performed on nanotechnology applications for wastewater treatment focuses on various applications such as nanosensors, nano adsorbents, nanomembranes and nanophotocatalysis. However, the difficulties encountered in most of water treatment studies performed with nanomaterials in the separation of the nanoparticles used to reuse from the aqueous media is an important limiting factor for industrial applications of this

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technologies. Therefore, in many studies, magnetic nanoparticles are more preferred because they can be easily separated by magnetic separation.

Magnetic nanoparticles are used in a wide variety of applications due to their unique structural, electrical and magnetic properties [4-9]. For this reason, there is a significant increase in the number of studies aiming to develop new methods for the synthesis of these particles. Among these studies, in order to increase their industrial use, studies involving lowering process costs, high volume production, simplifying processes and developing more environmentally friendly methods attract more and more attention every day.

Spinel ferrites, an important subgroup of magnetic metal oxide nanoparticles, can exhibit very unusual magnetic properties, depending on the type of metal in their structure, and thus they can be used for many different purposes in industry and technology [10, 11]. Spinel ferrites are defined by the formula MFe_2O_4. Here, the ions to the M site are Cd^{2+}, Ni^{2+}, Mn^{2+}, $Co^{2+,}$ Zn^{2+}, Cu^{2+} etc. a transition metal ion with +2 charge may come, while this site is expressed as tetrahedral. Fe ion with a +3 charge passes to the octahedral site [12, 13]. Spinel ferrites are known for their strong magnetic properties and are widely used in many different applications where magnetic material is required.

One of the most widely used types of spinel ferrites is zinc ferrites. Zinc ferrites ($ZnFe_2O_4$) are low-cost, non-toxic semiconductor materials with narrow band gap. Zinc ferrite ($ZnFe_2O_4$) nanoparticles, which have industrial use like other spinel ferrites, are also very important materials in the field of biomedical technologies due to their super-magnetic behavior at room temperature and their extraordinary properties such as biological compatibility [11]. Since zinc ferrites do not exhibit toxic properties in terms of human health, they can be used as drug carrier materials in biomedical applications. Moreover, their non-toxicity also provide important advantages when used for environmental purposes such as water and wastewater treatment. Therefore, the development of low cost, environmentally friendly, simple and high efficiency synthesis techniques for the production of zinc ferrites, which is considered as a very important commercial nanomaterial, maintains the importance.

There are many methods suggested in the literature for the synthesis of zinc ferrites. This material has been previously produced by many different researchers using various techniques such as solvothermal synthesis [14], combustion [10], coprecipitation method [15], thermal treatment [16], sol-gel [17], solution combustion method [18], and hydrothermal [19]. Some of these methods require very complex and expensive experimental setups, while others require expensive starting chemicals. Moreover, many of these methods require intensive energy consumption, yet produce a very small amount of product. Moreover, in many of these methods, water is used for the synthesis process, therefore, impurities from water reduce the purity of the products and create wastewater problems at the end of the process. These problems limit the ability to produce this material on commercial scale. In order to ensure that zinc ferrites can be used in industrial or environmental applications that require extensive use, new methods that will be alternatives to all the above mentioned methods need to be developed.

Accordingly, microwave assisted methods have brought a different dimension to the synthesis of nanomaterials. These techniques allow many different nano-sized materials to be produced simply and in large quantities at a lower cost and environmentally friendly approach. Microwave-assisted methods make it possible to synthesize nanostructures at relatively lower temperatures. Thanks to this technique, the heat required for the reaction is provided by using microwave irradiation instead of conventional methods, and thus the required heat penetrates into the reactive mixture more homogeneously and effectively. Microwave energy is homogeneously distributed not only on the outer surface of the reactive materials, but simultaneously inside the material, thus producing well-crystallized nano-sized powders with smaller particle size and high purity. In addition, this method is a low cost and simple method with uniform particle formation and short reaction times. It is also a suitable method for the preparation of various nanostructured materials with different sizes and shapes. On the other hand, many researchers today focus on combustion method for the synthesis of nanomaterials with small size and different morphology. This method stands out for having the advantages of being low cost, no need for complex devices and being able to work with non-toxic and cheap starting reagents. The most important disadvantage however is that the energy consumption is high as it requires working at high temperatures for long periods. When the combustion method is applied in conjunction with a microwave-assisted heating, heating costs are known to be significantly reduced [20].

Spinel $ZnFe_2O_4$ nanostructures attract more and more attention for environmental applications due to their strong response to visible light, magnetic properties, chemical and thermal stability, biocompatibility and low cost. It provides ease of filtration thanks to its suitability for magnetic separation. Since they are chemically and thermally very stable, they can be reused several times after their first use. [21-23].

It is known that spinel ferrites can be used as adsorbents or photocatalysts for environmental purposes. Zinc ferrite has been used as both an adsorbent and a photocatalyst in many previously published studies. Zn ferrite shows improved photocatalytic behavior and excellent reusability compared to other nano-sized spinel ferrite materials [24]. Spinel zinc ferrites, which are produced in different shapes and sizes by different methods, have been used as photocatalysts in the treatment of wastewater containing various dyes such as methyl orange, methyl red, thymol blue, methylene blue and toxic chemicals such as 4-chlorophenol (4-CP) by photocatalytic oxidation. [4, 21, 25-29].

