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# INVESTIGATION OF PHOTOCATALYTIC AND ANTIMICROBIAL PROPERTIES OF BORON DOPED IRON OXIDE NANOSTRUCTURED PARTICLES

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## Abstract

Iron oxide and boron doped iron oxide was synthesized by hydrothermal method. XRD and SEM measurements of these nanostructured particles were made and their structural and morphological properties were determined. XRD results are examined and it is seen that all nanostructured particles have Rhombohedral structure. It has been calculated with the Debye-Scherrer formula that these particles are nanostructured. As an application, the photocatalytic and antimicrobial activities of these nanostructured particles have been investigated. Photocatalytic analysis was carried out using ciprofloxacin under the xenon lamp. It has been observed that the photocatalytic degradation rates are high on ciprofloxacin. The antimicrobial activity of the synthesized particles was determined using the Kirby-Bauer Disk Diffusion Method. It has been determined that the boron additive contributes positively to the antimicrobial activity.

*Key words:* antimicrobial, iron oxide, nanostructured, photocatalytic properties

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## 1. Introduction

With the development of the industrial society, environmental pollution has emerged as a serious problem for mankind (Sun et al., 2019). An important topic of environmental pollution is the pollution of wastewater. Water is one of the most important basic needs for our world, however it is constantly polluted by mankind (Shah et al., 2018a). Water pollution is a problem that needs to be solved in order to maintain a regular life in nature. Water is polluted by many industries including petrochemical, textile and pharmaceutical industries (Helal et al., 2017).

One of the pollutants we encounter in wastewater is antibiotics. Antibiotic is an agent that prevents or destroys the growth of bacteria and fungal microorganisms. Ciprofloxacin is an antibiotic widely used in the treatment of human and animal diseases. CIP is partially metabolized after ingestion, but is mostly excreted in the aquatic environment. Although antibiotics have been used in large quantities, the presence of these substances in wastewater has not received much attention until recently (Kümmerer, 2009; Shah et al., 2019). Ciprofloxacin (CIP) has caused serious environmental problems due to its strong biological activity (Zhang et al., 2015).

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It has reported high rates of CIP in wastewater (Shah et al., 2020). The removal of wastewater from CIP has been an important issue that researchers are working on (Yang et al., 2017). For this reason, it will be in the nature's best interest to develop treatment technology to remove antibiotics from wastewater (Ji et al., 2014).

Recently, various techniques have been developed to remove such pollutants. These methods provide wastewater treatment through coagulation, precipitation, adsorption, ion exchange and membrane treatment (Sun et al., 2015). Although there are serious developments in this area, these techniques cannot be used because they cannot be applied on costs or large scales (Zhou and Smith, 2001). Unfortunately, many techniques do not have sufficient efficiency (Yan et al., 2013). Catalytic oxidation, removal of pollutants in water and wastewater is one of the remarkable technologies (Zhang et al., 2016). Fujishima is the pioneer of this innovative technology. Today, many scientists are working on photocatalysis to eliminate environmental pollution (Al-Hamdi et al., 2017).

The development of nanotechnology has had a serious impact in the modern age (Muhammad et al., 2019a). Many studies have shown that many properties of metallic nanoparticles produce better results than the bulk form of the metal (Hashmi et al., 2021). Synthesis of metal oxide nanostructures has provided opportunities for applications in many different fields (Qurashi et al., 2010). Semiconductor-based photocatalysis has proven to be a promising technology for treating wastewater (Wen et al., 2018). Nanostructures play an important role in the removal of dyes, organic and inorganic contaminants (Khan et al., 2019). Metal oxides has many uses such as electronic, magnetic,optical and catalytic applications etc. (Khan et al., 2020; Su et al., 2016). Iron oxide (IO) is a suitable material for photocatalysis due to its properties such as photochemical stability, band gap, and favorable optical photoelectrochemical capability in the visible light region (Lei et al., 2018). Iron is preferred because it is widely available in nature, low cost and non-toxic(Shah et al., 2018b).

Elements such as Mo-Cr (Kleiman-Shwarsctein et al., 2008), Ga (Xiao et al., 2014), Ba-Cd-Sr-Ti (Rahimi et al., 2013), S (Guo et al., 2010), Pd (Wei et al., 2012), Au (Thimsen et al., 2011), Cu (Reddy et al., 2019), Co (Suresh et al., 2017), Ni (Kerli et al., 2019) have been doped to IO by researchers in order to increase their photocatalytic activity.

