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Synthesis of TiO$_2$–Ag$_3$PO$_4$ photocatalyst material with high adsorption capacity and photocatalytic activity: application in the removal of dyes and pesticides

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The photocatalytic activity of TiO$_2$ can be enhanced by coupling it with other semiconductors and the semiconductor composites may find useful application in water treatment technologies. TiO$_2$–Ag$_3$PO$_4$ composites were synthesized and characterized with XRD, SEM-EDX and DRS. The synthesized TiO$_2$–Ag$_3$PO$_4$ showed high photocatalytic activity in the presence UV-vis light on rhodamine B, methylene blue and the pesticides imidacloprid, atrazine and pyrimethanil. LC-MS analysis of the photodegraded pyrimethanil led to the identification of hydroxylated and aliphatic derivatives of pyrimethanil. The photocatalytic activity of the coupled semiconductor was higher than that of the bare TiO$_2$ and Ag$_3$PO$_4$ and this was attributed to the unique band matching between TiO$_2$ and Ag$_3$PO$_4$ which resulted in efficient charge separation and subsequent reduction in the electron–hole recombination. In addition, the synthesized TiO$_2$–Ag$_3$PO$_4$ showed strong adsorption for water soluble dyes implying that TiO$_2$–Ag$_3$PO$_4$ can remove pollutants through photocatalysis and adsorption. The results from the study showed the potential application of TiO$_2$–Ag$_3$PO$_4$ composite in water treatment technologies.

1 Introduction

Increased population and industrial activities have resulted in industrial effluent generation and pollution of water bodies, harmful to humans and aquatic life especially when they contain substances such as dyes, pesticides, heavy metals and pharmaceutical wastes.[1]

The world production of dyes has increased dramatically over the past years and these azo dyes, reactive dyes, solvent dyes for instance are used by the textile, food, adhesive, cosmetics, arts, construction, paints, glass and ceramic industries extensively.[2] The release of these colored organic substances into our environment is a source of aesthetic pollution and is detrimental to the environmental ecosystems. In addition, large concentrations of organic dyes in the aquatic environment may be toxic to aquatic species and disulphonated azo dyes has been reported to be a major source of problem in drinking water plants globally.[3]

In addition there is high demand for pesticides globally as a result of increasing agricultural activities and the toxins in the pesticides are leached into surface and ground water sources which are detrimental to human health and aquatic life.[4] The alarming impact of these activities on the environment has prompted the European Union to set standards under the European Directive 2000/60/EC that establishes maximum concentrations for pesticides and related harmful chemical substances in drinking waters to safeguard its detrimental effects on humans.[5]

High chemical stability and low biodegradability of these organic pollutants have necessitated the search for suitable treatment methods that can easily break down inherent chemical components. Techniques such as adsorption, biodegradation, ozonation and photo-Fenton processes have been adopted in treating dyes and pesticides pollutants.[6] However, these methods have been reported to be ineffective in the treatment of polluted water bodies.[7] Recent studies have been focused on the use of advance oxidation processes such as photocatalysis for the removal of dyes and pesticides from wastewaters,[8] degradation of crude oil fractions,[9] and for aquatic disinfection.[10]

Photocatalysis involves the generation of reactive oxygen species (ROS) in the presence of sunlight, semiconductor, dissolved oxygen and water. These ROS are able to oxidize and mineralize organic contaminants into carbon dioxide and inorganic anions.[11] Hence, semiconductor based photocatalysts have received enormous attention because of their potential in solving some of the most challenging environmental problems. One of the most widely investigated photocatalyst is TiO$_2$. Though TiO$_2$ is chemically stable, its wide band gap energy limits its efficient utilization in sunlight irradiation. That is TiO$_2$ is active in the UV region of the electromagnetic spectrum

