Efficient One-Pot Synthesis of TiO$_2$/ZrO$_2$/SiO$_2$ Ternary Nanocomposites Using *Prunus × Yedoensis* Leaf Extract for Enhanced Photocatalytic Dye Degradation

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A simple, efficient, and ecofriendly method was employed to synthesize TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites using *Prunus × yedoensis* leaf extract (PYLE) that shows improved photocatalytic and antibacterial properties. The characterization of the obtained nanocomposites was done by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, field-emission scanning electron microscopy (FE-SEM), and energy-dispersive X-ray spectroscopic (EDS) analysis. The synthesized ternary nanocomposites with nanoscale pore diameters were investigated for the elimination of Reactive Red 120 (RR120) dye. The obtained results showed about 96.2% removal of RR120 dye from aqueous solution under sunlight irradiation. Furthermore, it shows promising antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*. The improved photocatalytic and antibacterial activity of TiO$_2$/ZrO$_2$/SiO$_2$ may bring unique insights into the production of ternary nanocomposites and their applications in the environment and biomedical field.

1. Introduction

The Reactive Red 120 is a cationic dye used in several industries such as paper, leather, cotton, pulp, and wool. This toxic aqueous solution causes various problems including human health issues such as abnormal heartbeat rate, shock, cyanosis, jaundice, tissue death, carcinogenesis, mutagenesis, teratogenesis, respiratory toxicity, kidney failure and malfunctioning,
and damage to the major organs like the brain, lung, liver, and sexual organs and causes emphysema [1–3]. The effluents released from the dyeing units are highly toxic, and it is directly discharged into the water bodies, which severely impact the environment. Due to the effluent’s resistance to light, heat, chemicals, and water, these effluents at low-level concentrations do not readily degrade in the environment [4]. The estimated annual production of dye products is 10 million kilograms, out of which up to 2 million kilograms of reactive dyes enter the biosphere [5]. However, over a long period, different methods are employed for treating dyes from aquatic media [6], which include catalytic oxidation, sonocatalytic degradation, ozonation, adsorption [7], electrochemical oxidation [8], and coagulation/flocculation [9]. But these technologies are not suitable to meet the required water quality standards [10]. Recently, semiconductor photocatalysis drags the attention because of its advanced and green technique that provides the potential to degrade the dye in wastewater. It also stands for environmental benignancy, stability, and safety [11].

The growing global research needs a fast and environment-friendly technology to remove wastewater pollutants. Recently, nanotechnology has helped researchers enable potential applications in environmental issues. Titanium dioxide (TiO₂) nanoparticles have been used as a benchmark photocatalytic material due to their high stability, nontoxicity, low cost, and strong oxidizing agent [12–15]. They have been used in various environmental applications such as high photocatalytic efficiency, optical, dielectricics, and antimicrobial devices [16–18]. TiO₂ has a unique series of reactive oxygen functional groups present on the surface, such as carboxylic acid, hydroxyl, and epoxide groups that are beneficial in preparing the TiO₂ nanocomposites [19] such as titanium oxide-reduced graphene oxide (TiO₂-rGO) [20], SiO₂–TiO₂/ZrO₂ [21], and Zr-TiO₂/SiO₂ [22]. Overall, titanium reveals a more extensive phi-conjugation system in a two-dimensional planar structure, a higher surface area, and a higher electron conductivity, including reactive oxygen and a carboxyl group which is present in titanium dioxide as a unique functional group would support strengthening the metal and metal oxide particles [23]. Under UV light irradiation [24], TiO₂/ZrO₂/SiO₂ photocatalyst had greater photocatalysis performance than the TiO₂/SiO₂ and TiO₂/ZrO₂ systems. Furthermore, TiO₂ is a promising material for removing dye from wastewater because of its high electron mobility and flexibility [25].