UV light-driven heterogeneous photocatalytic process is considered to be an effective alternative for the removal of environmental pollutants originating from

organic dyestuffs in wastewaters and has therefore been widely studied by many researchers in the literature. Today, many researchers prefer photocatalytic nanocatalysts to remove the color caused by organic environmental pollutants. Photocatalytic nanocatalysts are widely used for color removal from wastewater due to their high photocatalytic efficiency, low cost and non-toxicity [30, 31].

It is known that the synthesis method of nanoparticles is highly effective on the structural, magnetic, electrical and morphological properties of these materials. Therefore, it is predicted that the synthesis method can be highly influential on the photocatalytic properties of the materials. Accordingly, in this study, zinc ferrite spinel nanomaterials were synthesized by microwave-assisted combustion method, which is considered as an environmental method, and then used as a photocatalyst in the photocatalytic oxidation process of Procion Yellow HE-3G textile dye and its photocatalytic performance was investigated.

2. MATERIALS AND METHOD

2.1. Preparation of materials

In this experimental study, the experimental studies carried out were carried out in two stages. In the first step, the synthesis and characterization of zinc ferrite ($ZnFe_2O_4$) nanoparticles, which have a thermally and chemically stable structure, by microwave-assisted combustion method were investigated. Then, the use of the synthesized particles as photocatalysts in the removal of textile dyes from synthetic wastewaters by photocatalytic degradation process was investigated. In photocatalysis experiments, procion yellow HE-3G, a textile dye from the diazo dyestuffs group and widely used in industry, was used as dye.

In this study, zinc (II) nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), iron (III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$) and urea ($CO(NH_2)_2$) were used as synthesis reagents. All chemicals used were of analytical grade and were supplied from Sigma-Aldrich (Germany).

2.2. Characterization

In order to determine the structural, morphological and magnetic properties of the synthesized particles, X-Ray Diffraction (XRD), FT-IR, Vibrating Sample Magnetometer (VSM), Scanning Electron Microscope (SEM), and Transmission Electron Microscope (TEM) characterization tests were performed. Bruker D8 Discover model (Germany) XRD system was used for X-ray analysis (CuKα, λ = 1.5406 Å). Vibrating Sample Magnetometer (VSM) measurements performed at room temperature were made by Cryogenic Limited PPMS (UK) system. Perkin Elmer Spectrum Two model system was used for Fourier Transform Infrared Spectroscopy (FT-IR) measurements. The morphological properties of the synthesized zinc ferrite nanoparticles were analyzed with a FEI Talos F200S model Transmission Electron Microscope.

2.3. Synthesis procedure

A mixture consisting of Zinc (II) nitrate hexahydrate, Iron (III) nitrate nonahydrate and urea was prepared for the synthesis of zinc ferrite nanoparticles by microwave assisted combustion method. All reagents were mixed according to stoichiometric proportions in a wide open beaker. The mixture was made homogeneous by using a mechanical mixer. The resulting mixture was placed in a standard microwave oven and it was subjected to microwave irradiation for approximately 5 minutes. The reaction taking place in this process is thought to have taken place as given in Eq. 1.

$$3Zn(NO_3)_2 + 6Fe(NO_3)_3 + 20CO(NH_2)_2 \rightarrow 3ZnFe_2O_4 + 40H_2O + 32N_2 + 20CO_2 \quad (1)$$

At the end of the microwave process, a dark brown powder was obtained. Later, the products were subjected to heat treatment in a furnace for the purposes of improving their crystal structure and removing the impurities they contain. Characterization studies were carried out on the final products obtained. The schematic representation of the experimental procedure applied is presented in Fig 1.

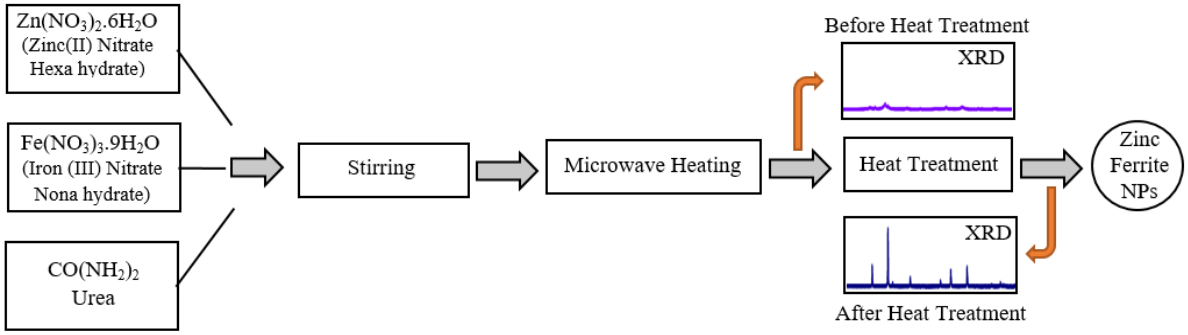

Fig 1. Schematic representation of the experimental procedure applied for synthesis

2.4. Photocatalysis experiments

A dye solution containing 100 ppm was prepared for photocatalysis experiments. 100 mL of this solution was measured and taken into a glass beaker. Then, 2 mL of hydrogen peroxide solution (ww, 0.30%) was added to the solution. A predetermined amount of zinc ferrite was added to the solution as catalyst. The

glass beaker was sealed with aluminum folio to increase the effectiveness of the UV lamp. During the process, the solution was mechanically mixed at a constant stirring speed. At the end of the experiment, catalyst particles were separated magnetically from the mixture. The concentration of the polluter matter was measured by an UV Spectrophotometer at specific time intervals during the experimental period. Removal efficiencies were calculated with the expression given by Eq. 2.

$$\%\ Removal\ Efficiency = \frac{C_o - C_e}{C_o}\ x100 \qquad (2)$$

Here, C_o (mg L^{-1}) is the initial contaminant concentration and C_e (mg L^{-1}) is the equilibrium concentration at any given time.