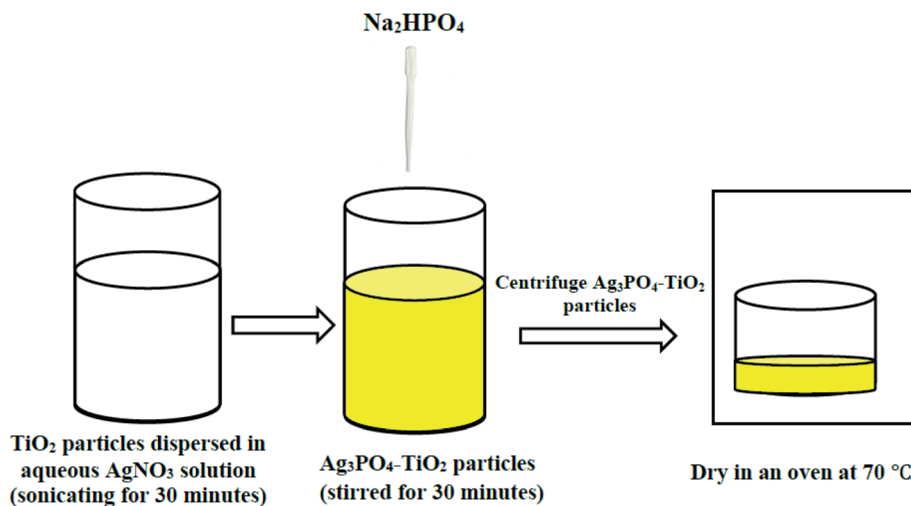*Department of Materials Science and Engineering, University of Ghana, LG 77, Accra, Ghana. E-mail: jkefavi@ug.edu.gh*

Fig. 1 Synthesis scheme of the Ag_3PO_4–TiO_2 nanocomposite.

which makes up only *ca.* 4–5% of the electromagnetic spectrum and this limits its practical application. Developing semiconductor materials that are very sensitive to visible light and can be effectively utilized in practical applications has become the focus of many researchers. Different visible light active photocatalysts such as Au/TiO_2,[12] $C–TiO_2/g-C_3N_4$,[13] $YFeO_3$,[14] defect ZnO nanorods[15] and ZnO/CuO[16] have been developed by researchers. These semiconductor photocatalyst may be decorated with bimetallic nanoparticle cocatalyst to enhance their degradation efficiency.[17] In addition, 3D graphene based photocatalyst have been developed and utilized in environmental pollutant degradation.[18] Ag_3PO_4 with extremely high visible light photocatalytic activity has also been reported.[19]

Photocorrosion which involves the conversion of Ag^+ to Ag^0 in the absence of an electron acceptor has been reported as a major drawback of Ag_3PO_4 photocatalyst. This occurs as a result of the solubility of Ag_3PO_4 in aqueous solution.[19a,20] In addition to using Ag_3PO_4 as a stand-alone photocatalyst, several composite photocatalyst have been developed by combining Ag_3PO_4 with AgI,[21] gC_3N_4,[22] carbon quantum dots,[23] $SrTiO_3$ (ref. 24) and TiO_2.[25] TiO_2–Ag_3PO_4 has been reported to be the most efficient among the

composite photocatalyst formed with Ag_3PO_4.[26] A photocatalytic system made up of carbon fiber cloth as a porous substrate and Ag_3PO_4/TiO_2 as a photocatalyst with a rhodamine B dye removal efficiency of ~99.5% has been reported.[27] Graphene oxide (GO) embedded ternary heterostructure nanocomposites of $N–TiO_2/Ag_3PO_4@GO$ with different weight ratios of $N–TiO_2$ to Ag_3PO_4 has also been developed.[28] It should however be mentioned that, to the best of the authors knowledge, efficiency of all the reported TiO_2–Ag_3PO_4 photocatalyst was examined using water soluble dyes and phenols,[29] and none of the articles reported a detailed adsorption kinetics and equilibrium studies. A detailed adsorption equilibrium and kinetic studies is required to understand the adsorption mechanism of Ag_3PO_4–TiO_2 towards organic molecules.[30]

