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The ultrasonic process with titanium magnetic oxide nanoparticles to enhance the amoxicillin removal efficiency

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ABSTRACT

The widespread use of antibiotics and their subsequent release into the environment has caused concern around the world. Incomplete metabolism releases these chemicals into the environment, and traditional purification systems are unable to remove them. As a result, it lingers in the environment and is one of the most serious environmental issues confronting public health. The goal of this study was to investigate the possibility of using ultrasonic and titanium dioxide nanoparticles as catalysts for the removal of amoxicillin from aqueous solutions, as well as to figure out the optimal conditions to maximize the efficiency of removal efficiency. Decomposition of amoxicillin in water in the presence of titanium magnetic catalyst with concentrations of 0.1, 0.25, 0.5, 1, and 2.5 g/L and amoxicillin concentrations of 1, 10, 25, 50, and 100 mg/L at different times of 10 to 180 minutes, pHs of 3, 4, 5, 7, 9 and 11, temperatures of 10 to 60 ºC and frequencies of 35, 300, and 700 kHz were examined. At a concentration of 1 g/L catalyst, a concentration of 10 mg/L amoxicillin, a standstill duration of 60 minutes, an acidic pH, a temperature of 40 °C, and a frequency of 35 kHz, the maximum removal of amoxicillin (91.7%) occurred. The use of an ultrasonic method in conjunction with titanium magnetic nanoparticles as an oxidizing agent proved to be a successful tool for lowering amoxicillin concentrations in aqueous media. As a result, advanced oxidation processes, particularly ultrasonic, can reduce pharmaceutical and organic contaminants in the environment.

Keywords: *Pharmaceutical contaminants, Water pollution, Advanced oxidation, Purification.*

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INTRODUCTION

Drugs are a large group of emerging pollutants and the presence and concentration of these pollutants in the environment is a serious threat to the environment. These pollutants accumulate in the environment mainly due to their stability, resistance to biodegradation, and low biological excretion, and do not decompose under normal conditions. In addition, the medicine must have a high solubility in water to be absorbed by the target cells in the living organism. Hence, drugs have inherently strong biological activity that affects living organisms [1]. Therefore, the existence and fate of medicinal compounds in the environment, especially in aquatic environments, has become one of the most important issues in the field of environmental pollutants. Meanwhile, antibiotics are being used more frequently due to their quantity, accessibility of supply, and therapeutic applications in human and animal diseases. Therefore, they can be found in wastewater, natural waterways, surface water, and groundwater [2].

Despite the low concentrations in the environment (nanograms per liter to micrograms per liter), the continuous and stable entry of

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antibiotics into aquatic ecosystems, and bacterial resistance generated by them and their metabolites, these drugs have become one of the most important environmental issues in the world [3]. Today, municipal, hospital and industrial wastewater, effluents, and solid waste are known as the main sources of drugs entering the aquatic environment. More than 80 different types of environmentally friendly drugs have been found in concentrations up to micrograms in the effluents of wastewater treatment plants, surface water, groundwater, and drinking water [4]. Among these, penicillins are one of the most important groups of antibiotics that are used in medicine and veterinary medicine as food additives and make up 70% of the antibiotics used in many countries around the world. Penicillins include amoxicillin, ampicillin, bacampicillin, epicillin, and metampicillin, which are among the most widely used antibiotics [5].

Amoxicillin is a beta-lactam antibiotic that is active against a wide range of gram-negative and positive bacteria and is used to treat bacterial infections in respiratory, urinary, gastrointestinal, and skin infections. Amoxicillin is also used to treat and prevent animal infections, as well as to stimulate the growth of veterinary animals such as fish and cattle [6]. One of this antibiotic's properties is its high instability, which is caused by hydrolysis and rapid decomposition into a variety of compounds, which can have many adverse effects [7].

Due to their strong complexes, most of the drugs used are non-biodegradable, and conventional wastewater treatment processes such as membrane filters, ion exchange, coagulation, flocculation, and oxidation are ineffective in removing them. This is especially true because conventional treatment methods usually result in other environmental issues by producing significant amounts of sludge [8]. In the recent decade, advanced oxidation processes (AOPs) have been used as a suitable high-efficiency procedure for the treatment of hazardous chemicals with limited degradability in groundwater, surface water, and wastewater. Methods used in AOPs include ultrasonic waves, electro-Fenton, photo-Fenton, ozonation, UV/ozone, electro/persulfate, ultrasonic/persulfate, photocatalytic, etc. The formation of free radicals with strong oxidizing power, great efficiency in breaking down organic materials, inexpensive start-up and operational costs, and a diversity of ways are all advantages of these processes [9]. AOPs lead to the formation of hydroxyl radicals as the primary oxidant. Oxidizing agents like H_2O_2 and O_3, ultraviolet, ultrasonic, and homogeneous or heterogeneous catalysts are used to create these radicals.

