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SOLAR PHOTOCATALYTIC DEGRADATION OF METRONIDAZOLE ANTIBIOTIC BY BIO-SYNTHESIS TIO_2 FROM AQUEOUS SOLUTION: EFFECT OF SOLAR INTENSITY AND PH

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Abstract
Biosynthesis of nanomaterials has piqued the interest of current researchers due to its low toxicity, reproducibility, environmentally friendly, economic viability, and low energy consumption. In this direction, for the first time, a biosynthesis titanium dioxide (TiO_2) nanoparticle was carried out by using Orange leaves (O-TiO_2) as reducing agents to synthesize TiO_2 from titanium (IV) isopropoxide (TTIP). Furthermore, the effectiveness of synthesized catalyst O-TiO_2 for degradation Metronidazole (MTZ) residue from aqueous solution was studied for the first time by changing different initial parameters such as pH (3, 5, 7, 9, and 11), and solar intensity while keeping other parameters constant 15 mg/L of MTZ initial concentration, 30mg/L of O-TiO_2 concentration, 200 mg/L of H_2O_2 concentration, and, and the results confirm the effectiveness of O- TiO_2 to remove MTZ as that of commercial TiO_2 and the maximum removal percentage was achieved to be 89.12% Its usage as a catalyst is viable because of its low cost and great output rate.
Keywords: Biosynthesis TiO_2; Orange leaves; Photocatalyst batch process; Metronidazole degeneration;

1. Introduction
Global climate change and population growth have put pressure on water supplies. New measures are needed to minimize the growing challenges to water sustainability. Reuse/recovery of treated wastewater generates a new resource while protecting current water supplies. Urban wastewater is a combination of household wastewater, industrial wastewater, and/or rainwater (Shevah, 2019). Urban wastewater is typically treated and released into receiving ecosystems. However, wastewater should be treated using advanced treatment techniques to remove micropollutants that represent a risk in their content. Water treatment plant secondary effluent contains chemical compounds, many of which are acutely or chronically harmful to aquatic creatures and human and animal health. They are micropollutants that do not disintegrate readily and can have long-term environmental impacts (Richardson, 2019; Gil et al., 2019). Chemical compounds, pharmaceuticals, personal care products, plasticizers, and industrial additives are examples of emerging pollutants that are not presently monitored by water treatment systems(Petrie et al., 2015).

With the increase in living standards, the production and widespread use of pharmaceuticals (medicinal drugs) and personal care products (emerging contaminants), their resistance to biological treatment and the absence of any legal regulation in their discharge into surface water bodies, and the presence of such compounds in aquatic environments pose potential health risks. The presence of emerging contaminants, especially drugs used in the treatment of human and animal diseases, and as growth promoters in animals has been found in natural waters (Milić et al., 2013). Antibiotics, depending on their physical and chemical properties, are absorbed into soil, sediments, and groundwater. These pollutants cannot be completely removed by conventional wastewater treatment plants. Meanwhile, if they do not biodegrade or cannot be removed from treatment plants, they can reach drinking water (Jueyi et al., 2010; Subedi et al., 2015). Traditional wastewater treatments are not intended to handle pollutants such as pharmaceuticals, they can only extract drugs with a low removal rate, allowing untreated components to mix with surface waters (Khan et al., 2020).To provide usable quality water, new methods are proposed to ensure that the contaminant is mineralized and transformed into non-toxic products rather than eliminated. Advanced oxidation processes (AOPs), which are insensitive to traditional treatment techniques, have been launched as ground-breaking water treatment technologies. AOPs generate strong oxidative species such as H2O2, O2•–/HO2•, and HO•, which are the most oxidative agents for the redox process, to destroy the contaminant and turn it into less harmful (Zeng et al., 2019; Gil et al., 2019). The AOPs can be classified into the Fenton-based, electro-chemical, and photocatalyst process using the generation mechanism of hydroxyl radicals. Heterogeneous AOPs in which semiconductor solid photocatalysts are activated under UV light are used in AOPs; they are simple, clean, effective, and cost-effective processes compared to other AOPs. TiO2 is a semiconductor with a wide bandgap that is used in the presence of UV light with a wavelength less than 380 nm or sunlight (Mohammed et al., 2020). TiO2 nanoparticle is the most widely used, as it is stable over a wide pH range, non-toxic and inexpensive compared to other photocatalysts. (Mahdi et al., 2021; Ribeiro et al., 2015). The chemical synthesis for the nanoparticle process involves the chemical reaction of several precursors to produce another nanometer-sized material. The drawbacks of physical and chemical methods are the use of toxic solvents, hazardous waste, and high energy consumption (Maurya et al., 2019). As a result, further developments are required to create ecologically safe and renewable nanoparticles.