3. RESULTS & DISCUSSION

3.1. XRD analysis

XRD analysis was carried out to determine the chemical composition of the samples obtained in the synthesis studies and to characterize their structural properties. The obtained X-ray diffractograms are given comparatively in Fig 2.

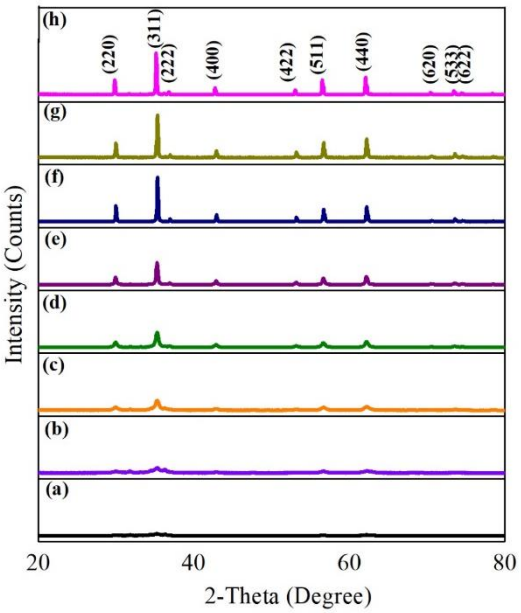

Fig 2. X-Ray diffractograms of zinc ferrite nanoparticles synthesized by microwave-assisted combustion method before and after heat treatment, (a) Precursor, (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C, (f) 700°C, (g) 800°C, (h) 900°C

The pattern shown as 2a from diffractograms presented in Fig 2, belongs to the precursor sample produced by only microwave effect. The X-ray pattern of this sample shows that the transformation in the sample was not completed. From the X-Ray diffractogram given in Fig 2a, it was determined that the sample produced by applying only microwave was in an amorphous structure. This result has been observed in other similar studies conducted before [20].

It is known that heat treatment has a significantly positive effect on improving the crystal structure of a substance. Accordingly, it was decided to subject the samples to heat treatment so as to complete their transformation and improve their crystal structure. Accordingly, the solid sample obtained from the microwave system was subjected to heat treatment at temperatures varying between 300°-900°C. For this purpose, the precursor sample was subjected to heat treatment for 4 hours in an muffle furnace at 300°C, 400°C, 500°C, 600°C, 700°C, 800°C and 900°C respectively.

Determining the minimum value of the heat treatment temperature required to complete the conversion is an important parameter in terms of the process economy. From the X-ray diffractograms presented in Fig 2, it is clearly seen that the structure shows a significant change after 500°. Moreover, in the comparison of the diffractogram of the sample prepared with heat treatment applied at 600° with the standard diffraction cards given for $ZnFe_2O_4$, it was seen that it is completely compatible with the JCPDS card No 74-2397. It was observed that all reflection peaks given on this card were obtained and the positions of the peaks were correctly also in place [10]. No additional peak of the second phase was observed in the XRD pattern, showing that the as prepared ferrite consisted of single spinel $ZnFe_2O_4$ phase. In the X-ray diffractograms of samples produced by heat treatment at different temperatures, a peak of 311 crystal planes is observed in the region between 2θ=36°-38°. This peak is the major peak in the diffractogram and is specific for spinel oxide structured materials. By using some data of this peak, the crystal sizes of the synthesized samples can be calculated with the Debye-Scherrer equation. The Debye-Scherrer equation is given below as Eq. 3.

$$D = \frac{-0.89\lambda}{\beta.Cos\theta} \qquad (3)$$

In this equation; "D" is the crystal size (nm), "β" is the radian value of the half height of the major peak in the x-ray diffractogram (FWHM), "λ" is the wavelength of the X-ray generator used in the XRD system (0.154 nm) and "θ" is the Bragg angle of the dominant peak. The crystal sizes of the samples produced at various temperatures were calculated with the Debye-Scherrer formula and then these values were plotted against the heat treatment temperature. The graphic obtained is presented in Fig 3.