Nowadays, ultrasonic technology can be utilized to eliminate organic contaminants from water and wastewater. Many complicated chemical molecules are decomposed into considerably simpler ones when this method is used. Ultrasonic radiation has several advantages, including the absence of any cancerous products, the lack of odor and taste, the elimination of the need to use and store hazardous chemicals, and the need for ultrasonic units to be installed in a small space, all of which have expanded its application [10]. A cavitation process occurs during ultrasound irradiation, which could induce a large number of small bubbles at specific frequencies and intensities of ultrasonic waves. The formation, oscillation, growth, contraction, and collapse of bubbles lead to hot spots and pressure in a very small space inside and around the cavity. These conditions destroy water molecules and H_2O_2; On the other hand, H^o and OH^o radicals with considerable oxidative activity are produced, which could degrade a variety of organic compounds in solution [11].

By adding catalysts to the ultrasonic process, degradation efficiency can be improved. The production of extra nuclei enhances the rate of cavitation bubbles when a catalyst is added. Ultrasonic radiation, on the other hand, can excite the catalyst and form electron-hole pairs. These synergistic effects increase the speed and efficiency of pollutant degradation. Among the existing catalysts, TiO_2 is a very essential catalyst due to its unique properties such as high specific surface area, strong oxidation capability, high stability, and the fact that it has two band gaps: anatase (3.2 eV) and rutile (3.0 eV). However, the high rate of electron-hole recombination and the resulting huge band gap could be limiting factors [12]. To control this limitation, the recombination rate can be reduced by doping metal elements such as Fe_3O_4. On the other hand, since iron has magnetic properties, it could assist in nanoparticle recycling in addition to enhancing oxidation properties [13].

The goal of this study was to use a two-component Fe_3O_4/TiO_2 catalyst in the sonocatalyst technique to improve amoxicillin removal efficiency. The hybrid catalyst has excellent efficiency for eliminating organic pollutants due to its low electron-hole recombination rate, the efficiency of separation and charge transfer, high surface area, and high oxidation capability. The pH, temperature, frequency, time, and concentrations of titanium dioxide and amoxicillin were also optimized to improve amoxicillin removal. A magnet could also be used to recycle the produced catalyst.

MATERIALS AND METHODS

Raw materials and equipment

99% pure amoxicillin, sodium dodecyl sulfate (SDS) ($NaC_{12}H_{25}SO_4$), iron chloride ($FeCl_2.4H_2O$), titanium tetra butoxide, hydrochloric acid, and sodium hydroxide were purchased from Sigma Aldrich. The equipment used includes a pH meter (Istek, 915PDC), spectrophotometer (Bio spec-1601), and ultrasonic device (PARSONIC 7500 S, 220 VAC).

Synthesis of nanoparticles

Synthesis of Fe_3O_4 magnetite nanoparticles

A solution of 0.625 percent (weight/volume) SDS, a solution of 0.5 M sodium hydroxide, and a solution of iron chloride (5 g/l Iron) were first produced at room temperature for manufacturing magnetite nanoparticles. The iron chloride solution was then gently mixed into the SDS solution, drop by drop. At 80 rpm, the solution was stirred for 30 minutes. Sodium hydroxide was used to alter the pH of the solution to between 11 and 12. The solution was then agitated at 120 rpm for an hour. The resulting black solid was rinsed with distilled water many times before being dried at 40 degrees Celsius. The resultant material was pounded in a mortar and then soaked for 15 minutes in a 0.1 M sodium hydroxide solution. Finally, it was washed several times with distilled water and dried at 40 °C until Fe_3O_4 magnetite nanoparticles were obtained [1].

Synthesis of Fe_3O_4/TiO_2

The sol-gel technique was used to synthesize Fe_3O_4/TiO_2. 0.3 g of magnetite nanoparticles were dissolved in 60 ml of ethanol without water at this point, and 14 ml of titanium tetrabutoxide was gently added to it. The mixture was placed in a mixer and swirled at 600 rpm for three hours. It was then magnetized and washed multiple times with distilled water and ethanol before being dried for one hour at 450°C [14].

Optimization of the examined parameters

The method of optimizing one factor at a time was adopted. The study parameters include pH (3, 5, 7, 9, and 11), ultrasonic time (10, 30, 60, 90, 120, and 180 minutes), ultrasonic frequency (35, 300 and 700 kHz), temperature (10, 20, 40, 50, 60 °C), amoxicillin concentration (1, 10, 25, 50, and 100 mg/l), and catalyst concentration (0.1, 0.25, 0.5, 1, and 2.5 g/l). The pH of the solution is changed with 0.01 M HCl and NaOH. One parameter was changing in each stage, while the others remained constant. The solution is sampled at the necessary times following the ultrasonic procedure, and the samples are processed for reading by passing them through Whatman 0.45 filter paper. A spectrophotometer is used to determine the concentration of amoxicillin. Finally, the best values for each parameter were found, and amoxicillin elimination was achieved under ideal conditions.