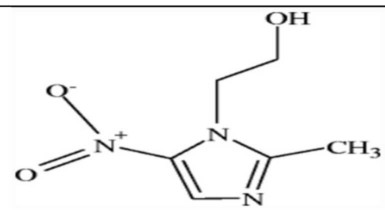
The biosynthetic process (also known as green synthesis) is a technique for creating nanoparticles that utilize reducing agents obtained from plants and microorganisms. It offers several advantages, including environmental safety, economic effectiveness, biocompatibility, renewable energy, and non-toxicity (Jalill et al., 2016). Sugars, terpenoids, polyphenols, alkaloids, phenolic acids, and proteins are all compounds that can play a role in the biosynthesis of nanoparticles (Parveene et al. 2016).The ability to generate a usable product from bio-based waste would significantly improve and ensure global economic development along with waste management issues . To achieve this criterion, Orange leaves extract was used in this study to synthesize TiO2, then their photocatalytic ability for MTZ was studied under different operating conditions in a batch reactor system.

2. Material and method

2.1 Chemical reagents:

All the chemicals used in this study were of analytical grade and used directly in the experiments as received without prior purification, which was purchased from Merck. Metronidazole ($C_6H_9N_3O_3$), was chosen as a target pollutant, its chemical properties were shown in Table 1. Titanium tetra isopropoxide TTIP (containing 95% anatase and 5% rutile) has been utilized to synthesize TiO_2 nanoparticles. Fresh Orange leaves were collected from one farmer in Diyala Provinces / Iraq. The pH value of the aqueous solution was adjusted by using (0.1M) HCl and/or NaOH.

Table 1. Physical and chemical characteristics of MTZ (Kulkarni et al., 2019).

Characteristic	antibiotic
Molecular structure	
Molecular formula	$C_6H_9N_3O_3$
Molecular weight (g/mol)	171.2
Water solubility (mg/ml) at 20 °C	10.0
pK_a	2.55
Melting point (°C)	159-163
K_H (mol/dm^3.atm)	5.92×10^7
V_p (Pa)	4.07×10^{-7}

2.2 Methodology of Preparation

2.2.1 Green synthesis of TiO_2 nanoparticles

Fresh orange leaves were gathered, and they were properly cleaned with distilled water. These leaves were submerged in distilled water, cooked for two hours at 70 degrees Celsius, strained, and kept for further use. While the distilled water was continually agitated for 30 minutes, 10 ml of titanium isopropoxide (TTIP) was added drop by drop to 250 ml of distilled water. A precursor (extract) was then added to this solution until the pH of the solution reached 7. The entire mixture was stirred at 980 rpm for 4 hours and then set aside. The solution was filtered after 12 hours to remove by-products, and the wet cake was collected and dried in a hot air oven for 12 hours at 70°C as shown in Figure 1.The collected nanoparticles called O-TiO_2 were stored for later use this method was adopted (Kantheti and Alapati, 2018).

