Polyaniline-Coated TiO₂ Nanorods for Photocatalytic Degradation of Bisphenol A in Water

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ABSTRACT: Polyaniline (PANI)-wrapped TiO₂ nanorods (PANI/TiO₂), obtained through the oxidative polymerization of aniline at the surface of hydrothermally presynthesized TiO₂ nanorods, were evaluated as photocatalysts for the degradation of Bisphenol A (BPA). Fourier-transform infrared spectroscopy analysis revealed the successful incorporation of PANI into TiO₂ by the appearance of peaks at 1577 and 1502 cm⁻¹ that are due to the C=C and C=N stretch of the benzenoid or quinoid ring in PANI. Brunauer–Emmett–Teller analysis revealed that PANI/TiO₂ had almost double the surface area of TiO₂ (44.8999 m²/g vs 28.2179 m²/g). Transmission electron microscopy (TEM) analysis showed that TiO₂ nanorods with different diameters were synthesized. The TEM analysis showed that a thin layer of PANI wrapped the TiO₂ nanorods. X-ray photon spectroscopy survey scan of the PANI/TiO₂ nanocomposite revealed the presence of C, O, Ti, and N. Photocatalytic activity evaluation under UV radiation through the effect of key parameters, including pH, contact time, dosage, and initial concentration of BPA, was carried out in batch studies. Within 80 min, 99.7% of 5 ppm BPA was attained (PANI/TiO₂), obtained through the oxidative polymerization of aniline at the surface of hydrothermally presynthesized TiO₂ nanorods. The quantum yield (QY) of these photocatalysts was evaluated to be 9.86 × 10⁻² molecules/photon and 2.82 × 10⁻² molecules/photon for PANI/TiO₂ and TiO₂, respectively. PANI/TiO₂ showed better performance than as-synthesized TiO₂ with a rate constant of 4.46 × 10⁻² min⁻¹ compared to 2.18 × 10⁻² min⁻¹. The rate of degradation of PANI/TiO₂ was also superior to that of TiO₂ (150 mmol/g/h vs 74.89 mmol/g/h). Nitrate ions increased the rate of degradation of BPA, while humic acid consistently inhibited the degradation of BPA. LC–MS analysis identified degradation products with m/z 213.1, 135.1, and 93.1. The PANI/TiO₂ nanocomposite was reused up to five cycles with a removal of at least 80% in the fifth cycle. LC–MS results revealed three possible BPA degradation intermediates. LC–MS analysis identified degradation products which included protonated BPA, [C₁₀H₁₃O₄⁺], and [C₄H₄O⁺]. The PANI/TiO₂ nanocomposite demonstrated superior photocatalytic activity with respect to improved QY and figure of merit and lower energy consumption.

1. INTRODUCTION

Water is regarded as the most vital of natural resources worldwide for the sustainability of life, yet freshwater systems are directly threatened by human activities. Currently, the world is facing a serious challenge in saving the few available sources of “clean” water. Rapid industrialization has led to high discharge of organic pollutants into the environment, causing serious damage to aquatic life and human well-being.2,3 Among these pollutants that are well-reported for their negative impact on water quality are a unique class of compounds referred to as emerging organic pollutants. Bisphenol A (BPA) is one of these emerging organic pollutants and is a synthetic organic compound, widely used in food packaging and production of pesticides, flame retardants, polycarbonate, and epoxy resins.4–8 BPA has been reported to act as an endocrine disruptor.4–8 It enters the aquatic system during the manufacturing process or through leaching from the products.9–11 BPA has a high water solubility (120 mg/L at 25°C) and KOW ~ 3.4, which is considered as a moderate potential for bioaccumulation.12 It acts by binding to the estrogen receptor or membrane-bound estrogen receptor in the cellular nucleus and influences cellular activities.9,10 In addition, BPA has been shown to affect metabolism through influencing enzyme activity in animal tissues.7

To date, various methods have been reported for the removal of BPA from wastewater. These include adsorption, biological treatment, chemical oxidation, and advanced oxidation processes.13–16 However, some of these methods...
have proven to be inefficient or are prone to generating a large amount of sludge. Advanced oxidation processes, on the other hand, have been consistently identified as effective methodologies for the removal of persistent organic pollutants from an aqueous environment. Among the advanced oxidation processes, the photodegradation technique, which is based on the ability of semiconductor materials to absorb a photon of energy equal to or greater than its band gap energy and generate hydroxyl (·OH) and superoxide (·O₂⁻) radicals, has been consistently used to degrade organic contaminants. Photodegradation offers the advantages of high efficiency, low toxicity, simplicity in design, and ease of operation.

Several catalysts have been reported in the literature for the photodegradation of BPA. Taking into consideration the TiO₂ properties, including strong oxidizing power, large surface area, corrosion resistance, nontoxicity, and cost effectiveness, this semiconductor has been widely used as a photocatalyst for the degradation of organic pollutants. However, its application has been hindered by the high recombination rate of the electron–hole pairs. Surface modification of TiO₂ with a polyaniline (PANI)-conducting polymer has been reported to alleviate this challenge by effecting charge separation. For example, commercially available irregularly shaped polyhedra P25 deposited by PANI has been found to exhibit an improved photocatalytic performance toward methylene blue because of electrons being gathered in the conduction band of TiO₂, while holes are trapped in the highest occupied molecular orbital (HOMO) of PANI. On the other hand, spherical black anatase TiO₂ nanoparticles, synthesized via a hydrothermal procedure, were deposited onto a PANI matrix, resulting in improved light absorption for photocatalytic degradation of methyl orange.