Evaluation of amoxicillin removal efficiency

A spectrophotometer with a wavelength of 230 nm was used to determine the concentration of amoxicillin. Standard amoxicillin solutions were first made, and then the amoxicillin calibration curve was developed based on the absorption rate and specificity of the drug content. Finally, the amoxicillin removal efficiency was determined as follows [15]:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

where in:

R = Contaminant decomposition efficiency in solution (percentage)

C_0 = initial concentration of contaminant in solution (mg/L)

C_e = final concentration of contaminant in solution after decomposition (mg/l)

RESULTS AND DISCUSSION

Properties of synthesized nanoparticles

XRD analysis: XRD patterns of Fe_3O_4 nanoparticles, TiO_2 nanoparticles, and titanium magnetic oxides are shown in Fig. (1a). As can be seen, these nanoparticles have a crystalline structure with TiO_2 nanoparticles with 2θ equal to 25.16°, 37.88°, 48.67°, 54.35°, 55.18°, and 63.73°, which correspond to Miller indices (101), (112), (200), (105), (211), and 204, respectively, indicating an anatase structure [9]. Also, 2θ equals 30.23°, 35.58°, 43.13°, 54.53°, 57.18°, and 62.63° belong to Fe_3O_4 nanoparticles which are related to crystal

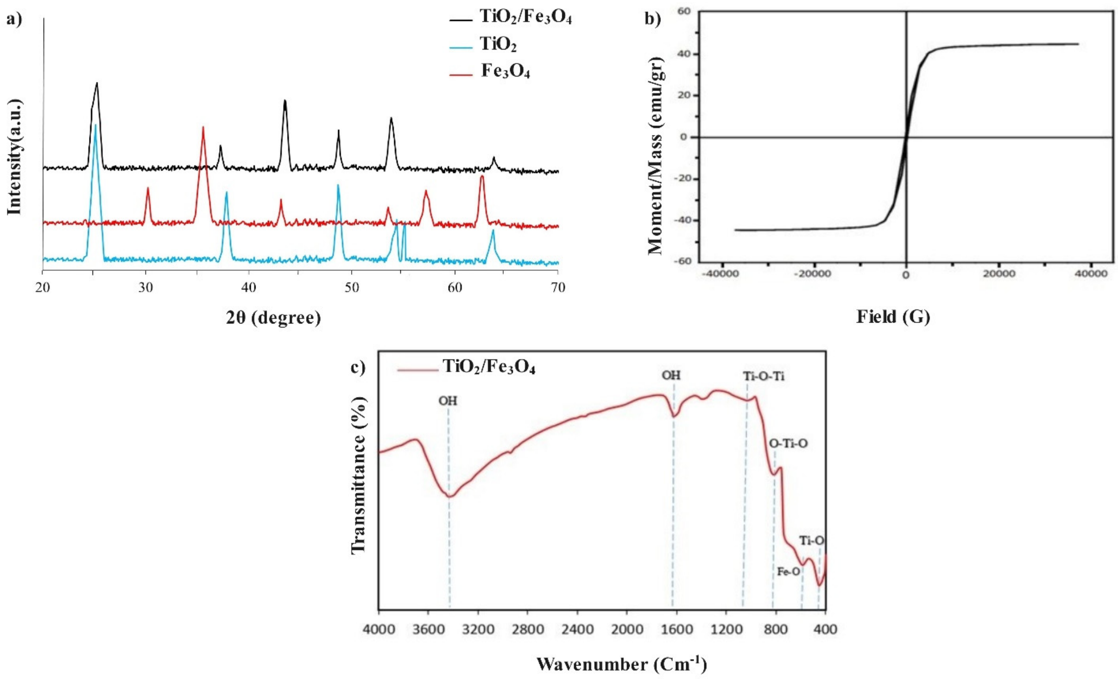

Fig. 1. a. XRD Patterns b. VSM pattern, c. FT-IR pattern of Fe_3O_4/TiO_2 nanocomposite

planes (220), (311), (400), (422), (511) and (440) respectively [8]. The Fe_3O_4 and TiO_2 phases in the structure of the Fe_3O_4/TiO_2 magnetic composite are represented by the 2θ equal to 25.28°, 37.25°, 43.53°, 48.73°, 53.83°, and 63.78 peaks.

VSM analysis: The magnetic characteristics of Fe_3O_4/TiO_2 nanocomposites were estimated using the VSM model, as shown in Fig. (1b). The synthesized nanocomposite, according to this study, has soft magnetic characteristics and exhibits superparamagnetic behavior in the presence of a magnetic field [8]. The photograph does not show any magnetic residual effects or phenomena. Furthermore, the composite's greatest magnetic saturation is 44.56 (emu/g) [16].