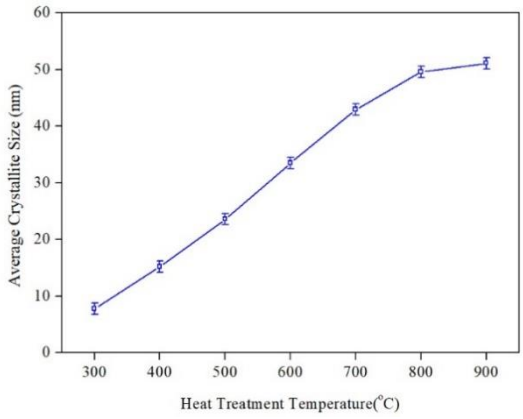

Fig 3. The variations of the average crystallite sizes with increasing heat treatment temperature

According to Fig 3, it is seen that the crystal size of the samples distinctly increases with increasing heat

treatment temperature. It is estimated that this growth originates from sintering occurring with the effect of high temperature. On the other hand, it is known that increasing crystal size may cause a decrease in the surface area. Accordingly, the heat treatment temperature must be optimized to prevent sintering. Accordingly, while the improvement in the crystal structure continues with the increasing temperature, it was determined that the heat treatment applied after 700°C did not cause any change. According to these results, 700°C has been evaluated as the optimum heat treatment temperature for this process.

3.2. FT-IR analysis

Fourier transform infrared spectroscopy is one of the most common analytical techniques used to examine chemical changes and the interactions between reactive substances. Fourier transform infrared spectroscopy analysis was performed on all of the samples obtained in order to evaluate the possible chemical changes originated from the applied heat treatment. FT-IR spectra of the samples were measured between 450 cm^{-1}- 4000 cm^{-1} and obtained spektra are presented comparatively in Fig 4.

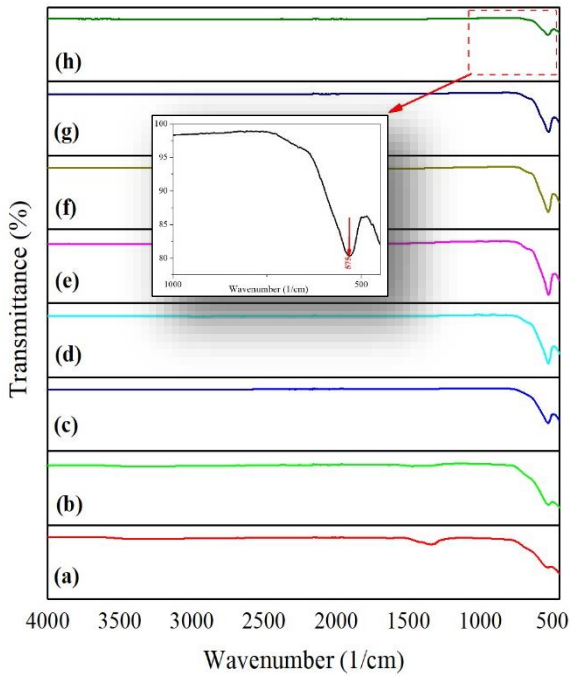

Fig 4. FT-IR spectra of zinc ferrite nanoparticles obtained before and after heat treatment, (a) Precursor samples, (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C, (f) 700°C, (g) 800°C, (h) 900°C, (i) 1000°C

When the FT-IR spectra given in Fig 4 are examined, a strong absorption band can be observed at 575 cm^{-1} caused by Fe-O tension vibrations [32]. In the FT-IR spectrum of the precursor sample presented in Fig 4a, an absorption band is observed at 1360 cm^{-1}. However, it has been observed that this peak disappears after heat treatments at high temperatures. It was evaluated that this absorption band is due to C–O stretching vibration which is originating from organic residue emerging with degradation of urea used as fuel [33].

3.3. TEM analysis

Transmission Electron Microscope is an important advanced characterization technique that allows for the microstructure and crystal structures of nanomaterials to be examined. This technique provides simultaneous access to crystallographic and morphological information of nano-sized particles. TEM examination of the $ZnFe_2O_4$ samples obtained before and after heat treatment was performed and the obtained images are presented in Fig 5.

From the TEM images given Fig 5, it can be seen that the sample, which was not heat treated, consisted of smaller particle size particles, but at the same time they were present in large lumps. It is estimated that this clumping is caused by combustion residual organic materials. After the applied heat treatment, it is thought that the pellets are relatively dispersed, however, it was observed that the average particle size is increased due to the sintering that occurs under the effect of high temperature.

3.4. VSM analysis

Zinc ferrite is a material that is widely used in many different areas due to its strong magnetic properties. It is known that the synthesis method of nanoparticles causes significant changes on magnetic properties. Accordingly, in order to characterize the magnetic properties of zinc ferrite nanoparticles produced by microwave-assisted combustion, Vibrating Sample Magnetometer (VSM) measurements were made in the samples obtained. Hysteresis loops created using the measurement results obtained are presented in Fig 6.

According to the magnetic hysteresis curves given in Fig 6, it is seen that the magnetic properties of the synthesized particles have improved significantly with the increase in the heat treatment temperature in parallel with the results observed in XRD and FTIR analyzes. The similar observations can be seen in some previous studies [20]. These observations show that there is a direct and strong relationship between crystal structure and magnetic properties.

The saturation magnetization value is a characteristic commonly used to evaluate the magnetic properties of ferromagnetic materials. Saturation magnetization defines the maximum magnetization value that a ferromagnetic material can reach. The saturation magnetization value of a sample is determined from magnetic hysteresis loops. In this study, the saturation magnetization values measured at room temperature were determined from hysteresis loops. The variation of saturation magnetization values with increasing heat treatment temperature is presented in Fig 7.

It is clearly seen that the saturation magnetization value increases in parallel with the development of the crystal structure. These results indicate a strong relationship between magnetic properties and crystal structure. The data obtained are compatible with those reported in the literature [20].