The conducting polymer PANI has been utilized as a polymer of choice because of its easy synthesis, relatively low cost, nontoxicity, and modifiable surface chemistry. In addition to the stated desirable properties of PANI, we chose it for our study for its added ability to adsorb organic molecules via π–π interactions and hydrogen bonding. Furthermore, the incorporation of the TiO₂ photocatalyst into a PANI polymer alleviates the problem of agglomeration that may occur if powders are used. In addition, we envision an improved photodegradation performance of the nanocomposite because of the large surface area offered by nanorods compared to other forms of TiO₂.

Although there have been numerous reports on the structural properties of TiO₂/PANI such as magnetic properties, conductivity, and crystallinity which can impact their application in photocatalysis and wastewater treatment, there are still no studies reported on PANI-wrapped TiO₂ nanorods for the degradation of BPA under UV radiation as per the authors’ knowledge. It is important to investigate the synergistic effect of enhanced surface area offered by PANI-wrapped nanorods in which PANI acts as the adsorbent for BPA and the TiO₂ nanorods degrade BPA, leading to enhanced adsorptive photocatalytic degradation. The advantages of adsorptive photocatalytic degradation cannot be overemphasized. Indeed, the adsorption of the pollutant molecules onto the surface of the catalyst plays an important role in enhancing degradation, and composite materials, which are good adsorbents, are crucial in terms of promoting the synergy between simultaneous adsorption and degradation of pollutant molecules.

When engaging in research on photocatalytic studies pertaining to industrial wastewater, it is also imperative to examine the effects of other interfering species which can coexist in industrial wastewater. Till date, the authors are unaware of any such studies which have been conducted for PANI/TiO₂-based photocatalysts. Moreover, other important parameters such as quantum yields (QYs), figures of merit (FOMs), and energy consumption, which are important in assessing the photocatalytic efficiency for industrial applications, have not been reported for PANI/TiO₂ photocatalysts. In addition, there are no reports with experimental data to explain the mechanism of degradation by PANI-supported TiO₂ which was conducted in this study.

Based on the abovementioned consideration, in the present work, PANI-wrapped TiO₂ nanorods were prepared for the degradation of BPA under UV radiation. The effect of nitrate and humic acid, which are likely to coexist with BPA in real industrial wastewater samples, is also reported. The QYs, energy consumption, and FOMs have been evaluated and compared with those of other nanocomposites which have been reported for BPA in order to assess the efficiency of this photocatalyst for BPA degradation in industrial applications. A detailed mechanism of degradation is further provided.

2. MATERIALS AND METHODS

2.1. Reagents. All chemicals used in present research were of AR grade except the ones highlighted. Titanium isopropoxide (TTIP), isopropanol alcohol, acetic acid, sodium hydroxide (NaOH), nitric acid (HNO₃), iron(III) chloride (FeCl₃), aniline, BPA [2,2-bis(4-hydroxyphenyl) propane, BPA], methanol (HPLC Grade), acetonitrile (HPLC Grade), benzoquinone, potassium iodide, potassium nitrate, ammonium acetate, humic acid, and acetone were acquired from Sigma-Aldrich and used without further purification. Ultrapure water was obtained from a Merck water system (Milli-Q).

2.2. Synthesis of PANI. PANI was synthesized following a method adopted from the literature with slight modification. In a typical synthesis, FeCl₃ (6 g) was dissolved in 40 mL of distilled water and 0.8 mL of aniline monomer was rapidly added to the oxidant solution under stirring. Distilled water (40 mL) was slowly added to the solution while stirring for about 5 min and then left to stand for 12 h. The green product was washed with acetone to stop further polymerization and then further washed with distilled water at ~pH 7. The green product was filtered under vacuum and dried in an oven at 60 °C.

2.3. Synthesis of TiO₂ Nanoparticles. TiO₂ nanoparticles were synthesized using a hydrothermal method. Typically, 5 mL of TTIP was dissolved in a mixture of isopropl alcohol and water (5:3). The solution was poured into a 100 mL beaker and stirred. Concentrated acetic acid (6 mL) was added to the solution while stirring. The solution was stirred for 3 h and then heated to 180 °C in an autoclave for 24 h. The solution was then cooled at room temperature and washed with excess ethanol to yield a white precipitate. The precipitate was washed with distilled water until ~pH 7. The precipitate was then dried in an oven at 60 °C and calcined at 500 °C in a muffle furnace in air, producing TiO₂.
The solution was then cooled at room temperature and then washed with dilute HNO₃ and then with distilled water until pH 7. The precipitate was then dried in an oven at 60 °C and then calcined at 500 °C in a muffle furnace in air, producing TiO₂ nanorods.

2.5. Synthesis of PANI/TiO₂. The PANI/TiO₂ nanocomposite was synthesized as follows: varying amounts of TiO₂ nanorods were dispersed in 20 mL of distilled water and stirred continuously. FeCl₃ (6 g) was added to the mixture and 0.2 mL of aniline monomer was rapidly added to the oxidant solution under stirring. Distilled water (60 mL) was slowly added to the solution under stirring for about 5 min and then left to stand for 12 h. The green product was washed with acetone to stop further polymerization and then further washed with distilled water at pH 7. This product was filtered under vacuum and dried in an oven at 60 °C.