FT-IR analysis: The results of FT-IR analysis show that peaks at 3439 and 1627 cm^{-1} correspond to tensile and flexural vibrations of the OH group, respectively (Fig. 1c). The bond vibrations in the range of 458 and 817 cm^{-1} are Ti-O tensile vibration bonds and O-Ti-O flexural vibration bonds, respectively. In the 1029 cm^{-1} peak, Ti-O-Ti tensile vibration bands have also been found [14]. The Fe-O bond is shown by the spectra in the 586 cm^{-1} range, confirming the existence of Fe_3O_4 nanoparticles in the structure of this composite.

Investigation of parameters affecting the amoxicillin degradation

Effect of ultrasonic process on degradation efficiency

Because the physical effects and amount of OH° formation can vary depending on the ultrasonic frequency, it's critical to examine the effects of ultrasonic frequency on the oxidative elimination of organic contaminants [18]. The size of the cavitation bubbles increases as the frequency lowers. Until the crucial resonance level is reached and the explosion occurs. This explosion produces tremendous pressure and temperature, which shatters the covalent link of water, and produces OH°. Amoxicillin can be degraded by free OH° points and built-in hotspots. As a result, at ideal frequency, ultrasonic oxidation of organic matter can be significantly increased [9]. The ultrasonic frequency effect was got in this work by sonocatalytic oxidation of amoxicillin at frequencies of 35, 300, and 700 kHz for 180 minutes. To evaluate the effect of sonochemical frequency of 25 mg/l amoxicillin at pH 7 and concentration of 0.5 g/l titanium dioxide magnetic catalyst at 30 °C was used and the results are presented in Fig. (2a).

The fixed amoxicillin removal rates for sonocatalysis were 91.23, 88.64, and 76.21,

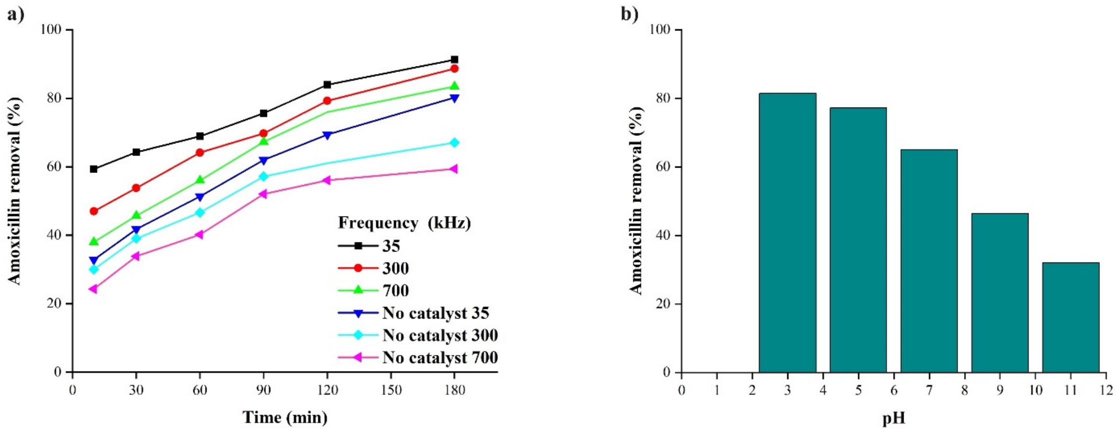

Fig. 2. a. Effect of ultrasonic frequency b. Effect of pH on amoxicillin removal

respectively, for 35, 300, and 700 kHz (US frequency). At 35 kHz, the maximum amoxicillin oxidation rate was achieved. On this basis, it can be deduced that amoxicillin removal is dominated by OH° generation. The removal efficiency rises with time in all treatments, as shown in Fig. (2a), with the highest removal occurring after 180 minutes. Experiments with and without catalysts at a frequency of 35 kHz indicated a higher removal rate than frequencies of 300 and 700 kHz at all times investigated.

As shown in Fig. (2a), the rate of amoxicillin degradation increased with the addition of catalysts at frequencies of 35, 300, and 700 kHz. The low removal rate in the presence of ultrasonics without the use of catalysts is due to the low production rate of OH° free radicals in the presence of ultrasonics alone. In the attendance of ultrasonic waves, the only source of OH° free radicals is water sonolysis, which is as follows:

1) $H_2O + US \rightarrow H^\circ + OH^\circ$

2) $H^\circ + O_2 \rightarrow 2HO^\circ$

Amoxicillin's decomposition power is minimal under these conditions since the number of radicals created during this process is negligible. As a result, the higher the solution's ion strength, the more effective the ultrasonic process is at removing contaminants. Because the ions in the solution can behave as free radical accelerators because of water sonolysis [17]. The results showed that the lower the frequency, the higher the ionic strength of the solution. As a result, the ultrasonic process is more efficient at removing pollutants, which is consistent with other studies. Low ultrasonic radiation has a higher energy content, which causes the activation of the synthesized catalyst. The ions produced during the induction of ultrasonic radiation act as cavitation nuclei, increasing the ultrasonic process' efficiency [18].