In this study, a one pot method was used to synthesize Ag_3PO_4–TiO_2 photocatalyst. The synthesized photocatalyst was characterized with XRD, SEM-EDX, and DRS. The photodegradation efficiency was examined using rhodamine B dye, methylene blue dye and three pesticides; atrazine, imidacloprid and pyrimethanil. Detailed adsorption kinetic and equilibrium studies was conducted on the Ag_3PO_4–TiO_2 using methylene blue dye. The
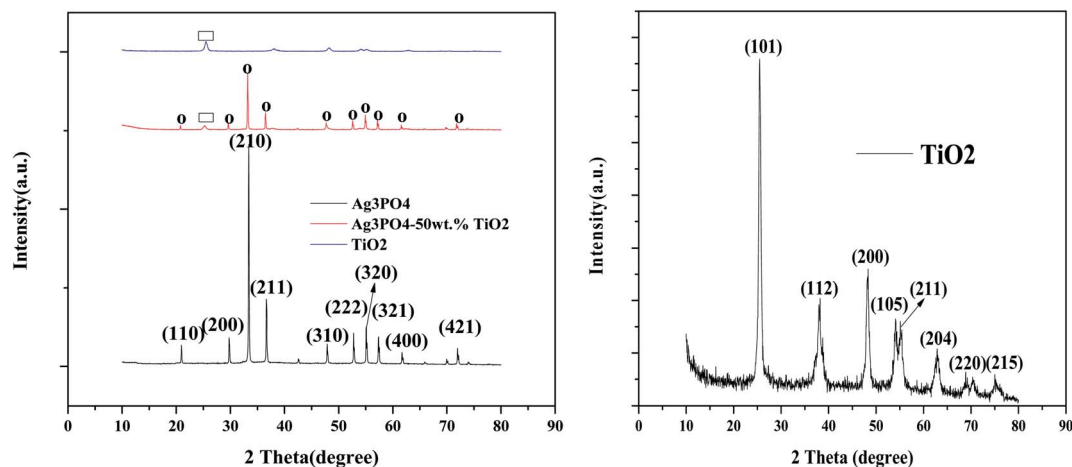

Fig. 2 XRD patterns for (A) Ag_3PO_4, TiO_2 and Ag_3PO_4-50 wt% TiO_2, (B) enlarged XRD pattern for TiO_2 [O = Ag_3PO_4, □ = TiO_2].

photodegradation by-products obtained after subjecting pyrimethanil to photocatalysis were identified using LC-MS.

2 Experimental procedure

2.1 Materials

All chemical reagents used in this study were analytical grade and were purchased from Sigma Aldrich, U.K. The chemical reagents were used without further purification. Deionized water was used throughout this study.

2.2 Synthesis of Ag$_3$PO$_4$–TiO$_2$ nanocomposite

In a typical synthesis, a calculated amount of TiO$_2$ (P25) was dispersed in 150 mL of 0.02 M AgNO$_3$ by sonicating for 30 minutes. 122.5 mL of 0.2 M Na$_2$HPO$_4$ was then added dropwise while stirring. The resulting bright yellow solution was continuously stirred for 30 minutes and then centrifuged to collect the bright yellow precipitate. The collected precipitate was washed repeatedly (three cycles) with deionized water and dried at 70 °C to obtain Ag$_3$PO$_4$–TiO$_2$ nanocomposite. Different amounts of TiO$_2$ were used in the synthesis to obtain samples with 10 wt%, 25 wt%, 50 wt% and 75 wt% TiO$_2$. A similar procedure was used to obtain Ag$_3$PO$_4$ but without the addition of TiO$_2$. The synthesis scheme of the Ag$_3$PO$_4$–TiO$_2$ nanocomposite is provided in Fig. 1 below.