Several investigations are currently being conducted on the heterogeneous photocatalytic degradation of dye exposed to UV-A or visible light [26]. The oxidative technique has decolorized and mineralized the variety of azo dyes on a workbench scale using artificial illumination and solar energy [27]. Wang et al. successfully demonstrated the photocatalytic degradation of eight commercial dyes by using solar energy, including MeO, in the TiO₂ mixture [28]. The plant-mediated synthesis of ternary nanocomposites is a safe, ecofriendly, rapid, and more stable approach due to the presence of numerous bioactive compounds such as alkaloids, flavonoids, terpenoids, tannins, saccharides, phenol, vitamins, amino acids, proteins, and various enzymes [29, 30]. Antibiotic resistance of microorganisms poses a serious problem. Thousands of people succumb to the harmful microorganisms and die due to hospital pathogens being resistant to the antibiotics. Hence, there is an ultimate need for novel antimicrobials, and the synthesized ternary nanocomposites exhibit a biocompatible structure which provides great convenience for medical applications. These phytochemicals present in the PYLE extract act as a reducing agent in the bioreduction of ions for the synthesis of TiO₂/ZrO₂/SiO₂ nanocomposites. Controlled pore size distribution, density, compressive strength, and other unique characteristics are important properties of nanocomposites synthesized using the one-pot method. Moreover, the use of solar irradiation, instead of UV light, is another attractive point that fits today’s requests for more intense use of renewable energies. The present study deals with the photocatalytic degradation of RR120 dye obtained by the one-pot solar photoreduction (with the intensity of ~50000 lx) to avoid the high temperature and pressure required for the standard hydrothermal reaction. Additionally, the antibacterial activity of the green synthesized TiO₂/ZrO₂/SiO₂ nanocomposites was also investigated.

2. Experimental Sections

2.1. Materials. Titanium tetraisopropoxide (C₁₂H₂₈O₄Ti) assay ≥ 98%, Sigma), zirconium (IV) acetylacetonate (Zr(C₅H₇O₂)₄ > 98%, Sigma), sodium silicate (Na₂SiO₃•9H₂O), and methanol (Daejung Chemicals Reagents, South Korea) were used as precursors to prepare oxide composites. Reactive Red 120 was supplied by SD Fine Chemicals, Mumbai, India. Stock solutions of 1000 mg/L of the dye were prepared, and further concentrations were obtained by diluting the stock solution. Mueller Hinton Agar (MHA) was purchased from MB cell, South Korea. All solutions were prepared using Milli Q water with of conductivity 18 μΩ/m.

2.2. Biological Materials. Staphylococcus aureus and Escherichia coli were collected from the Korean agriculture culture collection (KACC) in Suwon, South Korea. The collected organisms were subcultured in nutrient agar and incubated at 37°C for 24 hours; after incubation, the plates were stored at 4°C until the experiment.

2.3. Prunus × Yedoensis Leaf Extracts (PYLE) Preparation. 50 grams of Prunus yedoensis leaves was collected from the plants in and around the Chonbuk National University, Iksan campus, South Korea. The collected leaves were washed in distilled water to remove the impurities, and then these leaves were sheared into small pieces. After shearing, it was boiled with 200 mL sterile Milli Q water for 30 min in a heating mantle to obtain the decoction. The obtained decoc- tion was subjected to filtration using a Whatman No.42 filter paper. After filtration, it was stored at 4°C until further process.

2.4. One-Pot Green Synthesis and Calcination Treatment of TiO₂-Coated ZrO₂/SiO₂ Nanocomposites. 100 mL of 0.1 M titanium tetraisopropoxide (C₁₂H₂₈O₄Ti assay ≥ 98%,
Sigma) solution was added to 300 mL of *Prunus × yedoensis* leaf extract mixture was vigorously stirred for one hour and ultrasonicated for 15-30 min. Followed by adding 100 mL of 0.1 M Zr(C₅H₇O₂)₄ and 100 mL of 0.1 M Na₂SiO₃·9H₂O to the sonicated reaction mixture using a peristaltic pump (flow rate-0.5 mL/hour) at 80°C. Then the reaction mixture was subjected to centrifugation at 12000 rpm, the pellets were collected, and then the pellets were washed subsequently with distilled water and methanol to remove organic material present in the final product. The obtained product was subjected to calcination at 800°C for two hours in a muffle furnace. The final product obtained was designated as TiO₂/ZrO₂/SiO₂ ternary nanocomposites and subjected to characterization and investigation of photocatalytic and antibacterial activities.