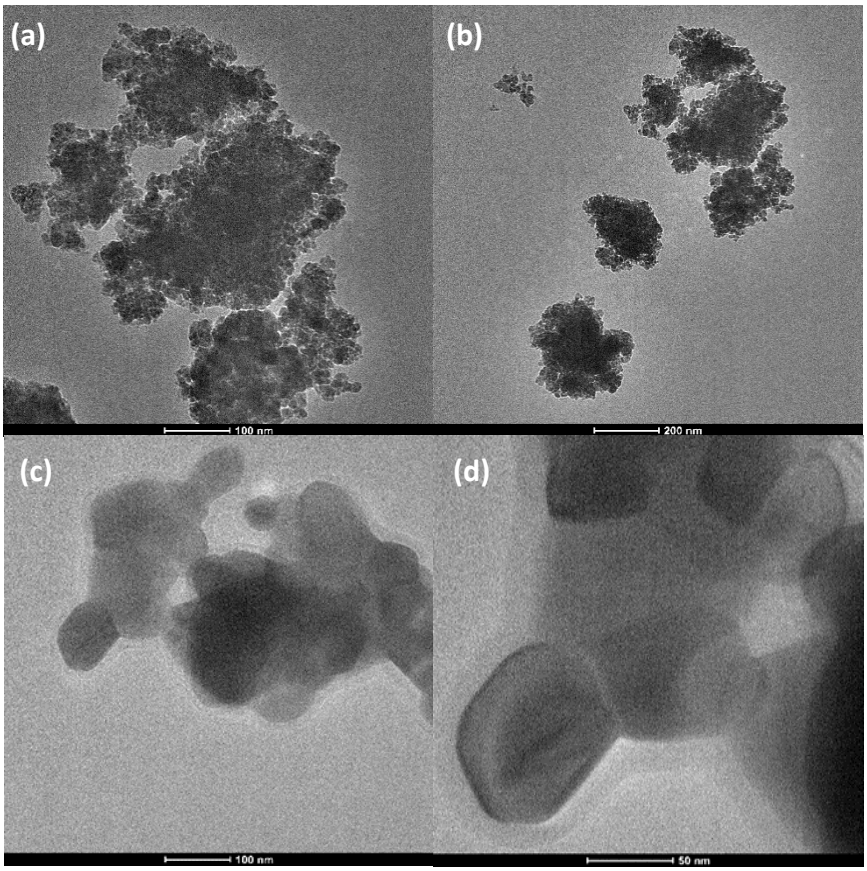

Fig 5. TEM images of $ZnFe_2O_4$ samples obtained before and after heat treatment; (a-b) sample produced without heat treatment, (c-d) sample produced by heat treatment at 700°C

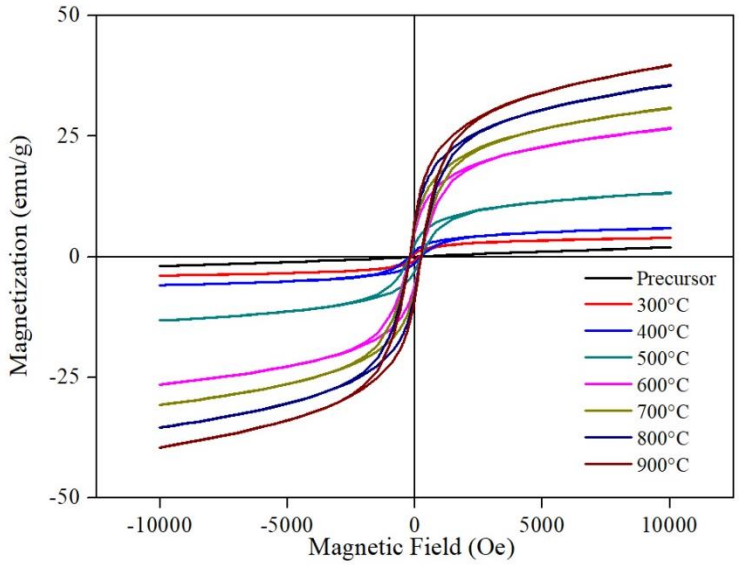

Fig 6. Magnetic hysteresis curves of $ZnFe_2O_4$ nanoparticles heat treated at different temperatures

One of the most important problems encountered in studies carried out with nanoparticles in an aqueous environment is the separation of the particles used from the environment. It is aimed to separate nanoparticles used as photo-catalysts in the system under study by magnetic separation techniques from the aqueous environment. In some previous studies, it was stated that when the saturation magnetization value of magnetic nanoparticles is about 20 emu g^{-1} and above, they can be separated from the aqueous environment by applying an external magnetic field [34, 35]. Accordingly, from the particles synthesized in this study, it is seen that the particles subjected to heat treatment at temperatures of 600° and above provide this conditions.