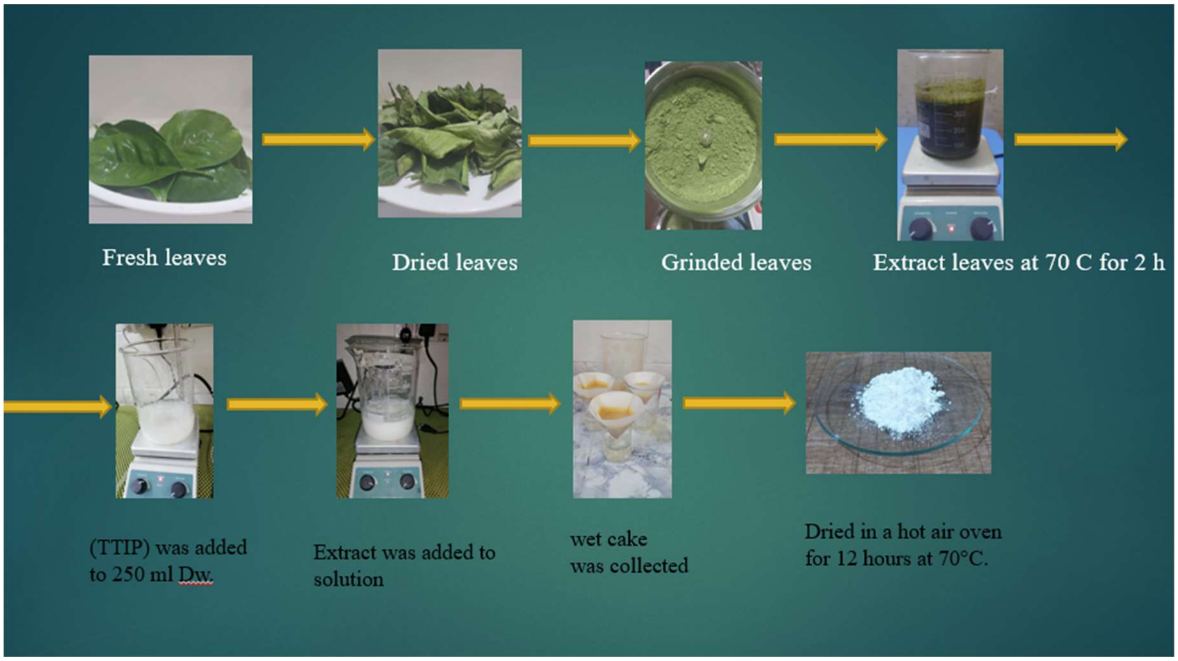


Figure 1: Schematic diagram of nanocomposite process manufacturing.

2.3 Photocatalytic Performance

Under solar irradiation, the photocatalytic degradation procedure was conducted in a batch-mode reactor. The reactor was made of Pyrex glass (1 L) that had been coated with silver nitrate in order to prevent sunlight scattering and at the bottom, there was a piece of the mirror (used as a reflector). Solar radiation was assessed using the (SPM- 1116SD) device, the instrument was pointed toward the sun with an average solar UV power of (150-850) W/m^2, UV measurements were taken for the range between 300 and 400 nm. MTZ solution was prepared at 15mg/L then pH was adjusted, (using pH meter type INOLAB 72, WTW Co., Weilheim, Germany). Subsequently, O-TiO_2 (30) mg/L was added, and finaly 200mg/L of H_2O_2 was added. The suspension was stirred at 200 rpm with a stirrer type (MSH-300N, BOECO, Hamburg, Germany), first in the dark for 30 min to achieve primary adsorption equilibrium, and then start the solar photocatalyst reaction. To separate the catalyst, 10 mL of the sample was extracted and centrifuged at 200 rpm for 15 minutes at predetermined time intervals. A spectrophotometer (UV-Vis Spectrophotometer PerkinElmer 55 OSE) was used to quantify the concentration of MTZ in each sample at a wavelength of 320 nm. The removal performance of the target chemicals, on the other hand, was calculated using the equation:

$$\text{MTZ Removal efficiency} = \frac{\text{MTZ}_o - \text{MT}_e}{\text{MTZ}_o} \times 100\% \;\ldots\ldots\ldots\ldots\ldots\ldots.. (1)$$

Where MTZ_o and MTZ_erepresent both the primary and the equilibrium concentration of MTZ (mg/L), respectively.

3. Results and discussions

3.1. Fourier-transform infrared spectroscopy (FTIR):

FTIR spectra of O-TiO_2 are confirming the composition and structure of the nanocomposites before treatment. As shown in Figure 2 (black line). The peaks observed from 500 to 800cm^{-1} were most likely caused by the Ti-O stretching bands, linked to the creation of the TiO_2 nanoparticles, while the peaks at 1113.86, 1369.21, 1634.38 cm^{-1} are associated with the vibration mode of the Ti-OH bond (Rehman et al., 2020) were attributed to the titanium carboxylate. Bonds within the range of (1200-1600) cm $^{-1}$ can be associated with the carbon functional groups such as CH, CH_2, CH_3, or O-CH_3, which might be coming from the plant extracts (Vijaylaxmee et al., 2014; Johari et al., 2021), which gave rise to the CH_3 stretching frequency peaks at 2921.36 cm^{-1}, and the $^{-}$OH group stretching and bending vibration maxima were seen at 3423.28cm^{-1}. The Ti-O-Ti stretching frequency was noted to peak at 1395.25 cm^{-1} (Aminuzzaman et al., 2019).
After the removal of the drug only the transmittance was reduced and the behavior of some peaks had changed suggesting that this drug had great affinity towered the functional groups located on its surface as shown in Figure 2(red line).