2.6. Characterization of the Photocatalysts. The morphology of TiO₂ nanorods and the PANI/TiO₂ nanocomposite was analyzed using a VEGA3 TESCAN (Bruno, Czech Republic), scanning electron microscopy (SEM), and a JEOL JEM-2100 transmission electron microscope (Peabody, Massachusetts, USA). The structural properties were analyzed by X-ray diffraction (XRD) (Philips, X’Pert PRO MPD, mineral powder diffraction) analysis, which was carried to investigate the crystallinity of the nanocomposite. The instrument uses an X-ray source of Cu Kα-radiation beam with an excitation wavelength of 0.15406 nm for the analysis. The functional groups of the materials were analyzed by Fourier transform infrared (FTIR) spectra that were recorded using a Shimadzu FTIR 8400 spectrophotometer with Al Kα as the excitation source. Photoluminescence measurements were performed using a PerkinElmer LS 45 fluorescence spectrometer.

2.7. Photocatalytic Degradation Studies. The photocatalytic degradation studies were carried out in a photocatalytic reactor with a capacity of 1000 mL. A glass column housing a UV lamp was fixed inside the reactor with tap water circulating around the glass column, cooling the solution. The wall of the glass column has a thickness of 3 mm. The reactor was made of Perspex, and during reactions, it was placed on a magnetic stirrer to keep the solution under agitation. The mixture of the catalyst and BPA solution was left in the dark under magnetic stirring for an hour until adsorption–desorption equilibrium was established. The mixture was irradiated with a UV lamp light at a predominant wavelength of 365 nm. The photocatalysis study was investigated as a function of time. The initial solution pH was adjusted to 10 from the solution pH of 6.5 with 0.1 M HCl or 0.1 M NaOH for experiments investigating the influence of pH. The suspension was continuously stirred in the dark for 30 min using a magnetic stirrer to ensure the adsorption–desorption equilibrium of BPA on the catalyst. Aliquots (10 mL) were removed from the sample at varied time intervals and filtered through 0.45 μm membrane filter discs for analysis by an Agilent high-performance liquid chromatograph (HPLC) using acetonitrile/water (40/60, v/v) as the mobile phase, an elution time of 15 min, and a detector wavelength of 275 nm.

A C18 reversed-phase column (4.6 mm × 150 mm) was used for chromatographic analysis. Repeatability of the measurements was ensured by performing three experiments. The effect of pH on the photodegradation was examined by keeping 0.1 g of the photocatalyst in contact with 500 mL of BPA solutions of 5 ppm concentrations, set at pH 4.5, 7, and 10 and at a temperature of 25 °C. Similarly, the effect of photocatalyst dosage was investigated for the photodegradation of BPA by varying the mass of the photocatalyst from 10 to 250 mg in 500 mL of 5 ppm BPA solution. The effect of initial BPA concentration was investigated at different initial BPA concentrations from 1 to 30 ppm. The presented data points are mean values. The removal efficiency of BPA was calculated using eq 1

\[
\% \text{ removal} = \frac{C_i - C_f}{C_i} \times 100
\]

where \(C_i\) (mg/L) is the initial concentration of the adsorbate in solution and \(C_f\) (mg/L) is the final concentration of the adsorbate in the filtrate.

In order to test the validity and reproducibility of the analytical data, the photodegradation experiments were conducted in triplicate and an average of three results is reported. The relative standard deviation was found to be within ±0.05%.

2.7.1. LC–MS Conditions. The analysis was conducted using a Shimadzu UHPLC-MS/MS 8030 instrument (Tokyo, Japan). The chromatographic separation was performed using a RAPTOR AR C18, 2.7 μm 100 × 2.1 mm column. The column was previously conditioned with MeCN: (5:95 v/v) at a flow rate of 0.1 mL/min. The column temperature was set at 40 °C. BPA solutions were separated following a gradient elution program shown in Table 1. To prevent sample carryover, 100% MeOH was used as blank and was injected after every standard and sample injection. A flow rate of 0.2 mL/min was used for the elution of BPA in UHPLC. For tandem mass spectrometry, the deprotonated molecule [M + H]⁺ was used as the precursor ion. Tandem mass spectra were acquired between m/z 30 and m/z 300 in the enhanced mass resolution mode Q3. A nebulizing gas flow rate of 3 L/min was used. A drying gas flow rate of 15 L/min was used for the mass spectrometry.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis of TiO₂, PANI, and PANI/TiO₂. FTIR spectroscopy analysis revealed the incorporation of PANI into a nanocomposite of PANI/TiO₂ as shown by the functional
groups of PANI that are present in the PANI/TiO$_2$ nanocomposite. The main peaks of PANI were all confirmed in the spectra (b) with peaks appearing at 3662, 2955, 1577, 1502, 1301, 1250, and 827 cm$^{-1}$.42 The band at 3662 cm$^{-1}$ corresponds to the N–H stretching mode and the peak around 2955 cm$^{-1}$ corresponds to the aromatic C–H vibration.42 The peaks appearing at 1577 and 1502 cm$^{-1}$ are due to the C=C and C=N stretch of the benzoide and quinoid, respectively (Figure 1). The peak appearing at 1301 cm$^{-1}$ is due to the C=N vibrations.42 The peaks due to PANI were clearly observed in the PANI/TiO$_2$ sample. The spectrum displays the major peaks of PANI such as the peak at 3662 cm$^{-1}$ which is due to the N–H stretching and other peaks due to the benzoide and quinoid rings which appear at 1577 and 1502 cm$^{-1}$.40 The new weak peak appearing at 917 cm$^{-1}$ is probably due to the C–H out-of-plane bending vibration of the PANI composite.39 These bands reveal the existence of PANI in the synthesized PANI/TiO$_2$ sample. At 700 cm$^{-1}$, a peak assigned to Ti–O–Ti bridging stretch modes was observed on the TiO$_2$ spectra.43