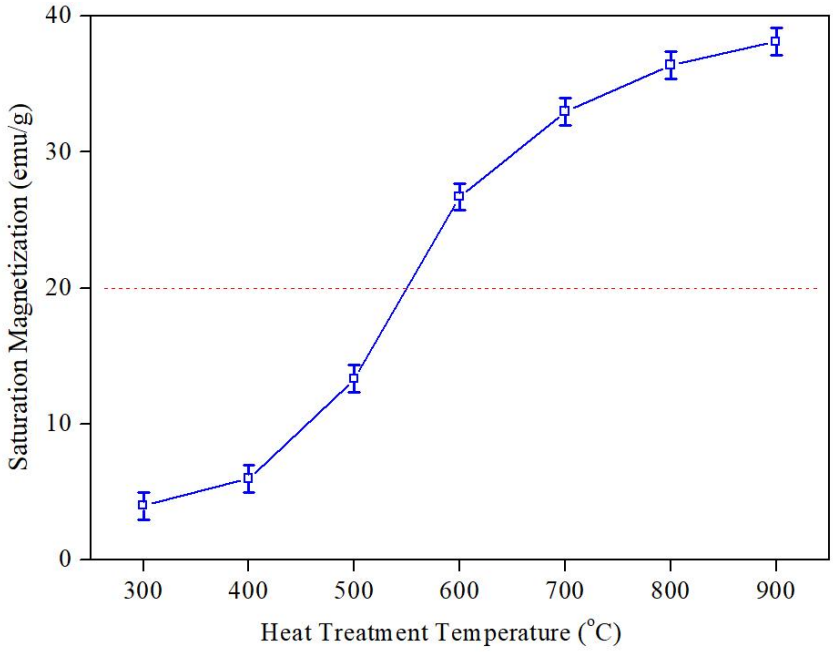

Fig 7. The variation of saturation magnetization values with increasing heat treatment temperature

3.5. The analysis of the surface properties

One of the most important problems encountered in studies conducted with nanoparticles in an aqueous environment is the separation of the particles used from the environment. In the system under this study, it is aimed to separate nanoparticles used as photo-catalysts from the aqueous environment by magnetic separation techniques. In some previous studies, it was claimed that when the saturation magnetization value of magnetic nanoparticles is about 20 emu/g and above, they can be separated from the aqueous environment by applying an external magnetic field. The surface areas of nanoparticles are a highly influential characteristic on their catalytic performance. Generally, photocatalysts with larger surface area are expected to exhibit as more much catalytic performance. Because photocatalysis process starts with the adsorption of the organic pollutant on the catalyst surface.

The Brunauer - Emmett - Teller theory (BET) is a commonly used theory to explain the physical adsorption of gas molecules on a solid surface. The specific surface area of many different types of materials is measured by an analysis technique based on this theory. Surface properties of zinc ferrite nanoparticles were measured with a surface analyzer that performs measurements based on bet theory. The adsorption desorption isotherms measured at 77 K for the zinc ferrite nanoparticles produced under optimum conditions are given in Fig 8.

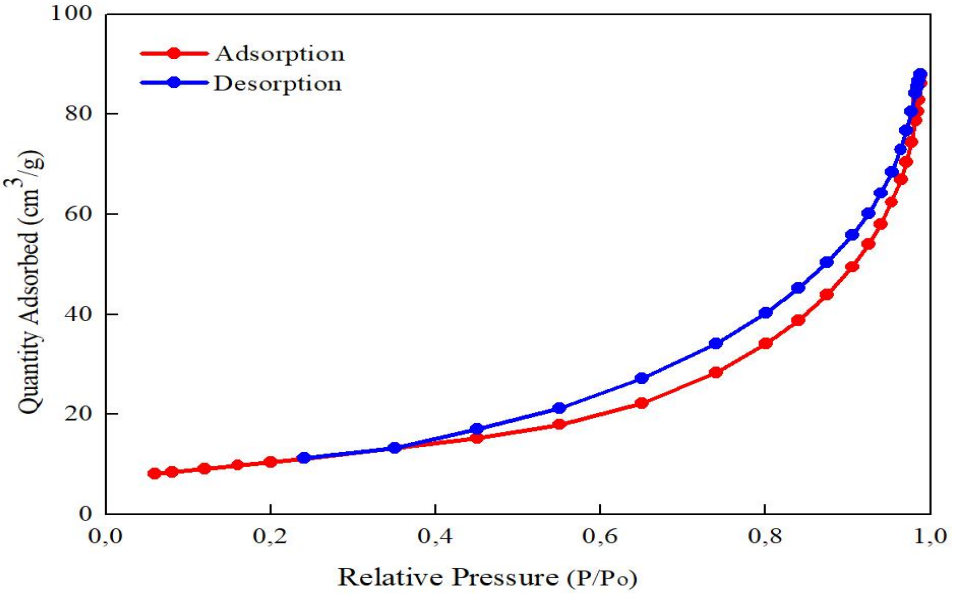

Fig 8. Adsorption-Desorption isotherms of the zinc ferrite nanoparticles prepared in optimum conditions

When the adsorption desorption isotherms presented in Fig 8 are examined, it is seen that the obtained isotherm is substantially similar to the type 3 isotherm according to the IUPAC classification. The classification made by IUPAC for the adsorption hystereses loops is an approach that is widely accepted by many researchers. The IUPAC classification is an empirical classification of hysteresis loops, based on a previous classification made by de Boer [36-38].This classification claims that there is a correlation between the shape of the hysteresis loop and the texture (e.g., pore size distribution, pore geometry, and connectivity) of a mesoporous material [36]. When isotherms presented in Fig 8 are evaluated according to the IUPAC classification, it is seen that the resulting adsorption desorption isotherm has substantial similarities with the Type II isotherm. Type II, is generally used to describe adsorbents whose pore size distribution and pore shape are irregular. Specific surface areas of zinc ferrite nanoparticles synthesized in optimum conditions by microwave-assisted combustion method were calculated with various theories such as BET, Langmuir, t-plot, and single point. The data obtained are presented in Table 1.