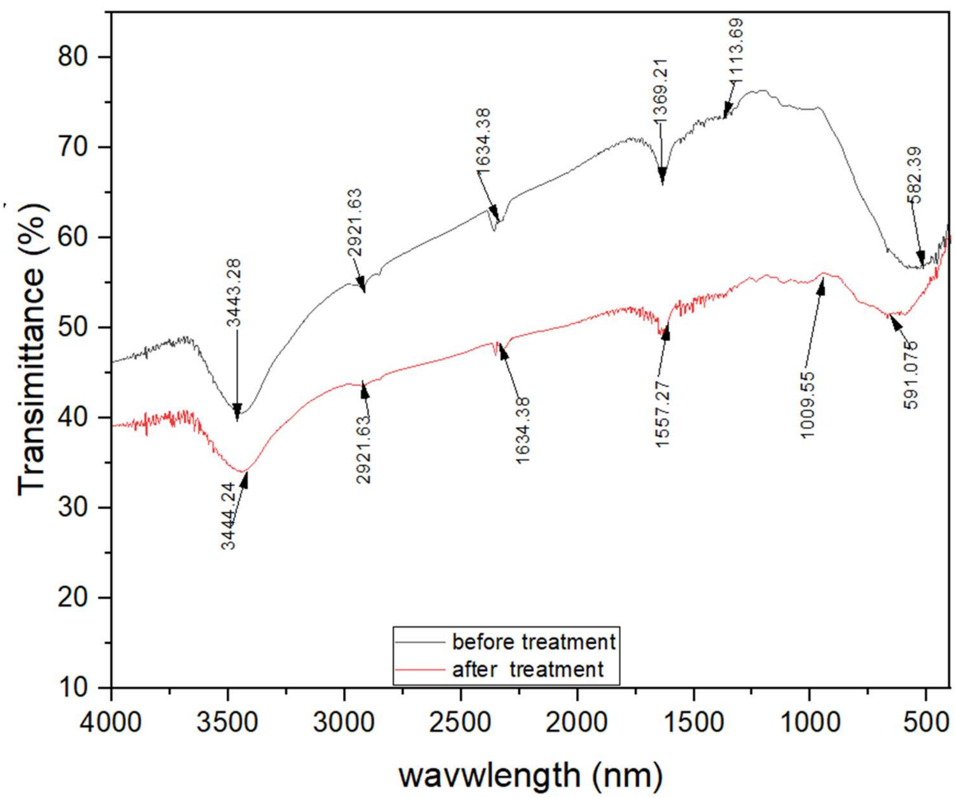


Figure 2: FTIR spectrum of O-TiO_2 nanoparticles before and after photocatalytic.

3.2. Comparison of MTZ Removal by Various Techniques:

The results plotted in Figure 7 demonstrated the relationship between different techniques of AOP to remove MTZ (solar radiation only, solar radiation/H_2O_2, O-TiO_2 only, and solar/ O-TiO_2 /H_2O_2). The experiments were conducted at MTZ concentrations of 15mg/L, pH 5, temp.25°C and 200 mg/L H_2O_2 and 45 mg of O-TiO_2 concentration. The results indicated that only a 33.29% removal percentage was reached by using solar radiation only. However, when H_2O_2 was added to the solar radiation experiments increased the removal efficiency to (72.63%). Whereas, with only O-TiO_2, the removal percentage was (39.82) %. The use of sunlight, H_2O_2 in addition to O-TiO_2 enhance the degradation rate of MTZ residue to 89.12%. Therefore, in this research, the four techniques of treatment were applied.