Effect of pH on degradation efficiency

The pH of the aqueous phase is critical in the sonolysis or sonocatalyst process, and it can lead to complicated consequences since it affects OH° production, pollutant characteristics, and particle aggregation. Because all catalytic reactions take place on the surface, the adsorption of target pollutants on the catalyst surface is a critical factor that is mostly determined by the catalyst's isoelectric pH and the pollutant pKa. Also, one of the most critical parameters impacting the efficiency of chemical and biological processes, particularly in advanced oxidation processes, is pH [19]. In the advanced oxidation process, pH can affect the rate of amoxicillin decomposition. The difference in amoxicillin degradation in the initial concentration of 25 mg/l amoxicillin, 0.5 g/l TiO_2, and pHs (3, 5, 7, 9, and 11) was identified and investigated in this work. The effect of different pHs can be explored by determining the point of zero charges (pzc), the pH at which the net charge of the total particle surface is equal to zero. In this experiment, the pHpzc was found to be 7.2. As shown in Fig. 2b, the rate of amoxicillin removal changes with pH, and the rate of degradation at an acidic pH (pH = 3) is higher than at an alkaline pH. The removal rate of amoxicillin at pH 3 is 81.43.

pH impacts the oxidation of organic materials and the rate of chemical processes directly and indirectly by creating free radicals. Due to the reduced oxidation potential of hydroxyl radicals as pH increases, the rate of amoxicillin removal reduces; thus, high concentrations of H^+ ions in acidic conditions result in the production of H^o radicals. H^o creates HO_2° radicals from oxygen in solution, which are then transformed into OH^o radicals. The formation of insoluble compounds reduced the intensity of sonolysis and hydroxyl radicals, reducing the rate of amoxicillin degradation at pH 11. It has also been reported that in acidic conditions, the aggregation of titanium dioxide magnetic particles diminishes compared to neutral conditions, increasing the effective surface area of the catalyst and potentially boosting sonocatalytic degradation [20]. The creation of hydroxyl radicals is the basis of advanced oxidation processes; however, at higher pHs, H_2O_2 decomposes quickly, decreasing free radical formation. Also, the effect of pH on the degradation of amoxicillin depends on its PKa value. The amount of amoxicillin PKa is 2.75. As a result, it will often be molecular in acidic liquids. The bubble transfer area, where there is a high concentration of OH^o, is where most molecular forms are directed.

According to Villaroel et al., acetaminophen in acidic solutions with a PKa of 9.5 is in molecular form and has a higher degradability, which is compatible with the findings in this study[21]. The study also indicates that when the pH of the solution falls, the decomposition of the compounds increases, which is due to an increase in hydrophobicity in an acidic environment [22]. Tan et al. also reported that $Fe_3O_4@TiO_2$ in an acidic environment with a pH of 6 caused the maximum uranium uptake [23]. The fact that amoxicillin molecules are positively charged in acidic conditions causes them to accumulate in the negatively charged liquid-bubble interphase, where the concentration of active radicals and temperature is higher, leading to an increase in amoxicillin removal. As a result, a larger rate of removal occurs [24].

Effect of temperature on degradation efficiency

Experiments were carried out at 5 different temperatures in the range of 10 to 60 °C at a constant value of other parameters (pollutant concentration: 25 mg/L, TiO_2 magnetic oxide catalyst concentration: 0.5 g/L, and time: 90 minutes) to investigate the effect of temperature on amoxicillin degradation, and the optimized value of frequency and pH were also used. The removal rate increased with rising temperature, especially from 10 to 40 °C, but there was a consistent trend in removal from 40 to 60 °C, according to the results given in Fig. (3a). Increasing the temperature significantly increases cavitation intensity and decreases amoxicillin concentration. As the temperature goes up, the water vapor pressure rises, resulting in the formation of additional cavitation bubbles. The concentration of hydroxyl radicals is reduced when the bubble bursts at a lower temperature, reducing pollutant degradation [25]. At temperatures below 25 °C, cavitation bubbles form and have a lower density. At higher temperatures, the reaction improves for compounds with low solubility. Because organic molecules are moved from the solution to an area with a high hydroxyl radical concentration, the rate of breakdown of organic compounds is directly related to temperature.