2.3 Product characterization

2.3.1 X-ray diffraction (XRD).
The X-ray diffraction patterns were obtained with Bruker D8 advanced focus diffractometer fitted with position sensitive detector (LynxEye) and standard detector. Cu-Kα radiation ($\lambda = 0.15405$ nm) and a 2theta angular range of 10–80° were used.
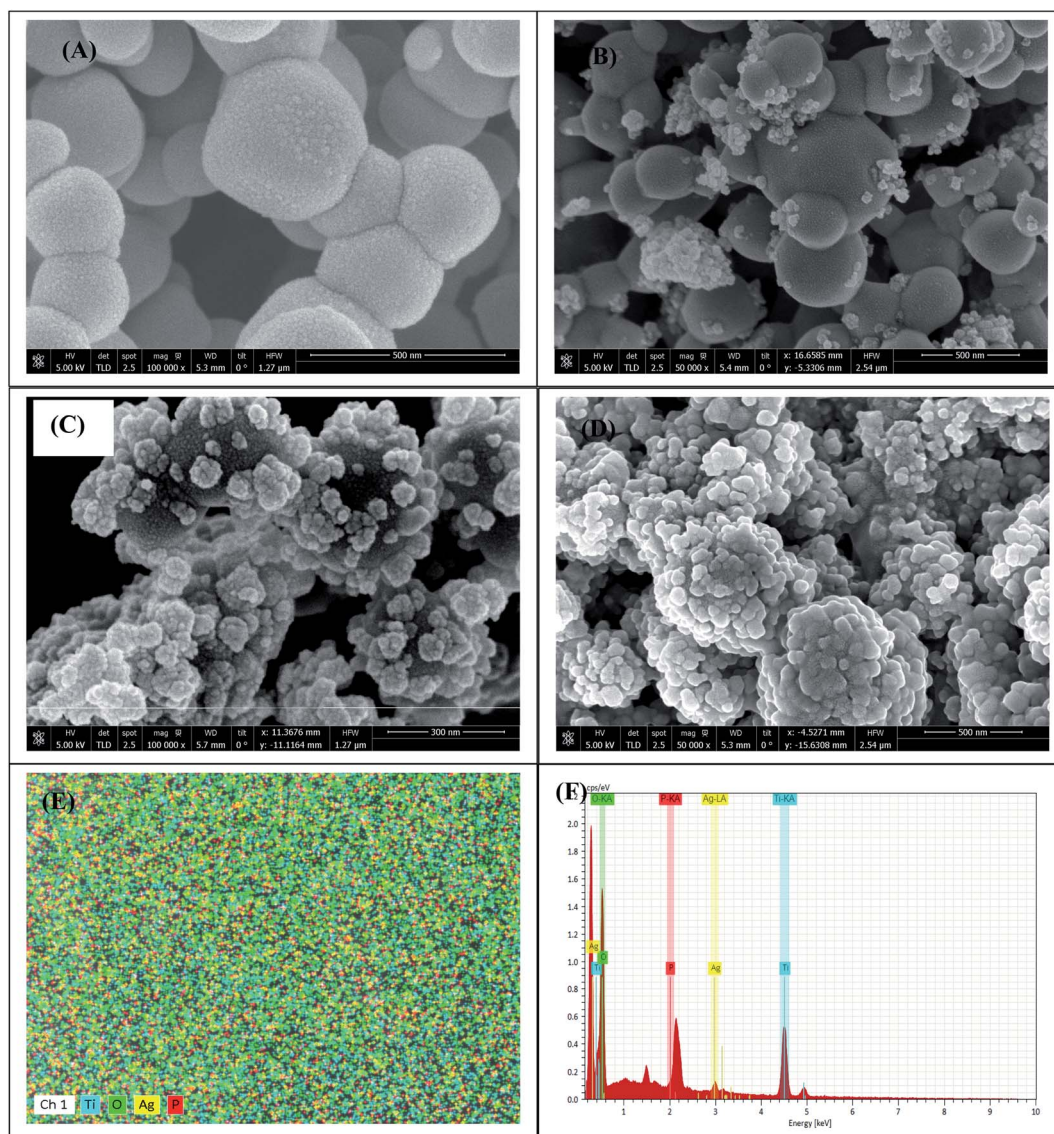