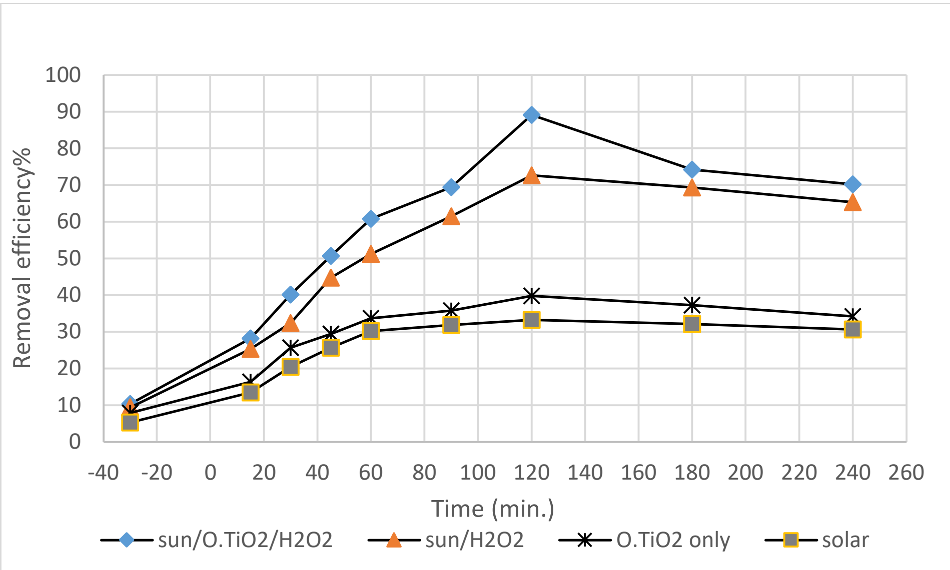


Figure 3. Removal of MTZ as a function of different oxidation systems using solar radiation.

3.2.1 The Effect of pH:

According to (Dabirvaziri et al. 2019), pH is one of the most important elements affecting the rate at which antibiotics degrade and the charge on the catalyst's surface regulates the removal of MTZ by affecting the production of hydroxyl radicals and, in turn, the effectiveness of oxidation. To reach the adsorption/desorption equilibrium in the initial tests, reactants were mixed for 30 minutes in the dark before being exposed to sunlight for 120 minutes. Following the completion of the dark run, the concentration of MTZ was measured in the first sample, and the effects of varied beginning pH values (3,5,7,9, and 11) on the solar photocatalytic degradation reaction were then investigated while maintaining H_2O_2=200 mg/L, MTZ conc. of 15 mg/L, 120min irradiation time, and 45 mg/L of O-TiO_2.

Their results were plotted in Figure 4, which demonstrates that a minor degradation was noticed in the dark after 30 minutes, indicating minimal MTZ adsorption. When the irradiation time began, however, the degradation efficiency increased. The outcomes also show that raising pH from 3 to 5 increased clearance %. The removal efficiency is reduced with each additional increase over 5. Antibiotics may degrade more quickly at acidic pH levels due to their hydrolysis, which also causes the pH of the solution to rise because it is below pHpzc. (González-Casamachin, 2019).

Low efficiency at alkaline conditions can be explained by the negative charges that MTZ and O-TiO_2 have because of their electrostatic attraction to one another, as well as by the dissociation and auto-decomposition of H_2O_2, whereas reduced degradation at pH 5 can be explained by H^+ ability to scavenge hydroxyl radicals, (Eq.4), (Pascariu et al., 2019).

$OH^{\bullet} + H^+ + e^- \rightarrow H_2O$ ……(4)

The highest removal efficiencies were 89.12 at pH=5. It is crucial to analyze pH of point of zero charges (pHpzc), the pH value at which catalyst surfaces are neutrally charged. In other words, when pH values are lower than pHpzc and vice versa, the surface charge of the catalysts is negative (Pan et al., 2021). The equations that follow demonstrate that, depending on whether the environment is acidic or alkaline, the photocatalyst surface can get ionized and then deionized.

$pH < P_{zc} \quad TiOH + {H_2}^+ \rightarrow TiOH_2^+$ …. (5)

$pH > P_{zc} \quad TiOH + OH^- \rightarrow TiO^- + H_2O$ …. (6)

The result of pHpzc of O-TiO_2 was demonstrated in Figure 5, the value was approximately pH 6.89. Lowering pH value (acidic condition) less than 6.89, according to (Eq.5), While raising the pH above this value, the negative charge on the surface of TiO_2 grows with increasing pH, according to (Eq.6) (Ahmed et al., 2010).