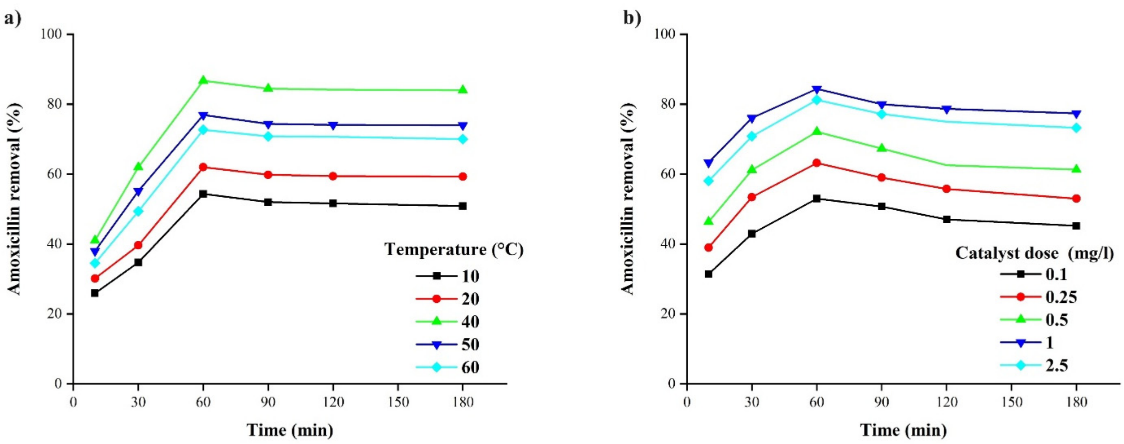

Fig. 3. a. Effect of temperature b. Effect of TiO_2 magnetic catalyst concentration on amoxicillin removal

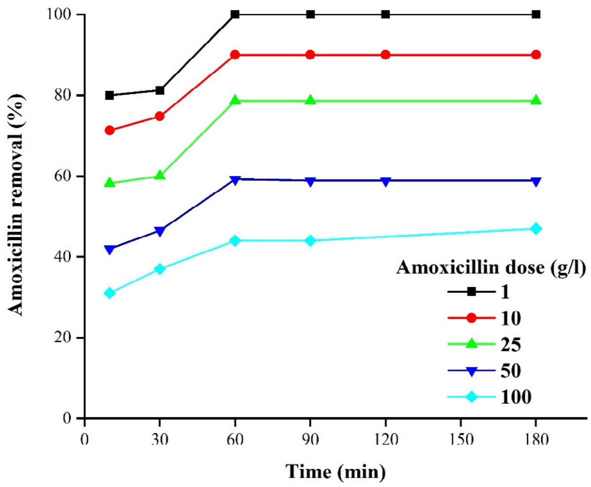

Fig. 4. Effect of amoxicillin concentration on removal efficiency

Investigation of the effect of titanium dioxide magnetic catalyst

The presence of a catalyst can speed up the decomposition of water molecules, resulting in more free radicals and hence a faster rate of organic compound degradation. The concentration of TiO_2 during the ultrasonic process was changed from 0.1, 0.25, 0.5, 1, and 2.5 mg/l to evaluate the effect of the TiO_2 magnetic catalyst on the sonication degradation of amoxicillin. The removal efficiency of amoxicillin increased with increasing catalyst concentration at 180 minutes, frequency of 35 kHz, and pH 3, and it was discovered that the removal efficiency of amoxicillin improved with increasing catalyst concentration. At a concentration of 1 g/l catalyst, 84.39 percent of amoxicillin was removed in 60 minutes of sonolysis. During the sonolysis process, the rate of amoxicillin breakdown rises when magnetic TiO_2 particles are present. The removal of amoxicillin increased with increasing catalyst exposure duration (10–60 minutes) in this investigation, as seen in Fig. (3b), possibly due to increased cavitation activity. Ultrasound is commonly used as an activation energy source. Nanoparticles tend to accumulate due to their high specific surface area and energy, however, ultrasonic waves cause them to scatter rather than accumulate. When the concentration of nanoparticles exceeds a particular value, however, ultrasonic vibrations are insufficient to deflect them, therefore the removal efficiency is proven by adding more TiO_2 [24]. Excessive concentrations of TiO_2 magnetic particles also generate interactions that prevent some organic pollution molecules from receiving ultrasonic wave energy. Contact with the base catalyst, as well as the aggregation and deposition of nanoparticles, have been shown in some experiments to inactivate activated nanoparticles when their concentration exceeds a particular threshold. Nadeo et al. also stated that the addition of TiO_2 magnetic catalyst increases the antibiotic removal efficiency to a certain extent and then proves that it is consistent with the results of the present study [26].

Investigation of the effect of amoxicillin concentration

For initial concentrations of 1, 10, 25, 50, and 100 mg/l of amoxicillin, the effect of amoxicillin concentration on the rate of sonocatalytic degradation in 1 g/l of TiO_2 magnetic nanoparticles, frequency 35 kHz, and pH 3 was investigated. The effect of drug concentration on the rate of sonolysis is shown in Fig. (4). As can be observed, the relative percentage of degradation decreases as the initial concentration rises, but the degree of degradation increases as well. At a concentration of 10 mg/l of amoxicillin, the maximum removal efficiency was 91.7 percent, while the efficiency at concentrations of 1, 25, 50, and 100 mg/l was 100, 80, 61.9, and 46 percent, respectively. The reason for this increase in decomposition efficiency by reducing the initial concentration of amoxicillin is that the concentration of hydroxyl radicals in the solution remains constant under the same conditions; thus, the reaction of amoxicillin with hydroxyl radicals is higher at low concentrations, increasing amoxicillin degradation by free radicals. In addition, when the concentration of the primary solution rises, the intermediate products created compete for free radicals with the raw materials, reducing the rate of degradation [27]. According to studies, the lower the drug concentration, the higher the sonolysis reaction and oxidative generation in the solution, as well as the initial degradation rate, which is compatible with the findings of this study. At low concentrations, sonocatalytic breakdown of the medication is increased due to OH attack in the liquid bubble [28]. Serna-Galvis et al. found that the generation of hydrogen peroxide diminishes with increasing contaminant concentration in sonocatalytic degradation studies of the pharmacological composition fluoxetine [29]. When the contaminant concentration is higher, however, the fluoxetine molecules approach the bubble cavities and react with OH.