### 2.5. Characterization of TiO₂/ZrO₂/SiO₂ Ternary Nanocomposites

The green synthesized TiO₂/ZrO₂/SiO₂ ternary nanocomposites were analyzed by FE-SEM-EDS (SU-8240, Hitachi, Japan) to observe the surface morphology and appearance of the nanocomposite. EDS was used to confirm the element present in the nanocomposite. XRD patterns were obtained using a Rigaku X-ray diffractometer to find out the crystalline nature of the nanocomposite. The scanning was completed in the region of 2θ from 10°-80° at 0.041/min at a constant time of 2S. The functional groups in the prepared nanocomposite were analyzed using a Perkin-Elmer FTIR spectrophotometer (USA) with a range of 4000-400 cm⁻¹. Raman spectroscopy was carried out by XploRA Raman microscope equipped with laser light of wavelength 532 nm. The UV-visible spectroscopy was recorded on UV-1800, Shimadzu, Kyoto, Japan, with the variable wavelength from 300 to 800 nm.

### 2.6. Photocatalytic Activity of TiO₂/ZrO₂/SiO₂ Ternary Nanocomposites under Various Light Sources

![Figure 1: (a) XRD spectra, (b) FTIR spectrum, and (c) Raman spectra of TiO₂/ZrO₂/SiO₂ nanocomposite.](image)
The photocatalytic activity of TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites was conducted by the method proposed by Borthakur et al. [31] with modifications. Briefly, the reaction mixture was prepared by adding 10 mg of synthesized TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites in 100 mL of RR120 aqueous solution with an initial concentration of 10 ppm, and the suspension was stirred in the dark for 30 min before irradiated in the sunlight to establish the absorption-desorption equilibrium between the photocatalyst and RR120 dye. The sunlight irradiation was carried out between 11:00 a.m. and 2:00 p.m. on consecutive days (summer season) in June and July 2020 (GPS coordination: 35.84682° N, 127.12935° E). The photocatalytic activity of TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites was estimated by measuring the degradation of RR120 in an aqueous solution under sunlight irradiation using a UV-Vis spectrophotometer. A sample solution of RR120 was withdrawn within the fixed time interval and centrifuged at 12,000 rpm for 20 min during the photocatalytic reaction. After centrifugation, the supernatant was used to measure the amount of RR120 at $\lambda_{\text{max}}$ (515 nm) [26] using a UV-visible spectrophotometer. The following equation determined the percentage of RR120 degraded by the prepared nanocomposite from the photocatalytic activity [32].

$$\text{Percentage of degradation} = \frac{C_0 - C_t}{C_0} \times 100. \quad (1)$$

Here, $C_0$ is the initial concentration of the aqueous RR120 solution (mg/L), and $C_t$ is the concentration of the aqueous solution after irradiation (mg/L). The reaction mixture was also subjected to different pH (4–12), different initial concentrations ($C_0$) of RR120 (10 mg/L to 30 mg/L), and three different dosages of TiO$_2$/ZrO$_2$/SiO$_2$ (from 20 to 60 mg/L). The kinetics study of RR120 was carried out to find the reaction rate constant of as-synthesized TiO$_2$/ZrO$_2$/SiO$_2$ nanocomposites. The degradation of RR120 can be described by the pseudo-first-order equation [33].

$$\ln \left( \frac{C_0}{C_t} \right) = -k_{\text{app}}t, \quad (2)$$
Figure 3: Continued.
where \( C_0 \) is the initial concentration of RR120 aqueous solution, \( C_t \) is the final concentration of RR120 aqueous solution, \( k_{\text{app}} \) is the pseudo-first-order rate constant (min\(^{-1}\)), and \( t \) is time (min). \( k_{\text{app}} \) values were enumerated from the slope \( \ln (C_t/C_0) \) at a different time point observed for the sample solution without a catalyst, with the catalyst in a dark chamber, TiO\(_2\)/SiO\(_2\), TiO\(_2\)/ZrO\(_2\), and TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) photocatalysts. The \( k \)-rate constant was derived through the kinetic value.