Increasing bacterial resistance against antibiotics is a global health problem due to the high use of antibiotics today. A promising practice to combat microorganisms is the use of various nanostructures with antimicrobial properties (Arakha et al., 2015). Metal oxide nanostructures can be an effective way to eliminate contamination because of their resistance to microbial agents (Ali et al., 2020). The electrostatic interaction between the charge on the surface and the bacterial membrane transforms the nanostructures into an effective antimicrobial agent (Iqbal et al., 2020).

Many synthesis based on IO and their antimicrobial activity studies have been studied by many scientists. For example, biosynthesis was performed to study the antimicrobial activity of IO and different amounts were studied (Rana et al., 2019; Rufus et al., 2017). In addition, elements such as Si (Arshad et al., 2019), Au (Shams et al., 2019), Mn (Belkhedkar et al., 2016), Ag (Demarchi et al., 2018, 2020; Feng et al., 2019) have been doped to IO and many antimicrobial studies have been conducted. In our study, boron doped iron oxide nano structures (IONS) were synthesized, their photocatalytic effect and antimicrobial properties were investigated.

## 2. Material and methods

### *2.1. Materials and preparation of nanostructures*

By hydrothermal method, $Fe(NO_3)_3.9H_2O$ (Iron(III) nitrate nonahydrate, 99%, Merck), NaOH (Sodium hydroxide, 97%, Merck) and $H_3BO_3$ (Boric acid, 99.5%, Sigma aldrich) chemicals were used for the production of IO and doped IONS. The solutions were adjusted to have a concentration of 0.05 M, and the boron ratio was adjusted to 0%, 10% and 20% relative to iron, and will hereinafter be named to as $Fe_2O_3$, Fe10B and Fe20B, respectively.

The solutions were placed in an autoclave and kept in the oven for 10 hours at 180 °C. The solution was removed from the autoclave and dried at 70 °C. The obtained particles were washed with ethanol and distilled water. The particles were then annealed at 550 °C for 2 hours.

### *2.2. Characterization*

The crystal structure of the particles obtained was measured using the Philips X'Pert PRO brand XRD device. Morphological properties of the particles were observed with ZEISS EVO LS10 scanning electron microscope. UV-vis absorption spectra were detected with a Shimadzu UV-Vis 1800 spectrometer between 240-400 nm wavelengths.

### *2.3. Investigation of photocatalytic degradation*

Optical properties of nanostructures were measured with Shimadzu 1800 spectrophotometer. Ciprofloxacin (CIP) (98%, Sigma-Aldrich) were used to determine the photocatalytic properties. An absorption spectrum scan was taken between 240-400 nm for ciprofloxacin. 300W xenon lamp is used as the light source. Ciprofloxacin solution (10ppm) was prepared for the degradation measurement of each sample. Samples under the xenon lamp were measured every 20 minutes with UV.

Ciprofloxacin solution (10 ppm ) was prepared for the degradation measurement of each sample. 10 mg of particles were added to 50 ml of dyestuff. It was kept in the dark environment for 30 minutes to stabilize. Determined as the maximum absorption was 273 nm for the ciprofloxacin solution.

*2.4. Antimicrobial activities of the IONS*

Preparing and Sowing Strains, Gram-positive for in vitro testing of antimicrobial and antiyeast activity of samples prepared from IO and IO doped nanostructures; *Staphylococcus aureus Rosenbach ATCC-6538, Bacillus cereus ATCC 7064*, gram negative; *Escherichia coli* ATCC-8739, *Salmonella typhimurium* strains were inoculated at Muller Hilton Broth (MHB) and activated by incubating at 37 ± 1 °C for 18 hours.

*Candida albicans ATCC-90028* yeast strain has been inoculated to Malt Extract Broth (MEB). As a medium for antimicrobial activity; Müller Hilton Agar (MHA) was used for bacteria and Malt Extract Agar (MEA) was used for yeast strain. Bacteria in sterile prepared petri dishes were inoculated with 0.5 McFarland standard and incubated at 37 ± 1 °C for 1 hour. After this time, inhibition zones formed on the medium were determined as millimeters (mm) ( Balouiri et al., 2016; Cockerill et al., 2012). The disc containing Amikacin (AK, 30 mg) and Gentamicin (CN, 10 mg) were used for control.