3.2. XRD Analysis of Pristine PANI, TiO$_2$, and PANI/TiO$_2$. The results for XRD analysis are shown in Figure 2. XRD analysis of as-synthesized PANI showed two broad peaks at 2$\theta$ = 20.5 and 25.3$^\circ$. This suggested an amorphous structure of the PANI and the results are in agreement with results that were obtained by Haldorai et al.44 The XRD pattern of as-synthesized TiO$_2$ nanoparticles showed peaks at 2$\theta$ values of 25.30, 37.90, 47.99, 54.2, 62.72, 68.84, 70.28, 75.12, and 82.79$^\circ$. These peaks correspond to anatase TiO$_2$ with hkl crystal planes [101], [004], [200], [105], [211], [204], [116], [220], [215], and [303], respectively.46 This pattern confirms the formation of a pure anatase phase without any other phases with a JCPDS score of 97%. The observed 2$\theta$ values were consistent with the standard values and showed the anatase phase of TiO$_2$ as per Joint Committee on Powder Diffraction Standard (JCPDS) card no. 01-086-1157. The peaks in as-synthesized TiO$_2$ also appeared in the PANI/TiO$_2$ nanocomposite showing that the TiO$_2$ did not lose its crystallinity even after incorporation of PANI.

XRD analysis can be used to determine the crystallite size of the powdered material by treating the XRD data using the Scherrer equation.47 The particle size of the material has been reported to affect the overall performance of the photocatalyst.50 Small particle sizes have been reported to provide a high surface area to volume ratio, which improves the photocatalytic efficiency by improving the contact between the photocatalysts and the pollutant.50,51 In this study, the particle sizes were determined using the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where $D$ is the average size in nanometers, $k = 0.89$, $\lambda = 0.1540$ nm (Cu K$\alpha$), $\beta$ = fwhm $\times$ 0.01745 in radians, and $\theta$ is the peak position.

The results show an average particle size of 16.62 nm. The same peak positions were also observed in a nanocomposite of PANI/TiO$_2$ with a calculated average particle size of 16.6 nm.

3.3. BET Analysis of Pristine PANI, TiO$_2$, and PANI/TiO$_2$. The pore size distribution and specific surface area were determined via nitrogen adsorption–desorption isotherms. Figure 3 illustrates that all the as-synthesized photocatalysts can be identified as a Type V isotherm with the H4-type hysteresis loop according to the IUPAC–BET classification.52 This signifies the presence of the mesoporous structure in the photocatalysts.52 Table 2 summarizes the BET specific surface area, pore volume, and pore size of all as-prepared PANI, TiO$_2$, and PANI/TiO$_2$ photocatalysts. The BET data showed that
the addition of PANI to the calcined TiO$_2$ resulted in an increase in the surface area from 28.2179 m$^2$/g of TiO$_2$ to 44.8999 m$^2$/g of PANI/TiO$_2$. A similar trend was observed in the pore volume and pore size because of the incorporation of PANI into the PANI/TiO$_2$ nanocomposite. The increase in these important parameters may result in high degradation performance of PANI/TiO$_2$.

3.4. SEM Analysis of (A) TiO$_2$ Nanorods and (B) PANI/TiO$_2$. Figure 4 shows the rod-like TiO$_2$ photocatalyst (image A). Image B in Figure 4 shows denser rod-shaped materials of different sizes.

3.5. TEM Analysis of (A) TiO$_2$ Nanorods and (B) SAED Analysis TiO$_2$ Nanorods. Transmission electron microscopy (TEM) analysis confirmed that nanorods of TiO$_2$ were synthesized, as shown in Figure 5 a,b. These uniformly dispersed TiO$_2$ nanorods had a diameter size range of 40–100 nm. TEM analysis revealed that the TiO$_2$ nanorods were wrapped by a thin layer of PANI forming in the nano-

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**Table 2. BET Specific Surface Area, Pore Volume, and Pore Size of as-prepared PANI, TiO$_2$, and PANI/TiO$_2$ photocatalyst**

| photocatalyst | $S_{BET}$ (m$^2$/g) | pole volume (cm$^3$/g) | pore size (nm) |
|---------------|---------------------|------------------------|----------------|
| PANI          | 4.3093              | 0.033007               | 30.64          |
| TiO$_2$       | 28.2179             | 0.097520               | 13.82          |
| PANI/TiO$_2$  | 44.8999             | 0.145248               | 35.62          |

Figure 3. BET surface area of [A] pristine TiO$_2$ nanorods, [B] PANI/TiO$_2$, and [C] TiO$_2$/PANI.