2.7. Antibacterial Activity. The TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) ternary nanocomposite antibacterial activity was evaluated against the Staphylococcus aureus and Escherichia coli by the well diffusion technique. The bacterial suspension was swabbed on the Muller Hinton agar plate for antibacterial activity, and the different concentrations of nanocomposites (50, 75, and 100 \( \mu \)g/mL) were loaded in the respective well on the agar plates. Then the plates were incubated at 37°C for 24 h. The antibacterial activity of TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) ternary nanocomposites was identified by the clear zone around the well, which indicates the inhibition of bacteria by the composite.

3. Results and Discussion

This study prepared the green synthesis of TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) ternary nanocomposites using PYLE.

3.1. X-Ray Diffraction Analysis. Figure 1(a) illustrates the XRD pattern of TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) nanocomposites. The diffraction peaks at 25°, 36°, 48°, 54°, 55.5°, 69°, 70°, and 75° were assigned to the corresponding planes (101), (103), (200), (210), (211), (116), (220), and (215), respectively, which indicate the presence of anatase TiO\(_2\). Also, it can be evidenced that the moderate low-intensity peaks at 27°, 35.5°, 42°, 56°, and 63° correspond to the planes of (110), (101), (111), (220), and (002), revealing the presence of rutile TiO\(_2\). Similar interpretations were made by Chellappa and Vijayalakshmi [34]. The prepared TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) ternary nanocomposite might exhibit a mixed phase of anatase and rutile TiO\(_2\). A low intense peak at 30° indexed to (111) resembles the zirconia phase, which might increase the mechanical strength of the ternary nanocomposites. The diffraction peaks at 38°, 45°, and 65° correspond to (112), (211), and (023), respectively; these planes confirmed the presence of monoclinic ZrO\(_2\). This was in good agreement with the study conducted by [35]. The heterojunction of TiO\(_2\)-coated ZrO\(_2\)/SiO\(_2\) inhibits the conversion of TiO\(_2\) anatase to rutile at 800°C. In ZrO\(_2\)/SiO\(_2\), the low intense peak at 20° and 30° reflects the combination pattern of ZrO\(_2\)/SiO\(_2\) into TiO\(_2\) coated nanocomposite [36, 37]. In this study, all assigned diffraction peaks in TiO\(_2\)-coated ZrO\(_2\)/SiO\(_2\) revealed an enhanced photocatalytic activity compared with the pure TiO\(_2\) because of the anatase crystalline phase. From the XRD results, it can be assumed that the coated TiO\(_2\) nanoparticles might be entered into the channels of the ZrO\(_2\)/SiO\(_2\) binary particle network.

3.2. FTIR Analysis. The FTIR spectrum of the nanocomposites is shown in Figure 1(b). Several functional groups were present in the prepared nanocomposite within 4000-400 cm\(^{-1}\). The prominent peak at 3384 cm\(^{-1}\) corresponds to the O-H stretching group present on the composite surface. The bank at 1627 cm\(^{-1}\) corresponds to C=C stretching vibrations in aromatic functional groups [38]. It is well known that the surface hydroxyl group plays a significant role in photocatalysis by capturing the holes and generating reactive hydroxyl radicals with high oxidation capacity [36]. The band around 1122 cm\(^{-1}\) is attributed to C-O stretching vibrations from the alcohol group, and the band at 669 cm\(^{-1}\) is assigned to the C-Cl stretching vibrations in the alkyl halide group. However, introducing titanium atoms to SiO\(_2\) to form the tetrahedral structure gives a complete structure of adsorbent [39]. The small peak at 515 cm\(^{-1}\) corresponds to the alkyl group in the Ti-O stretching, confirming the metal-oxygen bonding to nanocomposite [40].
3.3. Raman Analysis. Raman spectra of TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites are shown in Figure 1(c). The sharp peaks at 140, 394, 510, and 635 cm$^{-1}$ were assigned to the anatase phase of TiO$_2$. No characteristic peaks of silica were observed in the spectra. It is well known that zirconia has three polymorphs, namely monoclinic, tetragonal, and cubic; however, no Raman bands were observed for all these polymorphs [21]. Therefore, the Raman results indicate that silica and zirconium oxide are amorphous in the prepared TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites and are probably present as dispersed surface species.