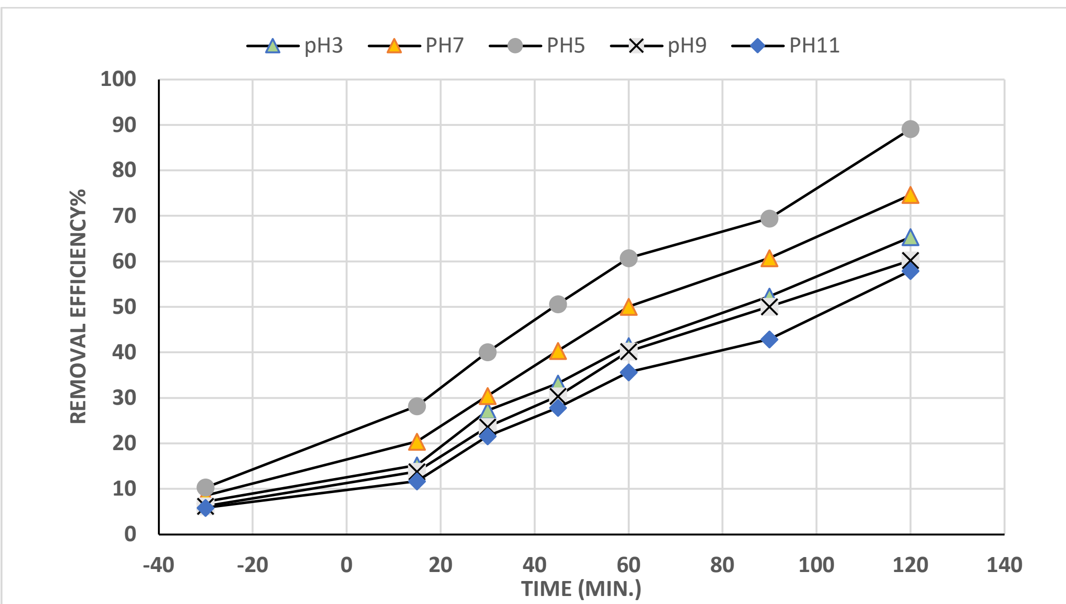


Figure 4: The effect of pH on the photocatalytic degradation of MNZ.

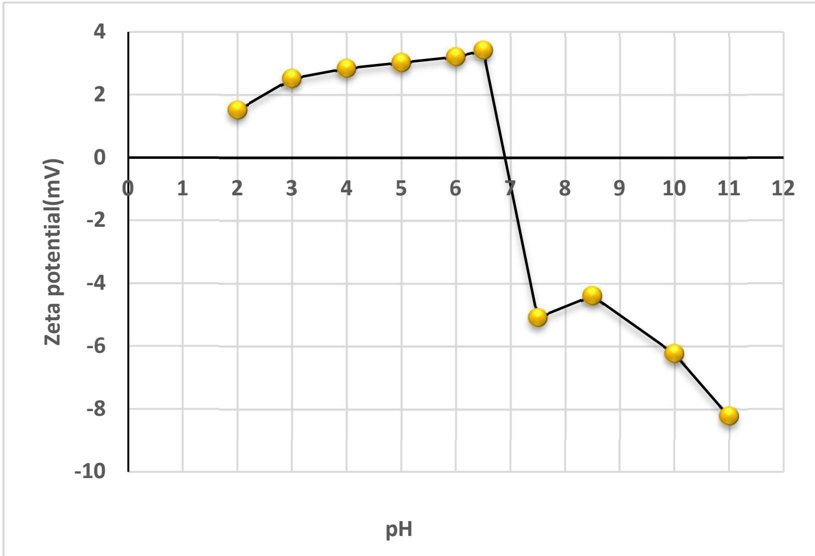


Figure 5: The point zero charge of O-TiO_2

3.2.2. The effect of Intensity:

Solar light possesses the energy equivalent to the wavelength needed for the degradation process, ensuring it to be a viable source for creating charge carriers across the TiO_2 (Shokri et al., 2020). Compared to the other alternative techniques, the use of natural solar UV energy (sunlight) over an artificial UV lamp may substantially minimize the expenses for photocatalytic oxidation (Hadjltaief et al., 2014). For that the effect of sunlight on the degradations of MTZ has been carried out early in the afternoon from 10:30 a.m. to 2p.m. during April, May and June, and their results were plotted in Figure 6.