Preparation and Application of Disks from Complexes, The antimicrobial activity of the synthesized particles was determined using the Kirby-Bauer Disc Diffusion Method (Bauer et al., 1966; Murray et al., 2007). 10 mg was taken from the synthesized particles and placed on 6 mm diameter discs. Samples prepared on bacteria cultivated in MHA and yeast strain cultures cultivated in MEA were placed. It was incubated at 37 ± 1 °C for 18-24 ± 2 hours to identify inhibition zones (Balouiri et al., 2016; Cappuccino et al., 2019; Cockerill et al., 2012). The study was performed in three replicates and mean values were given.

## 3. Results and discussion

IO and boron doped IO are synthesized by hydrothermal method. This process was carried out by keeping the prepared solutions in a Teflon-coated steel autoclave at 180 °C for 10 hours. Synthesized nanostructures were filtered then It was dried at 70 °C. It was annealed at 550 °C for 2 hours. Samples were prepared in accordance with the characterization procedures.

The crystal structure of nanostructured particles was measured using the X-Ray diffraction (XRD) device. XRD results of iron oxide(IO) and boron doped IO are shown in Fig. 1. When the XRD results of nanostructured particles are examined, it is compatible with the reference code PDF-2 00-001-1053 and has a Rhombohedral structure.

There is no new and different peak in XRD peaks of boron doped IO particles (Hu et al., 2012). However, it is seen that the peak intensity decreases with the addition of boron. It shows that the boron doping disrupts the lattice of $Fe_2O_3$, causing the crystal structure to deteriorate (Aydin et al., 2012). Various lattice defects and distortions may occur in the crystal lattice when atoms of different sizes are substituted in the lattice structure (Ilican et al., 2011). Some small peaks seen are thought to originate from the hydroxide compounds of iron.

The crystalline size of the nanoscale particles obtained was calculated by using the Eq. (1) (Debye-Scherrer formula).

$$D = \frac{0,9\lambda}{\beta \cos\theta} \tag{1}$$

where: $D$ is the crystal size. $\lambda$ is the X-ray wavelength used (1.5406 Å). $\theta$ is the diffraction angle. $B$ is expressed as the FWHM of the corresponding XRD peak at 2θ. Average crystal sizes were calculated 35nm for $Fe_2O_3$, 31nm for Fe10B and 34nm for Fe20B.