3.4. FE-SEM-EDS. The surface morphology of TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposite was observed under field-emission scanning electron microscopy (FE-SEM). TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites were almost spherical in shape [41]. The uniform distribution of particles on the nanocomposite surface has been observed. The formation of aggregation in the nanocomposite might be due to the presence of excess H$^+$ ions of H$_2$O molecules on the surface of the nanocomposite [42]. The particle size of the prepared nanocomposite was in the range of 2-20 μm, as shown in Figures 2(a)–2(c), where the prepared particles appeared to have a moderately rough surface [43]. Also, the surface roughness of nanocomposite was slightly increased due to the presence of TiO$_2$ on the surface [44]. The elemental composition of TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites was determined by energy-dispersive X-ray spectroscopy (EDS), as shown in Figure 2(d). It can be seen that the presence of different elements such as titanium (Ti), zirconium (Zr), and silica (Si) confirmed the configuration of the green synthesized TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites.

![Figure 4: UV-Vis spectra of RR120 removal at different time intervals: (a) TiO$_2$/ZrO$_2$, (b) TiO$_2$/SiO$_2$, and (c) TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites and (d) RR120 removal rate at different photocatalytic systems.](image)
Biofabrication of nanocomposites was reduced and capped by polyphenols, which was actively confirmed by EDS [42].

3.5. Elemental Mapping-EDS Analysis. Elemental mapping results of TiO$_2$/ZrO$_2$/SiO$_2$ nanocomposites are shown in Figures 3(a), 3(c), 3(e), and 3(g). The EDS results assessed the homogeneity of the nanocomposites. The distribution of Si, Zr, and Ti in the TiO$_2$/ZrO$_2$/SiO$_2$ nanocomposites is observed in Figures 3(b), 3(d), 3(f), and 3(h). Several earlier studies well coincided with the evenly distributed titanium over the SiO$_2$ spheres, which evidently confirms the active role of titanium in the nanocomposites [45, 46]. EDS measurements confirmed the presence of Ti, Zr, and Si. Furthermore, all other elements like Zr, Si, and O are uniformly dispersed without agglomeration, and similar results were obtained from the study conducted by Choi and Choy [47].

3.6. Photocatalytic Degradation of RR120 in the Presence of TiO$_2$/ZrO$_2$/SiO$_2$ Ternary Nanocomposites. The prepared TiO$_2$/ZrO$_2$, TiO$_2$/SiO$_2$, and TiO$_2$/ZrO$_2$/SiO$_2$ nanocomposites were tested for their photocatalytic activity. The photocatalytic degradation of the RR120 dye experiment was standardized with the pH, catalyst dose, concentration of RR120 dye, and time interval under the sunlight irradiation. We have identified that at pH of 5, a catalyst dose of 10 mg/L, the concentration of RR120 dyes with 30 mg/L, and initially at 15 minutes, steadily increasing the steady time of 75 minutes showed better photocatalytic activity. The RR120 dye absorption peak at 515 nm showed that the amount of dye is drastically decreased without shifting the peak position to the baseline, indicating the complete decomposition in the aqueous solution. Moreover, these bioreduced TiO$_2$/ZrO$_2$/SiO$_2$ nanocomposites toward RR120 exhibited a promising photocatalytic efficiency with a 96.2% removal rate within 75 min.

### Table 1: Comparison of photocatalytic activity of TiO$_2$/ZrO$_2$/SiO$_2$ nanocomposites with similar kinds of studies.

| S. No | Catalyst                              | % removal | Catalyst (mg/L) | Irradiation time | References       |
|-------|---------------------------------------|-----------|-----------------|------------------|------------------|
| 1     | Fe$_2$O$_3$/Ag nanocomposites         | 88.2%     | 60              | 140 min          | [64] Saranya et al. [64] |
| 2     | TiO$_2$ nanocomposites                | 94%       | 100             | 150 min          | [65] Khade et al. [65] |
| 3     | TiO$_2$/SiO$_2$-Ag nanocomposites     | 80%       | 50              | 4 h              | [66] Liu et al. [66] |
| 4     | Catechin@ZIF-L nanocomposites         | 92%       | 50 mg           | 150 min          | [67] Raju et al. [67] |
| 5     | TiO$_2$/ZrO$_2$/SiO$_2$ nanocomposites| 96.2%     | 10 mg           | 75 min           | Our study        |