Table 1. The various surface properties of the zinc ferrite nanoparticles prepared in optimum conditions

	BET ($m^2 g^{-1}$)	Langmuir ($m^2 g^{-1}$)	T-Plot ($m^2 g^{-1}$)	Single Point ($m^2 g^{-1}$)
Surface Area	38.0580	52.5293	37.2451	36.6986

BET surface area of the zinc ferrite nanoparticles subjected to heat treatment at 700°C was determined as approximately 38 $m^2 g^{-1}$. This value can be considered to be a very good surface area for a nanoparticle to be used as a photocatalyst.

3.6. Photocatalytic properties

A photocatalyst can be defined as an substance activating with a UV light beam coming onto it. It is known that zinc ferrite nanoparticles exhibit very good photo-sensitive properties. Accordingly, synthesized zinc ferrite nanoparticles were used as photocatalysts in the process of degradation of procion yellow HE-3G textile dye by photocatalytic oxidation and its effectiveness on removal efficiency was investigated for catalyst dosages of the 1 g L^{-1}, 0.5 g L^{-1}, 0.25 g L^{-1}, and 0,01 g L^{-1}, respectively. Absorption spectra obtained from experiment performed for each catalyst dosage are given in Fig 9.

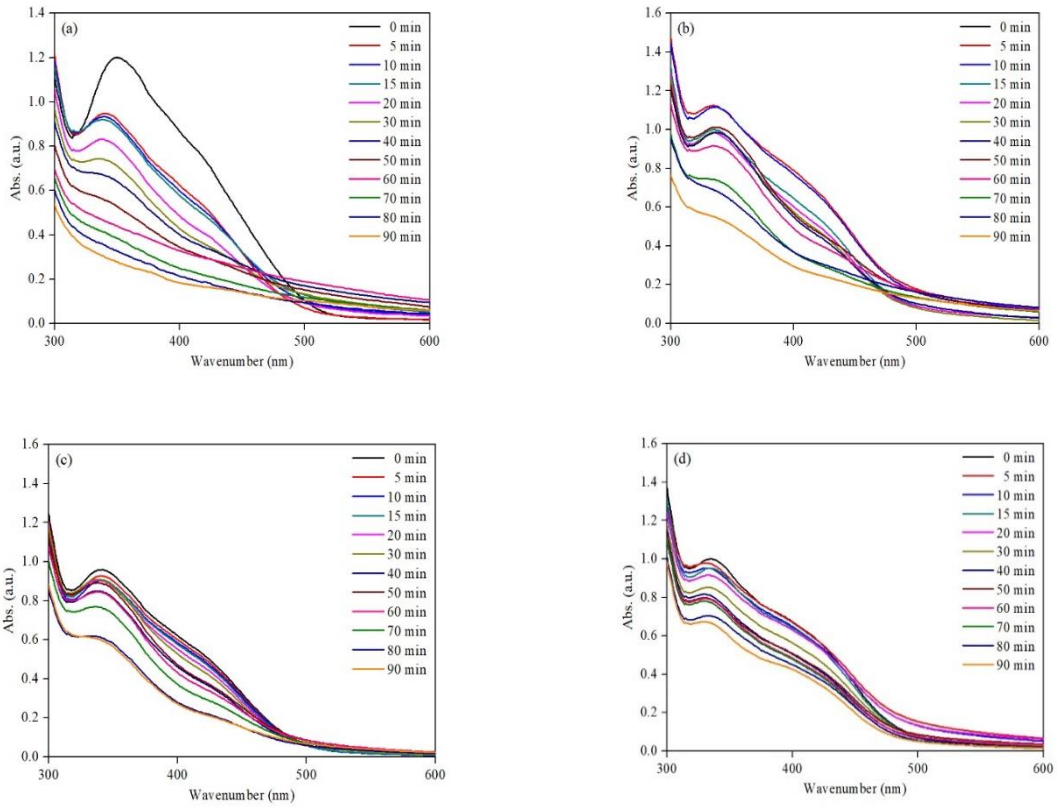

Fig 9. Absorption spectra obtained from experiments performed with different catalyst dosages a) 1g L^{-1}, b) 0,5 g L^{-1} c) 0,25 g L^{-1} ve d) 0.01 g L^{-1}catalyst dosage

When the absorbance curves given above are examined, it is seen that the removal efficiencies increase significantly with the increasing amount of catalyst as expected. However, results very close to each other were observed in experiments made with 0,25 g L^{-1} and 0.01 g L^{-1} catalyst dosages. A graphical figure showing the change in removal efficiency versus time is presented in Fig 10.