Effect of time on degradation efficiency

One of the variables affecting the oxidation process's performance is reaction time. Optimizing reaction time helps save money and energy. The results (Figs. 3 and 4) show that the removal percentage was incremental for the first 60 minutes of the experiment, and then there was no change. Increasing the reaction time allows more hydroxyl radicals to be produced, resulting in greater contact between these radicals and antibiotics, resulting in more amoxicillin degradation. The number of products produced by the catalytic reaction in the aqueous medium rises as the active sites for antibiotic absorption change over time, increasing the removal efficiency [7]. It costs a lot of money and energy to keep reacting for a long time so the optimum time is 60 min. Villegas-Guzman et al. [30] found that practically all pollutants are removed after 180 minutes of treatment in a study of the sonochemical degradation of the antibiotic dicloxacillin. They introduced 480 minutes of activity as environmentally acceptable while identifying 180 minutes as the optimal period.

Comparison of amoxicillin removal rate in different processes

The removal efficiency of amoxicillin utilizing TiO_2 magnetic nanoparticles, ultrasonic, and sonocatalytic methods is shown in Fig. (5). There are various techniques for the removal of pollutants in catalytic oxidation processes, as shown in this diagram. The performance of different methods under similar conditions was tested to determine the effectiveness of each agent on amoxicillin removal efficiency. Table 1 also compares the research results with other studies. The lowest removal efficiency of the ultrasonic process alone and without the use of a catalyst was 35.93 % after 180 minutes of reaction, demonstrating that sonolysis has a low oxidation potential in the removal of amoxicillin. TiO_2, Fe_3O_4, and TiO_2/Fe_3O_4 nanocomposites had removal efficiencies of 42.08 %, 50.3 %, and 56.9 %, respectively, owing to the adsorption procedure. When compared to TiO_2 and Fe_3O_4 nanoparticles, the high performance of TiO_2/Fe_3O_4 demonstrates a synergistic impact between TiO_2 and Fe_3O_4. It also demonstrates that TiO_2 loading on Fe_3O_4 nanoparticles provides an

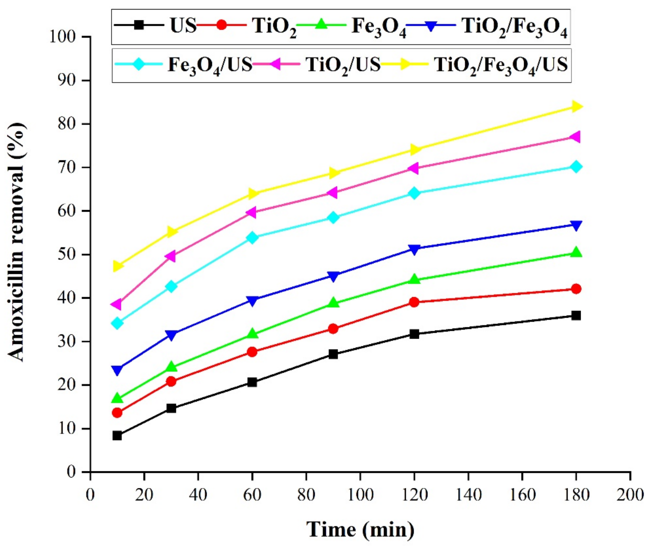

Fig. 5. Comparison of processes performed in the removal of amoxicillin under optimal conditions

Table 1. Comparison of research results with other studies

Method	Catalyst Type	Removal percent (%)	Refrences
Sonolysis	ZnO	46.87	32
Adsorption	carbon nanotubes	86.5	33
Photocatalyst	TiO_2	61	34
Photocatalyst	$CuI/FePO_4$	90	35
Photocatalyst	MIL-68(In)-NH_2/GrO	80	36
Sonocatalyst	ZnO@Fe_3O_4	90	37
Sonocatalyst	TiO_2/Fe_3O_4/US	84	This work