Figure 5: (a) Pseudo-first-order reaction kinetics of photodegradation of RR120 over various samples and (b) reusability of the prepared TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites.
absorbance spectra of the treated dye in the aqueous solution with the prepared composites were measured using a UV-visible spectrophotometer (Figures 4(a)–4(c)). The variations in the relative RR120 dye concentration \(C_t/C_0\) are presented in Figure 4(d), which shows the comparison of the photodegradation rate of RR120 dye in the presence of TiO\(_2\)/ZrO\(_2\), TiO\(_2\)/SiO\(_2\), and TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) nanocomposites, respectively. The variation in RR120 dye removal is influenced by sunlight sources irradiation time [48].

The obtained results clearly show that the RR120 removal efficiency of aqueous solutions without catalyst, with the catalyst in the dark, TiO\(_2\)/ZrO\(_2\), and TiO\(_2\)/SiO\(_2\) were less than that of the heterogeneous TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) ternary nanocomposites. The plant-based nanocomposite preparation is the most attractive approach for mass production at a minimal price that is safe for the ecosystem and human life. This nanocomposite might be an excellent potential photocatalyst for degrading pollutants utilizing sunlight [49].

The fact that the nanocomposites were synthesized by the sol-gel method could describe the photocatalytic improvement under natural sunlight with TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) ternary nanocomposites. In this case, nanocomposites with a large specific area would include more active surface sites for adsorbing water molecules and forming aggressive \(\bullet\)OH and HOO\(^{-}\) radicals by capturing the photogenerated holes [50]. The photocatalytic interactions are fueled by these active free radicals, resulting in the degradation of various pollutants from the aqueous medium [51]. However, the larger surface area still enables the dye molecule diminishment on the TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) photocatalyst surface. According to Abroushan et al. [52], the phosphate molecules are adsorbed on the surface of nanocomposite and generate

**Table 2: Antibacterial activity (zone of inhibition) of TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) nanocomposites against Gram-positive and Gram-negative bacteria.**

| S. No | Samples                        | Zone of inhibition (ZOI) in mm |
|-------|--------------------------------|-----------------------------|
|       |                                | 50 \(\mu\)g  | 75 \(\mu\)g | 100 \(\mu\)g | 50 \(\mu\)g | 75 \(\mu\)g | 100 \(\mu\)g |
| 1.    | PYLE                           | —              | —            | —            | —            | —            |
| 2.    | TiO\(_2\)/ZrO\(_2\)           | —              | 1 \(\pm\) 0.6 | 2 \(\pm\) 0.2 | —            | 1 \(\pm\) 0.8 | 2 \(\pm\) 0.4 |
| 3.    | TiO\(_2\)/SiO\(_2\)           | —              | 1 \(\pm\) 0.2 | 1 \(\pm\) 0.9 | —            | 1 \(\pm\) 0.5 | 2 \(\pm\) 0.3 |
| 4.    | TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) nanocomposites | 8 \(\pm\) 0.6 | 11 \(\pm\) 0.9 | 12 \(\pm\) 0.9 | 6 \(\pm\) 0.4 | 8 \(\pm\) 0.3 | 10 \(\pm\) 0.6 |
| 5.    | Chloramphenicol                | 10 \(\pm\) 0.7 | 12 \(\pm\) 0.7 | 15 \(\pm\) 0.3 | 12 \(\pm\) 0.4 | 15 \(\pm\) 0.3 | 16 \(\pm\) 0.6 |

**Figure 6: Variable numbers of colonies in agar plates (a) Staphylococcus aureus and (b) Escherichia coli exposed to different concentrations of TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) nanocomposites.**