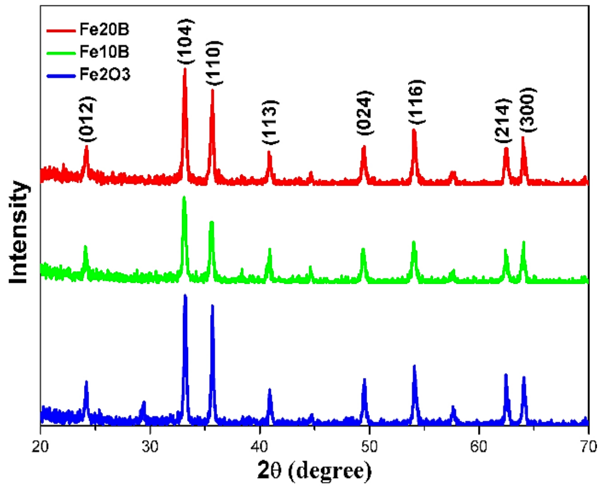


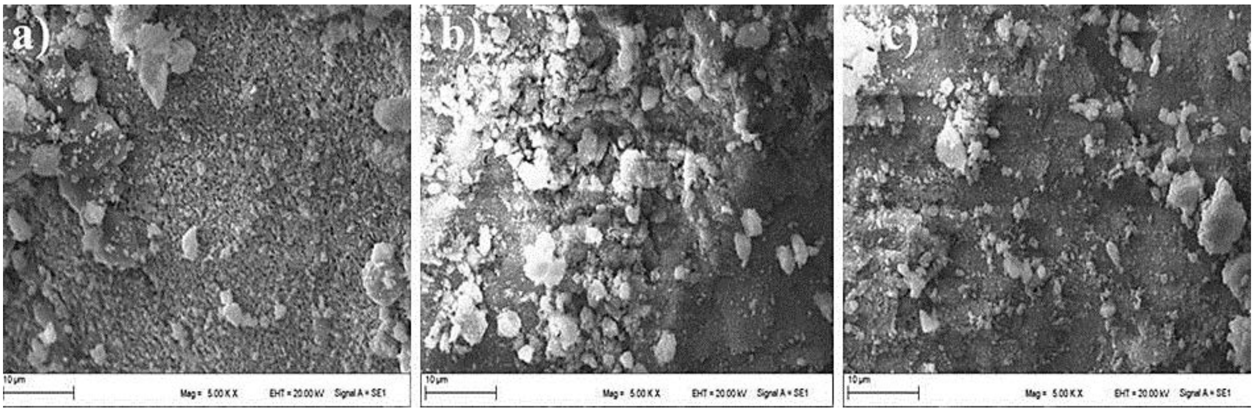

**Fig. 1.** XRD pattern of IO and boron doped IO

SEM images obtained to investigate the surface morphology of nano structures are given in Fig. 2. In SEM images, clustering is observed in some of the samples. These agglomerations are caused by the electrostatic interaction between IONS (Saqib et al., 2019). This may be attributed to the tendency of nanostructures to accumulate due to their magnetic nature (Duman et al., 2019).

The time-dependent photocatalytic degradation of ciprofloxacin for nanostructured particles was examined at room temperature under xenon light. Samples were taken every 20 minutes and scanned in a UV-Vis spectrophotometer in the range of 240-400 nm (Fig. 3). The maximum point in the UV-Vis absorption spectrum was determined by recording decreases in absorbance at 273 nm.

In Fig. 4, after 240 minutes, the degradation of nanostructured particles on ciprofloxacin was found to be about 81% for $Fe_2O_3$, 91% for Fe10B and 87% for Fe20B. In the time-dependent degradation graph in Fig. 4, It is seen that Fe10B performs more degradation compared to other samples. The least degradation was detected in $Fe_2O_3$ nanostructured particles.

In Fig. 5 the fragmentation rate constant is Fe10B, which is the largest.




(a) (b) (c)