Figure 4. SEM images of pristine TiO$_2$ (A) and PANI/TiO$_2$ (B).
composite of PANI/TiO$_2$ (Figure 5c,d). EDX elemental analysis in Figure 5e showed that the nanocomposite was mainly composed of carbon (C), oxygen (O), and titanium (Ti) elements. The chloride ion (Cl$^-$) species and Fe came from the preparation of the PANI/TiO$_2$ nanocomposite. Copper (Cu) atoms shown were due to copper grids used during TEM analysis.

3.6. TGA of Pristine PANI, TiO$_2$ Nanorods, and PANI/TiO$_2$. Thermogravimetric analysis (TGA) was employed to investigate the thermal stability of the TiO$_2$ and PANI/TiO$_2$ nanocomposite. TGA profiles of the TiO$_2$ and PANI/TiO$_2$ nanocomposite are shown in Figure 6. TGA results for PANI show four major weight losses. The weight loss in the first stage, from 50 to 150 °C for the peak of the pristine TiO$_2$ and PANI/TiO$_2$ nanocomposite, is due to the loss of adsorbed and bound water on the nanocomposite.$^{53}$ The weight loss at 150−250 °C was due to loss of water of crystallization.$^{54}$ The weight loss that occurred after 380−500 °C was due to the removal of functional groups and breaking of bonds forming the PANI polymers and also due to loss of gaseous emissions, for example, carbon monoxide, which might have occurred.$^{54}$ The weight loss at 150−250 °C was due to loss of water of crystallization.$^{54}$ The weight loss that occurred after 380−500 °C was due to the removal of functional groups and breaking of bonds forming the PANI polymers and also due to loss of gaseous emissions, for example, carbon monoxide, which might have occurred.$^{54}$ The final weight loss at 800 °C was due to the thermal degradation of the carbonaceous material.$^{55}$ TGA for the PANI/TiO$_2$ nanocomposite is shown in Figure 7. The results indicate three major weight losses. The first weight loss at 25−150 °C was due to loss of moisture.$^{56}$ Another weight loss observed from 180 to 700 °C was due to loss of low molecular weight oligomers of PANI.$^{26}$ After 700 °C, there was no weight loss observed for the nanocomposite because of the stability of TiO$_2$, which was incorporated into PANI to form a nanocomposite. This is in agreement with observations made on pristine TiO$_2$.$^{57}$

3.7. Photoluminescence and UV Absorption Analysis. Photoluminescence (PL) and UV spectroscopy provide information on the charge separation of materials.$^{55,56,59}$ PL reveals the migration of charges (electrons and holes) and the
formation of defects in the photocatalyst. This helps in understanding the recombination rate of charges at the surface of the photocatalyst. Figure 7a shows results of emission of the materials at 530 nm for all sample materials. The intensity of pristine TiO$_2$ spectra is higher than that of pristine PANI and that of PANI/TiO$_2$. The results show that the incorporation of PANI greatly improved the performance of the nanocomposite by reducing the recombination rate of the nanocomposite. This is attributed to the ability of PANI to affect charge separation by transferring electrons to the conduction band of TiO$_2$ and also trapped holes, leading to charge separation.

3.8. X-ray Photoelectron Spectroscopy. The surface characterization and chemical states of the PANI/TiO$_2$ nanocomposite were examined by X-ray photoelectron spectroscopy (XPS). Figure 8a represents the XPS survey scan of the PANI/TiO$_2$ nanocomposite, which revealed the presence of C, O, Ti, and N. The XPS results shown in Figure 8b reveal a peak at 284.75 eV, which was assigned to carbon from the PANI polymer. A small peak at 288.1 eV corresponding to C=O-Ti was observed. The peak in Figure 8c at 399.3 eV due to the N 1s peak corroborates positively with quinoid amine and benzenoid amine, which is consistent with the structure of PANI as reported by Golczak et al. Figure 8d presents the core level O 1s spectra (530 eV) due to O bonds such as Ti-O-Ti and Ti-O-H. Ti 2p core level spectra are presented in Figure 8e at 459.2 eV and 464.9 eV due to Ti 2p$_1/2$ and Ti 2p$_3/2$, respectively.

3.9. Application Results. 3.9.1. Selection of Photocatalysts. The photocatalytic action of pristine TiO$_2$ and PANI/TiO$_2$ was evaluated using a photocatalyst dosage of 0.2 g/L and 5 mg/L BPA solution at solution pH 6.5. Figure 9 shows the photocatalytic degradation of BPA under UV radiation. It is clearly observed that the photocatalytic degradation removal of PANI/TiO$_2$ was higher than that of pristine TiO$_2$. After 80 min irradiation, 79.8% degradation of BPA was achieved by PANI/TiO$_2$ compared to a removal efficiency of 60.7% that was observed for pristine TiO$_2$. The enhanced photoresponse of PANI/TiO$_2$ can be attributed to the modification of TiO$_2$ with PANI. This is in agreement with the observed results from BET analysis that showed an increase in the surface area of the nanocomposite after modification of TiO$_2$ with PANI (Figure 3). The contribution of PANI to the overall degradation efficiency is further highlighted by the increased removal efficiency of BPA in graph (b) compared to graph (a) under darkness. The removal in graph (b) can be attributed to adsorption via $\pi-\pi$ stacking and hydrogen bonding of BPA and PANI. The slight removal that was observed on graph (a) can be attributed to photolysis. PANI/TiO$_2$ was chosen for the rest of the experiments.