**Table 2: Antibacterial activity (zone of inhibition) of TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) nanocomposites against Gram-positive and Gram-negative bacteria.**

| S. No | Samples                        | Zone of inhibition (ZOI) in mm |
|-------|--------------------------------|-----------------------------|
|       |                                | 50 \(\mu\)g  | 75 \(\mu\)g | 100 \(\mu\)g | 50 \(\mu\)g | 75 \(\mu\)g | 100 \(\mu\)g |
| 1.    | PYLE                           | —              | —            | —            | —            | —            |
| 2.    | TiO\(_2\)/ZrO\(_2\)           | —              | 1 \(\pm\) 0.6 | 2 \(\pm\) 0.2 | —            | 1 \(\pm\) 0.8 | 2 \(\pm\) 0.4 |
| 3.    | TiO\(_2\)/SiO\(_2\)           | —              | 1 \(\pm\) 0.2 | 1 \(\pm\) 0.9 | —            | 1 \(\pm\) 0.5 | 2 \(\pm\) 0.3 |
| 4.    | TiO\(_2\)/ZrO\(_2\)/SiO\(_2\) nanocomposites | 8 \(\pm\) 0.6 | 11 \(\pm\) 0.9 | 12 \(\pm\) 0.9 | 6 \(\pm\) 0.4 | 8 \(\pm\) 0.3 | 10 \(\pm\) 0.6 |
| 5.    | Chloramphenicol                | 10 \(\pm\) 0.7 | 12 \(\pm\) 0.7 | 15 \(\pm\) 0.3 | 12 \(\pm\) 0.4 | 15 \(\pm\) 0.3 | 16 \(\pm\) 0.6 |
electrons when exposed to sunlight [52]. In the present study, these electrons are attracted by the surface adsorbed $O_2$ molecules, resulting in the formation of $O_2^{•–}$ and $HO^{•}$ radicals, which have a higher chance of contacting RR120 dyes due to a quicker reaction speed, and the RR120 dye may be mineralized over time by superoxide radical ions [53]. As an outcome, the relatively smaller crystalline size of TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposite is advantageous for reducing $O_2$ and oxidation of $H_2O$ molecules by capturing the electron, and the hole pair enhances the photocatalytic performance when exposed to sunlight [54]. According to the results, TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites as active photocatalyst have an excellent photocatalytic potential to discharge the RR120 dye in the aqueous solution. The results obtained were compared with the other green synthesized nanocomposites, as shown in Table 1.

3.8. Reusability Study. For assessing the reusability of TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites, photodegradation was checked by repeating the four cycles as shown in Figure 5(b). The photocatalytic experiments (300 min) were repeated in four cycles, with the same nanocomposites retained after each cycle [56]. At the end of each photocatalytic experiment, samples were recovered and washed with deionized water and then used to analyze their stability. The amount of photocatalytic reduction by the nanocomposites showed the best performance, and similar interpretations were observed in the study conducted by Hinojosa–Reyes et al. [57]). These results depicted the photocatalytic activity of the biogenic fabricated TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites with renewed management. It can be considered that the distinction in the degradation efficiency might be due to the various surface features, crystalline nature, and the optical properties of nanocomposites [58]. After recycling four times, there were no significant variations in the degradation efficiency. This clearly states that the synthesized TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites are reusable enough for industrial and environmental applications.

3.9. Antibacterial Activity. The bactericidal activity of TiO$_2$/ZrO$_2$/SiO$_2$ against S. aureus and E. coli is displayed in Figure 6. The antibacterial activity was carried out by a well diffusion method, and a zone of inhibition was observed for different concentrations (50, 75, and 100 μg/mL) of a nanocomposite (20 mg in 0.5 mL) [59]. While increasing the concentration of the nanocomposites, the zone of inhibition in the well plate also increases. The highest inhibition rate was observed in S. aureus at the concentration of 100 μg/mL, compared to E. coli (Table 2). The enhanced

![Figure 7: The proposed mechanism of RR120 degradation by TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites.](image-url)
antibacterial activity of TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites has been familiar to the generation of reactive oxygen species (ROS), which could disrupt the DNA, proteins, and lipids, and leads to the death of the bacteria [60]. Nanoparticles can easily penetrate through the cell membrane; consequently, accumulation inside bacterial cells damages membrane integrity and ultimately destroys the bacteria [61]. While the nanocomposite was in contact with the cell membrane of the bacteria, Ti$_2^{2+}$ was released and bound to the outer membrane; because the bacterial cell membrane was negatively charged [60]. Therefore, Ti$_2^{2+}$ positively charged might mutually attract negatively charged cell membrane and cause damage to the cell membrane, which undoubtedly leads to bacterial death [62].