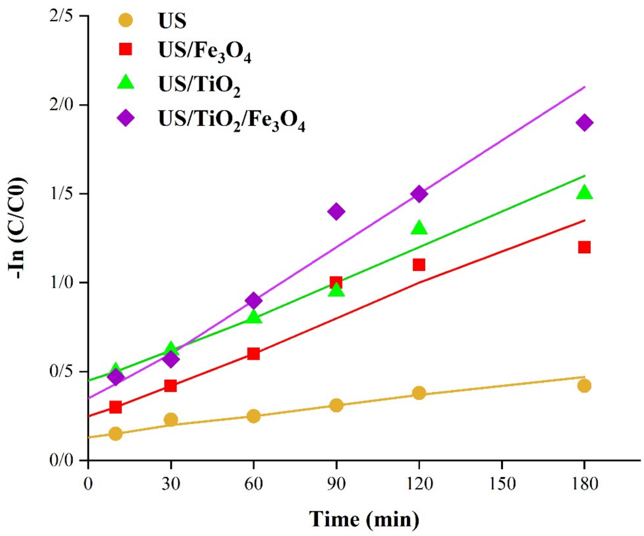

Fig. 6. Analysis of amoxicillin degradation kinetics

excellent adsorption ability for the synthesized composite to absorb amoxicillin, which could be useful in the sonocatalytic process.

The amount of amoxicillin removed by sonocatalysis processes is more than the amount received for the sonolysis process, as illustrated in Fig. (5). This significant difference can be indicated by the fact that more reactive radicals are created during sonocatalysis than during sonolysis alone when amoxicillin is degraded [31]. Fig. (5) shows that removing amoxicillin with Fe_3O_4 nanoparticles and ultrasonic (US/Fe_3O_4) increased greatly to 70.19 %, which is connected to the contribution of degradation and adsorption in amoxicillin removal. When compared to Fe_3O_4/US, TiO_2/US enhanced the percentage of amoxicillin removal at the same time, reaching 77.04 %, after 180 minutes. When the solution was subjected to TiO_2/Fe_3O_4/US, the greatest removal effectiveness (84%) was found. This suggests that the agents used to degrade amoxicillin and those employed to create reactive oxidants have a synergistic impact. The TiO_2/Fe_3O_4/US system's superior performance compared to other processes demonstrates that the synthesized catalyst has high catalytic activity in the production of reactive species in the presence of ultrasonic waves and can play an important role in the sonocatal degradation of organic matter through the formation of reactive species. As a result, bonding TiO_2/Fe_3O_4 and ultrasonic are viable strategies for producing free radicals and thus pollutant degradation. Fig. 4 also shows that the removal efficiency of amoxicillin increases with increasing contact time in all procedures, particularly sonocatalytic processes. Because of the high rate of sonocatalytic breakdown of amoxicillin caused by longer contact duration, more hydroxyl radicals are produced, as well as more electron holes are formed [11].

Kinetics of amoxicillin sonocatalytic degradation

Kinetic experiments of amoxicillin degradation were performed under pH = 3, with a concentration of 10 mg/l amoxicillin for 180 minutes in different processes (Fig. 6). The results reveal that the sonolysis process and the three sonocatalytic processes of amoxicillin follow first-order kinetics,

Table 2. Kinetic coefficients of sonocatalytic degradation of amoxicillin during different processes

processes	pH	Concentration of amoxicillin (mg/l)	k (min^{-1})(Constant)	R^2
US	3	10	0.0023	0.9159
US/ Fe_3O_4	3	10	0.0065	0.9386
US/ TiO_2	3	10	0.0076	0.9558
US/ TiO_2/ Fe_3O_4	3	10	0.009	0.9809

which agrees with the findings of Norzaee et al. [38]. The degradation of amoxicillin in various processes also shows that with the inclusion of a catalyst, the rate constant (k) increases, going from 0.0023 (min^{-1}) in the US process to 0.0099 (min^{-1}) in TiO_2/Fe_3O_4/US (Table 2).

CONCLUSION

Although medications are beneficial to creatures' health, their release into wastewater and the environment without treatment and care will have negative implications for humans and other organisms. Most researchers are currently attempting to develop practical yet economical strategies for treating industrial wastewater. The sonocatalyst process is an environmentally friendly way of reducing wastewater pollution and destroying dangerous contaminants. In this study, the possibility of degradation and removal of amoxicillin from aqueous solutions by an ultrasonic process was studied using a titanium oxide magnetic catalyst. The optimal amount of amoxicillin removal from aqueous solution at pH 3, temperature 40 °C, time 60 minutes, titanium oxide magnetic catalyst concentration 1 g/liter, and the beginning concentration of the pollutant 10 mg/L was determined based on the results of this study. The results demonstrate that adding catalysts improves degrading efficiency. When the solution was exposed to TiO_2/Fe_3O_4/US, the highest degree of degradation was found, with an 84 % removal efficiency. According to the findings of this study, the sonolysis process is an excellent method for purifying water from organic pollutants, particularly antibiotics, however, it is not economically viable by itself. As a consequence, using catalysts like TiO_2 and Fe_3O_4 improves degradation efficiency dramatically.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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