**Fig. 2.** SEM images (a) $Fe_2O_3$, (b) Fe10B, (c) Fe20B

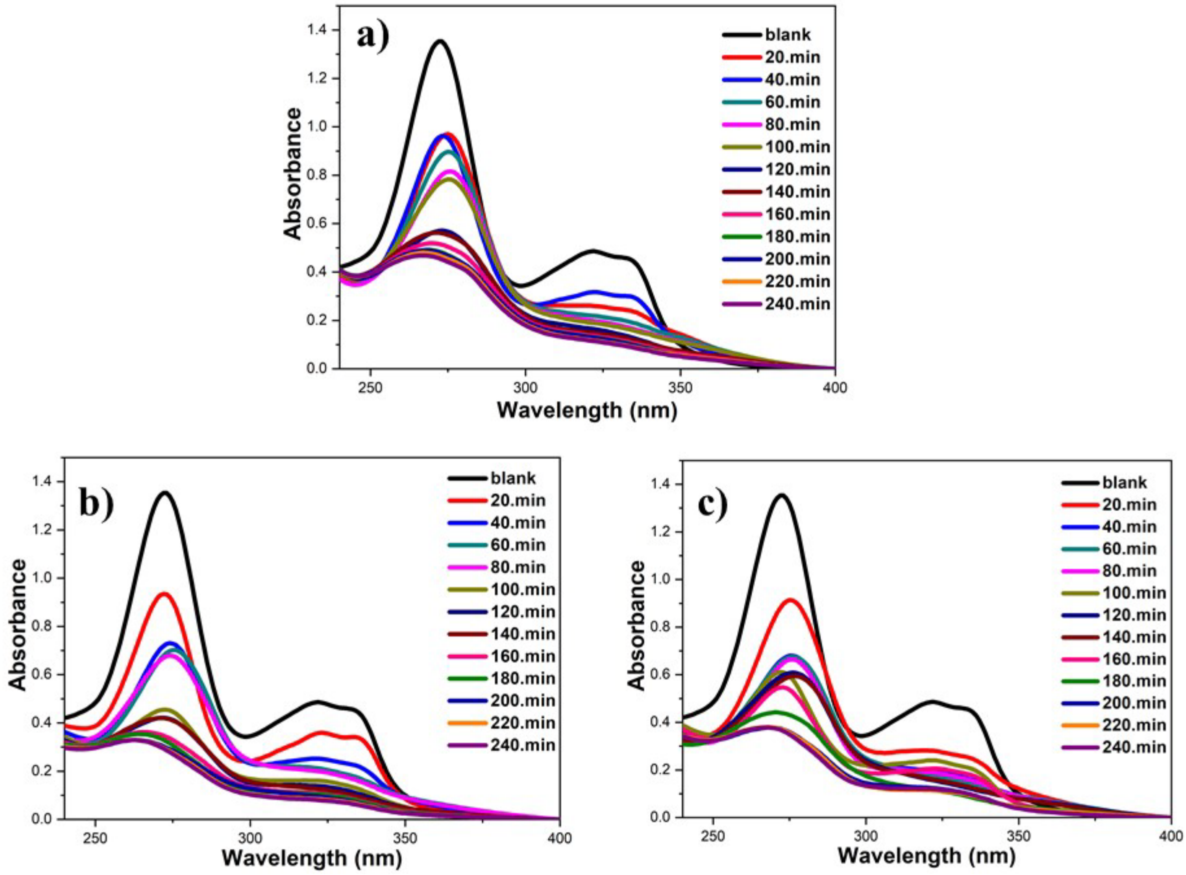



**Fig. 3.** Time-dependent UV–visible absorption spectra for ciprofloxacin in the presence of nanostructures particles, a) $Fe_2O_3$ b) Fe10B c)Fe20B

The speed constant of Fe10B was calculated to be k = 0.01352 $min^{-1}$. This situation overlaps with the degradation chart.

OH, which is a strong oxidizing agent, is thought to create the photocatalytic effect and OH radicals cause pollutants to degrade more quickly. It is thought by many researchers that hydroxyl radicals play a major role in contaminant degradation (Mishra and Chun, 2015). Boron additive can increase the light absorption capacity of $Fe_2O_3$. Boron additive increases the surface area of $Fe_2O_3$ (Hu et al., 2012). Boron addition caused an increase in the amount of degradation on ciprofloxacin. In general, nanostructured particles appear to have a high photocatalytic effect on ciprofloxacin.

Antimicrobial activity of IONS and boron doped IONS was tested. It was determined that Fe20B nanostructures showed high activity against gram-positive bacteria (*Staphylococcus aureus* and *Bacillus cereus*) compared to Amicacin and Gentamicin used as controls. It was observed that IONS does not have antimicrobial activity alone and does not show antiyeast activity against *C.albicans* strain. Moreover, it was observed that IONS alone had no antimicrobial activity and did not show antiyeast activity against the *C.albicans* strain.It is thought that higher bactericidal activity results are obtained due to differences in cell wall structure of gram-positive microorganisms (such as the presence of teichoic acids and lipotechoic acids responsible for adhesion).

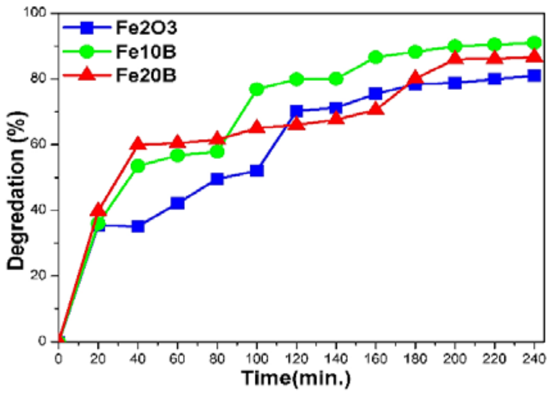



**Fig. 4.** The photocatalytic degradation of ciprofloxacin in the presence of all samples

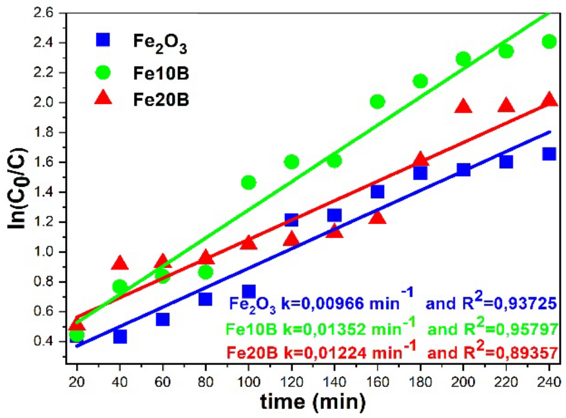



**Fig. 5.** The photocatalytic degradation of ciprofloxacin in the presence of all samples

It can be thought that the higher activity against control is due to the higher adhesion of the boron molecule to the cell wall than the iron molecule (Falk, 2019; Wu et al., 2020; Wang et al., 2021). In our study, it was determined that adding boron contributes positively to antimicrobial.