The experiments were conducted at the optimum conditions of the sun irradiation experiments (15 mg/L MTZ concentration, pH of 5, 30 mg/L of O- TiO_2, and 200 mg/L of H_2O_2 concentration).

It can be seen from this figure that light intensity from (342.5 MW/cm^2) to (1132 MW/cm^2) fluctuated the degradation from April to June. The formation of hydroxyl radicals has increased, which has improved removing rate. The number of photons absorbed by the catalyst depends on the intensity of the light; as solar power increases, more photons are absorbed by the catalyst, producing more hydroxyl radicals. As a result, there are more opportunities for photon activation on the catalyst surface, increasing the photocatalytic power (Oliveira et al., 2012).

The low rate of removal is explained by the fact that dust, the time of day, clouds, and other environmental factors prevent light from being absorbed and reaching the ground's surface. This is supported by the fact that the intensity of solar irradiance was variable and had an impact on the removal rate. (Benhabiles et al., 2018).

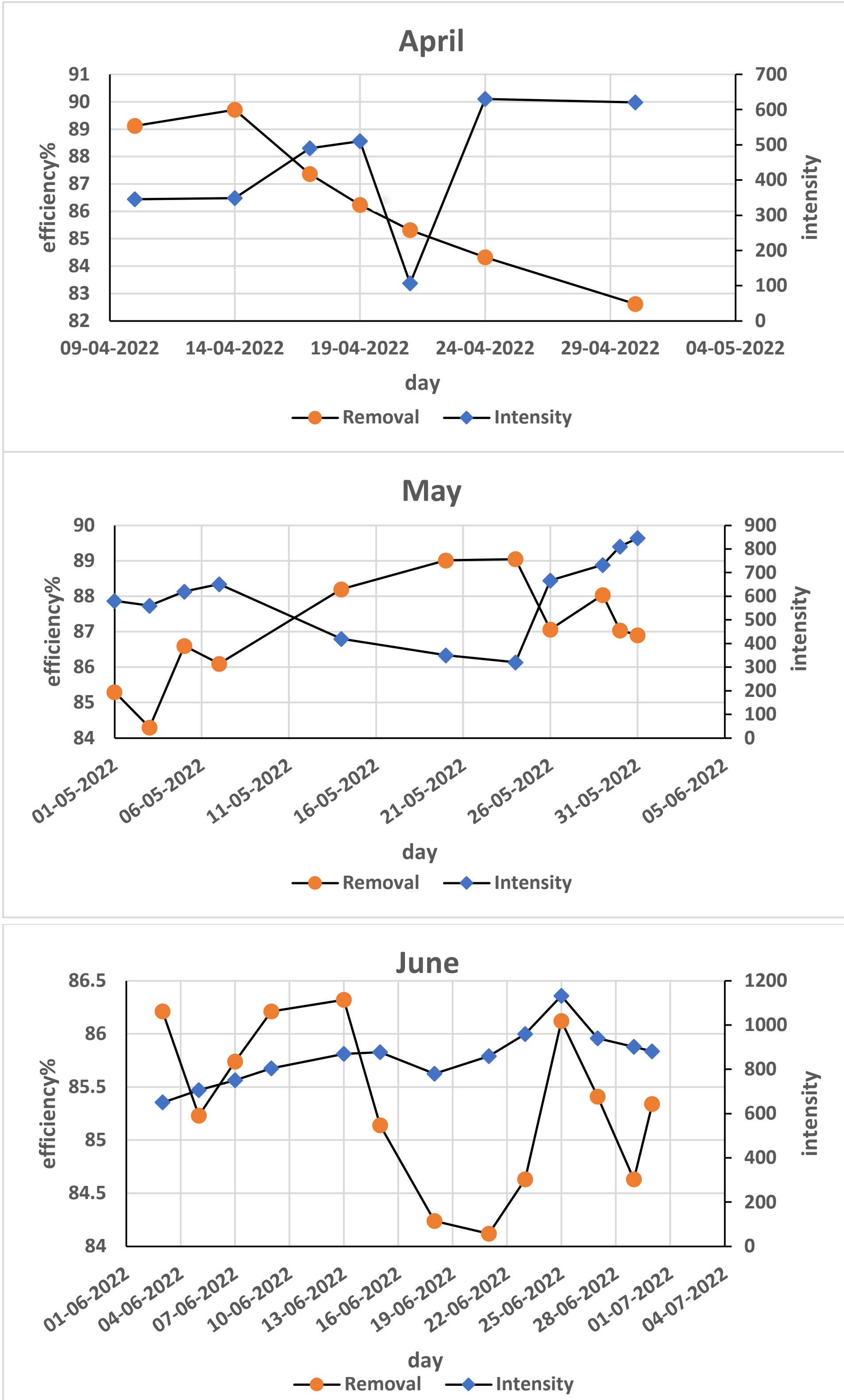


Figure 6: Effect of solar intensity on the removal efficiency.

3.2.7. Reusing and Recycling of Catalyst:

In practice, the good photostability of the as-prepared catalyst is conducive to reducing water treatment costs and avoiding secondary pollution. To test the stability of the synthesis nanoparticles, the photocatalytic performance for MTZ degradation of synthesis catalysis samples while keeping other parameters constant; pH= 5, 15 mg/L MTZ concentration, 200 mg/L of H_2O_2, and 45 mg/L of O-TiO_2 catalyst concentration. The