3.9.2. Effect of pH of BPA Solution on Its Photodegradation. Solution pH plays an important role in determining the efficiency of the photodegradation process. This is because it affects the adsorption-desorption of the organic molecules on the surface of the photocatalyst. In addition, pH influences the generation of hydroxyl radicals and active oxygen species that occur on the surface of the photocatalyst.
Figure 10 shows a comparison of the degradation of BPA (5 ppm) with a dosage of 0.2 g/L at different initial BPA solution pH’s ranging from 4 to 10. The results showed that the degradation of BPA depended strongly on the initial solution pH. The reported point of zero charge of TiO$_2$ from the literature is 6.25 while that of PANI is 5.8.$^{64,65}$ This implies that the surface of the PANI/TiO$_2$ was negatively charged in an alkaline solution and positively charged in an acidic solution. On the other hand, BPA had a negative charge because of the hydroxyl molecules in its structure.$^{66}$ These surface properties influenced the initial adsorption of BPA on the catalysts. The results in Figure 10 show that the BPA removal was 99.8% at pH 10 compared to 79.6% at pH 7 and the lowest removal was at pH 4 (50%). The high removal at pH 10 was due to an increase in diffused hydroxyl radicals in the bulk solution that degraded BPA.$^{41,42,67}$ Therefore, a pH of 10 was used as the optimum pH for the rest of the experiments.

Figure 8. (a) XPS survey scan for TiO$_2$/PANI. (b) Core level XPS spectra for (b) C 1s, (c) N 1s, (d) O 1s, and (e) Ti 2p of TiO$_2$/PANI.

Figure 9. Degradation of BPA on (a) pristine TiO$_2$ in the dark and (b) PANI/TiO$_2$ in the dark. Photocatalytic degradation on (c) pristine TiO$_2$ and (d) PANI/TiO$_2$. 
3.9.3. Effect of Photocatalyst Dosage on the Photodegradation of BPA. The effect of dosage on the photodegradation of BPA was determined in order to optimize the efficiency of the photodegradation process. Figure 11 shows a comparison of the degradation of BPA at different initial photocatalyst dosages. The results show that photodegradation efficiency improved with an increase in the dosage. The increase in dosage increased the number of \( \cdot \text{OH} \) radicals, which participated in the degradation of BPA.\textsuperscript{41} The results shown in Figure 11 show that the highest degradation of 99.9\% was attained within 80 min for dosages of 250 mg. However, despite achieving 94.5\% degradation efficiency after the same irradiation time, 100 mg dosage in 500 mL of BPA was chosen as the optimum dosage for the rest of the study. A high dosage may have reduced the degradation efficiency because of aggregation of the photocatalyst which may have reduced the surface area of the photocatalyst for light absorption.\textsuperscript{14} The BPA solution was degraded up to 40, 50, 59.6, and 80.5\% by 10, 20, 50, and 75 mg photocatalyst dosages after 80 min of irradiation, respectively.

3.9.4. Effect of Initial Concentration of BPA on Photodegradation. The effect of initial BPA concentration on its photodegradation was investigated over a concentration range of 1–30 ppm under an optimal pH of 10 and a photocatalyst dosage of 0.2 g/L. The photodegradation efficiency was influenced by the initial BPA concentration, as shown in Figure 12. Complete degradation of 1 ppm BPA solution was achieved within 80 min. 99.8\% degradation was attained for 5 ppm BPA solution within the same time and only 45.4\% was achieved when degrading 30 ppm BPA. After 80 min of irradiation, 68\%, 75.8\%, and 85\% degradation was achieved for 10 ppm, 15 ppm, and 20 ppm BPA solutions, respectively. The degradation efficiency decreases with increase in the concentration of BPA. This can be attributed to the increase in the BPA molecules that were adsorbed on the surface of the photocatalyst.\textsuperscript{19} This resulted in a reduction in the photons that were able to reach the surface of the photocatalyst surface, and therefore, less hydroxyl radicals were generated resulting in reduced photodegradation efficiency.\textsuperscript{14}

3.9.5. Kinetic Studies. A kinetic study was conducted on the degradation of BPA by as-synthesized PANI, TiO\(_2\), and PANI/TiO\(_2\). Table 3 shows the rate constants for the photodegradation of BPA by PANI/TiO\(_2\) corresponding to the Langmuir–Hinshelwood kinetics, which follows the relationship given below. The rate constant was calculated using the following expression\textsuperscript{68}

\[
\ln \left( \frac{C_0}{C} \right) = -kt
\]

(3)

where \( C_0 \) and \( C \) are the initial and final concentration, respectively, \( k \) is the rate constant, and \( t \) is the irradiation time. The rate constant for the degradation of BPA was calculated using the following expression\textsuperscript{68}

| photocatalyst | \( R^2 \) | rate constant (K min\(^{-1}\)) |
|--------------|----------|-----------------------------|
| PANI         | 0.6895   | 7.04 \times 10^{-4}         |
| TiO\(_2\)    | 0.9688   | 2.18 \times 10^{-2}         |
| PANI/TiO\(_2\) | 0.9589 | 4.46 \times 10^{-2}         |

The results show that PANI had the lowest rate constant of 7.04 \times 10^{-4} min\(^{-1}\). Pristine TiO\(_2\) had a rate constant of 2.18 \times 10^{-2} min\(^{-1}\). PANI/TiO\(_2\) shows a better performance than as-synthesized PANI and TiO\(_2\) with a rate constant of 4.46 \times 10^{-2} min\(^{-1}\). The results show a linear agreement with pseudo-first-order kinetics with high \( R^2 \) values. However, the \( R^2 \) value for the degradation of BPA by PANI was 0.6895,
which was the lowest, suggesting that the removal of BPA did not fit well with the pseudo-first-order kinetic model.