The MIC value of Ag-γ-$Fe_2O_3$ @ chitosan synthesized nanocomposite material against *E.coli* was expressed as 1.1 mg/L (Kaloti et al., 2016). The antimicrobial activity of the $Fe_3O_4$ / Ag @ nanofibrile cellulose construct has been reported to be 12 mg/L against the *S.aureus* strain (Xiong et al., 2013). In the antimicrobial activity study with $Fe_2O_3$ nanostructures, *P. aerugenosa*, *S. aureus B. cereus* and *S. typhii* strains were used. It was stated in the study that it showed the highest activity as 12 mm against S. typhii strain (Rana et al., 2019). In our study, in the study made from 10 mg sample, it was determined that it has an effect against *S. aureus* and *B. cereus* strains, which are gram negative bacteria. In addition, in similar studies in the literature, researchers said that iron oxide does not have antimicrobial activity (Borcherding et al., 2014; Chatterjee et al., 2011; Madubuonu et al., 2020; Vasantharaj et al., 2019). The schematic representation of the antibacterial mechanism of the samples is shown in Fig. 6.

In a study against S. aereus strain, it was stated that Boron doped nanocomposite shows synergistic effect and gives better results (Wang et al., 2016). In our study, parallel results were obtained. The values of the inhibition zones of the samples are given in Table 1. Although the nanostructures differ, the effect of boron doping is similar. Boron addition has been shown to increase antimicrobial activity.

## 4. Conclusions

In this study, the structural properties of iron oxide and boron doped iron oxide particles were investigated and their photocatalytic and antimicrobial properties were researched. In XRD analysis, it was observed that the boron additive did not cause a significant change in the peaks. The clustering of particles draws attention in SEM images of nanostructured particles.

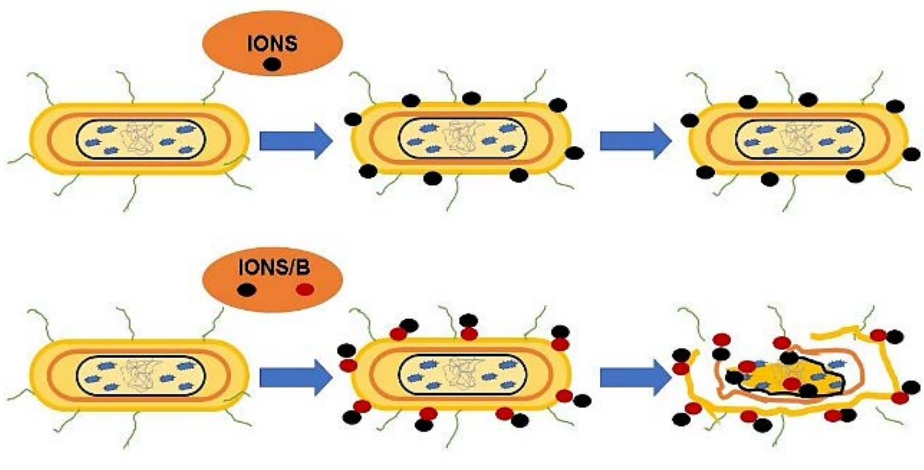



**Fig. 6.** Scheme of the antibacterial mechanism (decorated inspired by (Muhammad et al., 2019b))

**Table 1.** Inhibition zones of samples (mm)

| | *Gram Negative* | | *Gram Pozitive* | | *Yeast* |
|---|---|---|---|---|---|
| ***Samples*** | ***E. coli (1)*** | ***Salmonella typhimurium (2)*** | ***S. aureus (3)*** | ***Bacillus cereus (4)*** | ***Candida albicans (5)*** |
| **$Fe_2O_3$** | 0 | 0 | 0 | 0 | 0 |
| **Fe10B** | 0 | 0 | 12 | 10 | 0 |
| **Fe20B** | 0 | 0 | 16 | 16 | 0 |
| **Amicasin** | 16 | 18 | 18 | 22 | 0 |
| **Gentamicin** | 12 | 18 | 18 | 16 | 0 |

In photocatalytic experiments, it was observed that the particles have high photocatalytic degradation rates. In investigations on ciprofloxacin, it has been observed that boron doping increases photocatalytic degradation. In addition, as a result of the antimicrobial activity studies of the particles, it has been determined that the boron doping contributes positively to the antimicrobial activity.

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