catalyst was collected and washed thoroughly with distilled water and then dried to be used in subsequent experiments, and their results were plotted in Figure 15, it shows that the MTZ efficiency was (89.12, 67.21, 64.78, 54.87, and 34.26) % after the first, second, third, fourth, and fifth cycles. It indicated that our photocatalyst possessed reasonable stability for its practical application.

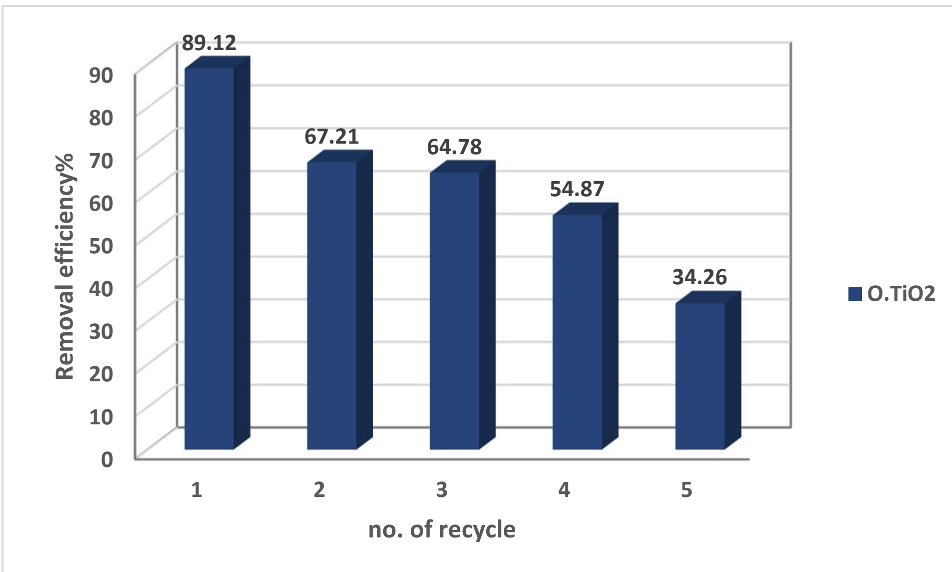


Figure 15: The relation between removal efficiency and the recycling runs

4. Conclusion

The research aimed to create a new green titanium dioxide and test its suitability for photocatalysts' removal of MTZ residues from aqueous solutions. As a reducing agent, Orange leaves extract was used to generate TiO_2 (denoted as O-TiO_2). UV-Visible spectrophotometer analyses were used to analyze the removal of MTZ antibiotics. Nanoparticles that had already been synthesized were satisfactorily characterized using FTIR method. The results of this study reveal that following calcination, the biosynthesized O-TiO_2 was used for the first time in a batch reactor to prove its potential for removing MTZ residue from aqueous solution by studying the effect of (pH, and solar intensity). The results confirm the effectiveness of O-TiO_2 to remove MTZ, with a maximum removal percentage of 89.12 %. In addition, increasing the solar light intensity confirms the removal rate of MTZ antibiotics. The results of this study confirm the effectiveness of using solar light and biosynthesis TiO_2 as a green and sustainable process for the elimination of antibiotics from wastewater.

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