The rate of degradation was further evaluated as 150 mmol/g/h for PANI/TiO₂ and 74.89 mmol/g/h for TiO₂. Thus, PANI/TiO₂ is almost 50% more efficient at degrading BPA than TiO₂ and even shows enhanced rates of degradation when compared to TiO₂ nanotubes developed for the degradation of CO₂ into CO and CH₄.⁶⁸

3.9.6. Effect of the Nitrate Ion on the Degradation of BPA. Nitrates have been reported to influence the degradation of organic matter in natural water as it is a source of hydroxide radicals.⁶⁹ However, some reports indicate that NO₃⁻ ions also negatively affect the process of degradation of organics in water as they can scavenge reactive oxygen species.⁷⁰ The effects of the NO₃⁻ ion on the degradation of BPA was investigated using environmentally relevant concentrations (0.05, 0.1, 0.5, and 1.0 mM) using 0.2 g/L photocatalyst dosage and 5 mg/L BPA solution with a pH of 6.5. The results in Figure 13 showed that the presence of nitrate ions in the BPA solution greatly influenced the degradation efficiency. The removal efficiency increased with an increase in the concentration of nitrates. The increase in the degradation rate was due to the ability of NO₃⁻ ions to induce the production of OH* radicals according to eqs 5-7.⁶⁹,⁷¹

\[
\text{NO}_3^- + h\nu \rightarrow [\text{NO}_3^-]^* \rightarrow \text{ONO}^- \quad (4)
\]

\[
[\text{NO}_3^-]^* \rightarrow \text{NO}_2^- + \text{O}^{(1)}\text{P} \quad (5)
\]

\[
[\text{NO}_3^-]^* \rightarrow \text{NO}_2^* + \text{O}^* + \text{H}_2\text{O} \rightarrow \text{NO}_2^* + \text{OH}^* + \text{OH}^- \quad (6)
\]

3.9.7. Effect of Humic Acid on the Degradation of BPA. Natural organic matter has been reported to have an influence in the fate of environmental organic contaminants. Guetzlof and Rice reported that the presence of humic acid resulted in an increase in the solubility of polycyclic aromatic hydrocarbon (PAH).⁷² Some reports also indicated that humic acids had no effect on degradation of organic pollutants.⁷³ In this study, the effect of humic acids in solution during degradation of BPA (5 mg/L) was investigated by adding 0, 1, 3, and 5 mg/L humic acid. The results shown in Figure 14 show that the presence of humic acids in solution at different concentrations consistently inhibited the degradation of BPA. The highest inhibition was observed with the addition of 5 mg/L. The inhibition was attributed to the blockage of the active sites by adsorbed humic acid on the PANI/TiO₂ photocatalyst.⁷⁴ Similarly, Li and Hu reported an inhibition of degradation of tetracycline in the presence of humic acid.⁷⁵ They concluded that humic acid quenched OH* radicals that are critical for the degradation process.

3.9.8. Byproduct Identification. BPA was degraded using PANI/TiO₂ and the intermediate products were identified using LC–MS. Samples were collected from the reactor at 0; 20; 60; and 120 min of irradiation. They were then filtered using 0.45 μm filter disc. The high-performance liquid chromatograms for BPA standard and the degradation products are shown in Figure 15a. The retention time (tᵣ) of BPA was shown to be at 4.4 min, which was evidenced by the single chromatogram in the samples for BPA standard and that at 0 min irradiation time. However, after irradiation, the peak due to the parent BPA reduced in size and completely disappeared with irradiation. Subsequently, new peaks appeared in chromatograms with tᵣ at 1.0; 1.7; and 3.0 that were attributed to degradation products. A peak with retention time ~0.7 was attributed to the degradation of the PANI polymer. However, there is need for other techniques to assist with its identification.

Figure 15b shows the full mass spectrum scans of the samples. The results show that BPA could be ionized in the positive mode producing a molecular ion abundance at m/z 229.1, which corresponded to the protonated BPA, [M + H]+. The results show that a fragment of BPA with a m/z of 213.1 was produced after 20 min of irradiation.⁷⁶ This fragment resulted from a loss of a methyl group, producing a carbocation, [C₁₄H₁₃O⁺]. Another peak with m/z 135.1 was produced and this was attributed to [C₆H₅O⁻] which was produced as a result of the cleavage of the alkyl-phenyl bond and possible degradation of BPA.⁷⁶ A peak observed at m/z 93.1 was attributed to the cleavage of two base phenolic molecules of BPA producing a fragment with the formula C₆H₅O. These degradation products were consistent with those reported in the literature.⁷⁵–⁷⁷

From the observed degradation products, a degradation pathway is proposed in Figure 18.