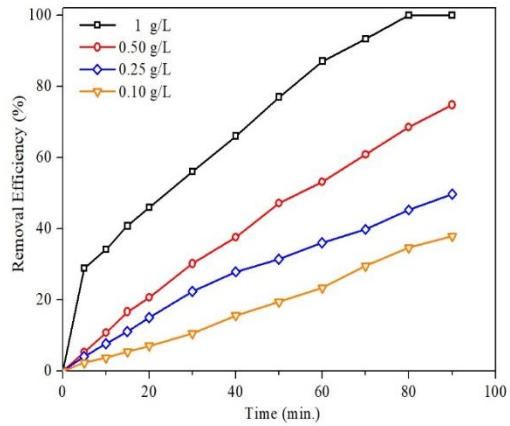

Fig 10. The changes in removal efficiency versus time in experiments performed with various catalyst dosages

The results given in Fig 10 show that the trial performed with a catalyst dosage of 1 g L^{-1} was clearly much faster than the others. In photocatalysis experiments, a removal efficiency of 100% was achieved at the end of the 80th minute for 1 g L^{-1} catalyst dosage, while at the end of the 90th minute in experiments made with the 0.5 g L^{-1}, 0.25 g L^{-1}, and 0.01 g L^{-1} catalyst dosages, respectively removal efficiencies of 74.8, 46.7% and 37.9% were observed. In order to determine whether $ZnFe_2O_4$ nanoparticles show a photo-catalytic effect during the chemical oxidation process of Procion Yellow HE-3G textile dye, an experiment was conducted by adding only hydrogen peroxide solution and catalyst to the paint solution and covering the surrounding of the beaker with aluminum folio in order to prevent the light exchange with the environment of the system. The absorption spectrum obtained from experiment performed without using any light source is presented in Fig 11.

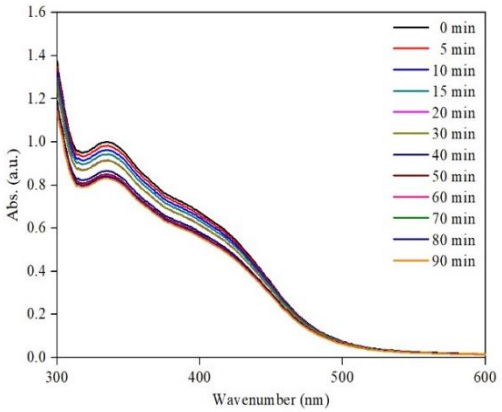

Fig 11. Absorption spectra obtained from the experiment in dark environment without using any light source

When the results given in Fig 11 are examined, it is observed that there is very little removal effect. It is estimated that this removal may have occurred with the adsorption rather than the oxidation. The graph prepared by comparing the results obtained from the experiment without using a UV light source with the results of the experiment carried out with UV irradiation under the same experimental conditions is presented in Fig 12.

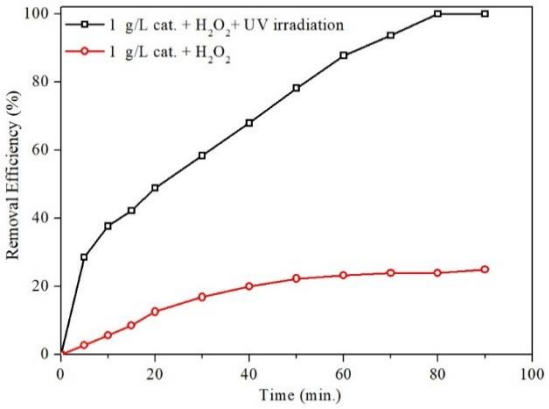

Fig 12. The comparison of the removal efficiency obtained from experiment made with UV effect and the removal efficiency obtained from experiment made without UV irradiation

When the removal efficiencies obtained from the experiments made with and without the UV irradiation are evaluated together, the positive effect of the applied UV irradiation onto removal efficiency can be clearly seen. Accordingly, the obtained results show that the $ZnFe_2O_4$ nanoparticles used in the process have a photocatalytic effect and this process is a phototocatalytic oxidation process.

4. CONCLUSIONS

In this experimental study, zinc ferrite ($ZnFe_2O_4$) magnetic spinel ferrite nanoparticles were successfully synthesized by microwave-assisted combustion method. Later, the synthesized $ZnFe_2O_4$ nanoparticles were used as photocatalysts in the process of degradation of Procion Yellow HE-3G textile dye by photocatalytic oxidation. The results obtained from the trials can be summarized as follows.

- The obtained results demonstrated that magnetic $ZnFe_2O_4$ zinc ferrite nanoparticles can be successfully produced by microwave-assisted combustion method.
- It was determined that zinc ferrite nanoparticles can be produced in a simple, fast and abundantly with the proposed method.
- It has been determined that the synthesized particles have a sufficient level of saturation magnetization to be able to be separated from the aqueous environment.
- The particles produced have demonstrated an effective photocatalytic performance in the process of degrading Procion Yellow H3-EG textile dye by photocatalytic oxidation. The removal efficiency was determined as 100% at the end of

80th minute in experiment made with 1 g L^{-1} catalyst dosage.

- The results obtained from trials carried out separately in the dark environment and under the influence of UV radiation clearly show that the process takes place photocatalytically.
- As a result, with the proposed synthesis process, zinc ferrite nanoparticles can be synthesized in a simple, fast, environmentally friendly and highly efficient. In addition, synthesized particles have the potential to be used as photocatalysts in dye removal by photocatalytic oxidation process from textile wastewater thanks to their very high photosensitivity.

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