3.10. Photocatalytic Mechanism. Figure 7 illustrates the proposed mechanism of RR120 degradation by TiO$_2$/ZrO$_2$/SiO$_2$ nanocomposites. The photocatalytic process consists of the photogenerated electron and hole and their transfer to the surface of the nanocomposites and creates active oxygen species. Under the irradiation of artificial sunlight, each oxide’s conduction and valence band contain the photogenerated hole and electron. According to the diagram, the position of the valence band of TiO$_2$ is higher than that of ZrO$_2$ and SiO$_2$. Therefore, the photogenerated hole transfer can take place from the valance band of TiO$_2$ to the valance band of ZrO$_2$ and SiO$_2$ [63]. However, in the case of photogenerated electrons, transfer takes place from the conduction band of SiO$_2$ to ZrO$_2$ and then to TiO$_2$. Such photogeneration effectively reduces the recombination of electron-hole pairs. Hence, during the photocatalytic reaction, the electron can be captured by O$_2$ to create a superoxide radical anion [55]. The hole can react with the hydroxyl group to generate hydroxyl radicals responsible for the degradation of RR120. It can be clear from the diagram that the hole and electron are effectively separated from each other at the surface of the TiO$_2$/ZrO$_2$/SiO$_2$ nanocomposite.

4. Conclusions

TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites were successfully synthesized by a simple, efficient, and ecofriendly method. The obtained results showed that TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposites have an excellent photodegradation activity and a promising bactericidal activity against the Staphylococcus aureus and E. coli. The high photocatalytic performance of TiO$_2$/ZrO$_2$/SiO$_2$ was achieved based on the electron transfer between TiO$_2$ NPs and ZrO$_2$/SiO$_2$. Also, the XRD pattern revealed the presence of monoclinic and tetragonal ZrO$_2$ and anatase TiO$_2$. The ternary nanocomposites decreased the recombination rate of electron and hole pairs; therefore, the superoxide anion, hydroxyl radical, and hydroxyl group play important role in the photodegrading and antibacterial activities. In nutshell, the one-pot green synthesized TiO$_2$/ZrO$_2$/SiO$_2$ ternary nanocomposite act as a promising photocatalyst to remove the recalcitrant dye pollutant in environmental applications and can be used for other industrial and medical applications.

Abbreviations

PYLE: Prunus × yedoensis leaf extracts
KACC: Korean agriculture culture collection
ROS: Reactive oxygen species
XRD: X-ray powder diffraction
FTIR: Fourier transform infrared spectroscopy
FE-SEM: Field-emission scanning electron microscopy
EDS: Energy-dispersive X-ray spectroscopy

Data Availability

All the data created were available within this manuscript.

Conflicts of Interest

The authors declare that they have no conflict of interest.

Authors’ Contributions

Velu Manikandan was responsible for conceptualization, methodology, and writing of original draft preparation. Saranya Packialakshmi was responsible for data curation and writing of original draft preparation. Bandha Bharti was responsible validation and writing of the draft. Palanivappan Jayanthi was responsible for conceptualization and supervision. Ranjithkumar Dhandapani was responsible for writing—review and editing—visualization. Palanivel Velmurugan was responsible conceptualization, validation, and formal analysis. Duraisamy Elango was responsible data curation, review, and editing, Ragul Paramasivam was responsible for software, review, and editing. Vinayagam Mohanavel was responsible for project administration. Asad Syed, Abdhallah M. Elgorban, and Ali H.Bahkali was responsible for funding acquisition. Saravanan Muthupandian was responsible for supervision, review, and editing. Velu Manikandan and Saranya Packialakshmi J contributed equally to this work and share the first authorship.

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