3.9.9. Proposed Mechanism for BPA Degradation. Reactive species such as hydroxyl (OH*), superoxide (O₂⁻), and holes (h⁺) are responsible for the degradation process (Figure 16).⁷⁸ In a study, Brooms et al. suggested a mechanism for the degradation of p-cresol by TiO₂/ZnO/PANI.⁷⁹ The authors suggested that PANI played an active role in the
degradation of p-cresol by TiO$_2$/ZnO/PANI by transferring electrons to the conduction band of TiO$_2$/ZnO and also trapped holes, leading to charge separation.$^{39}$ In another study, Masid et al. suggested the same mechanism when they used PANI/TiO$_2$ to degrade a dye, reactive blue 4.$^{79}$ However, there is no experimental data to support the suggested degradation mechanisms. In this study, we provide experimental data showing which reactive oxygen species were...
Different scavengers of reactive species were added to the degradation solution, and the degradation performance was evaluated after irradiation under optimized conditions. In this study, potassium iodide (KI) was used as a scavenger for positive holes. Figure 17 shows that only 30% degradation was achieved after the addition of potassium iodide (KI). This suggests that the positively charged holes were actively involved in the degradation of BPA. In the presence of benzoquinone (BQ) which was used as scavenger for superoxide radicals, 48% degradation was achieved, which is lower than the 99.8% achieved in the absence of quenchers. This suggests that the superoxide radicals were also involved in the degradation of BPA, although their involvement was not as dominant as that of the positive holes. In the presence of 10% volume isopropyl alcohol (IPA) which was used as a scavenger for hydroxyl radicals, a slight decrease in the degradation efficiency with an overall degradation of 70% after 80 min of irradiation under UV light was observed. This suggests that the hydroxyl radicals were not the dominant reactive species in the degradation of BPA by PANI/TiO2.

The mechanism for the degradation of BPA was therefore proposed to occur, as shown in Figure 18. After absorbing UV light irradiation, PANI can release electrons from the HOMO into the lowest energy unoccupied molecular orbital. PANI can transfer the photogenerated electron (e−) into the conduction band of the TiO2. The electrons were then scavenged by oxygen molecules, forming superoxides that are highly oxidizing, and they degraded BPA. Simultaneously, electrons might migrate from the VB of TiO2 to the HOMO of PANI, leaving behind positively charged holes (h+). The positive holes might react with moisture, forming hydroxyl radicals that are also highly oxidizing, and they degraded BPA.

3.9.10. Performance Efficiency of PANI/TiO2. In order to assess the efficiency of PANI/TiO2 as a photocatalyst for the degradation of BPA, the following parameters were evaluated.

\[
\text{quantum yield (QY)} = \frac{\text{decay rate (molecules per second)}}{\text{photon (photons per second)}}
\]

\[
\text{figure of merit (FOM)} = \frac{\text{product obtained (L)}}{\text{catalyst mass (g)} \times \text{time (h)} \times \text{energy consumption (Wh/mol)}}
\]

These parameters are tabulated for comparison with those of other photocatalysts developed for BPA degradation. Table 4 clearly shows that PANI/TiO2 supersedes most photocatalysts developed for BPA with respect to the QY, energy consumption, and FOM. Moreover, this photocatalyst also surpasses the degradation performance of the rGO/ZrO2/Ag3PO4 developed by Anwar and Park82 for the degradation of 4-nitrophenol and also gave the same FOM. It further shows a higher QY than that developed by Cortes et al.83 for the degradation of CO2. Hence, PANI/TiO2 can be considered as a highly efficient photocatalyst for industrial applications because of its relatively higher QY and FOM and lower energy consumption.

4. CONCLUSIONS

PANI-wrapped TiO2 nanorods were successfully synthesized by oxidative polymerization of aniline on hydrothermally presynthesized TiO2 nanorods. The photodegradation of BPA under UV radiation was investigated. The use of nanostructured TiO2 wrapped in PANI improved the photo-
Table 4. Comparison of Efficiency Parameters for the Degradation of BPA (Anwer and Park, 2018)

| photocatalyst       | light source | energy consumption (W h/μmol) | photocatalyst dosage (g/L) | QY (molecules per photon) | FOM |
|---------------------|--------------|------------------------------|---------------------------|--------------------------|-----|
| Ag2PO4−graphene     | vis          | 14.6                         | 0.5                       | 4.69 × 10^-6             | 69  |
| GO/BiFeO3           | UV           | 135.0                        | 0.5                       | 7.24 × 10^-7             | 50  |
| GO/BiFeO3           | vis          | 165.5                        | 0.5                       | 3.65 × 10^-7             | 50  |
| PANI/TiO2 (this study) | UV          | 1.46                         | 0.5                       | 9.86 × 10^-3             | 100 |

The degradation efficiency of the photocatalyst because of the synergistic effect of adsorption by PANI and photodegradation by TiO2. PANI affected charge separation and reduced the rate of recombination. LC−MS analysis identified degradation products with m/z 213.1, 135.1, and 93.1. The performance metrics showed that PANI/TiO2 had a relatively higher QY and FOM than most developed photocatalysts and lower energy consumption and enhanced rates of degradation and hence is a highly favorable photocatalyst for industrial applications. The degradation was however enhanced in the presence of nitrate ions and inhibited in the presence of humic acid. In summary, we report that the degradation of BPA using PANI/TiO2 nanocomposite has the potential to help alleviate the threat of water contamination by BPA and it is a highly efficient photocatalyst. However, humic acid must be removed from the wastewater sample matrix, as this inhibits the photocatalytic activity.

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**Notes**

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