Fig. 3 SEM images (A) Ag$_3$PO$_4$, (B) Ag$_3$PO$_4$-25 wt% TiO$_2$, (C) Ag$_3$PO$_4$-50 wt% TiO$_2$ and (D) Ag$_3$PO$_4$-75 wt% TiO$_2$; (E) EDX mapping for Ag$_3$PO$_4$-50 wt% TiO$_2$, (F) EDX spectrum for Ag$_3$PO$_4$-50 wt% TiO$_2$.

2.3.2 Scanning electron microscopy/energy-dispersive X-ray spectroscopy. The morphology of the synthesized nanocomposites was examined with scanning electron microscopy (FEI Nova NanoSem) connected to EDX acquisition detector. The elemental composition was determined through EDX.

2.3.3 Diffuse reflectance spectroscopy (DRS). DRS was conducted using Ocean Optics USB-4000 spectrometer with a dedicated reflectance probe. Illumination was supplied with a Deuterium/Halogen source across the UV-VIS range. The synthesized nanocomposites are compressed into a flat film between glass microscope slides prior to measurement and a commercial PTFE reflectance standard was sued as reflectance calibration.

2.3.4 Adsorption studies. The adsorption capability of the synthesized nanocomposite was examined using methylene blue dye. 100 mg of Ag_3PO_4–TiO_2 was added to 200 mL aqueous solution of methylene blue (5 mg L^{-1}). Aliquots of the methylene blue solution were taken at specified time intervals. The sampled solution was centrifuged at 6000 rpm for 5 minutes to remove the powdered nanocomposite. The concentration of methylene blue was obtained by measuring the absorbance at 655 nm wavelength using Ocean Optics 4000 USB modular UV-VIS spectrometer.

2.3.5 Photocatalytic methylene blue, rhodamine blue and pesticide degradation. The photocatalytic activity of the synthesized Ag_3PO_4–TiO_2 was examined using rhodamine B (6 mg L^{-1}) and methylene blue (8 mg L^{-1}) dyes and pesticides (pyrimethanil, imidacloprid and atrazine). In a typical photocatalytic degradation of rhodamine B dye, 200 mL of rhodamine B solution in deionized water was used with a photocatalyst suspension concentration of 0.5 g L^{-1}. A jacketed glass reactor with a quartz tube immersion well was used with illumination from 300 W Tungsten Halogen lamp. For each of the experiments, the solution was stirred in the dark for 30 minutes (24 hours for pesticide solutions) to attain an adsorption–desorption equilibrium for illumination. 2 mL aliquots were taken at specific time intervals and centrifuged at 6000 rpm for 5 minutes to remove the powdered photocatalyst. The dye concentration was quantified using Ocean Optics 4000 USB modular UV-vis spectrometer with an absorbance values taken at 554 nm. A similar procedure was used for the photocatalytic degradation of the methylene blue and pesticides. However, the absorbance values were taken at 665 nm for methylene blue, 269 nm (pyrimethanil), 270 nm (imidacloprid), and 222 nm (atrazine). The degraded pesticide solution obtained from pyrimethanil was analyzed with LC-MS to identify photodegraded products.

3 Results and discussion

3.1 Characterization of Ag_3PO_4–TiO_2

The XRD patterns of the pristine P25 TiO_2, Ag_3PO_4, and Ag_3PO_4-50 wt% TiO_2 are presented in Fig. 2. The XRD pattern for the Ag_3PO_4 showed well defined crystalline Ag_3PO_4 with sharp and intense diffraction peaks that can be indexed to the body-centered crystal structure (JCPDS no. 06-0505).

The dominant peaks at 33.4° and 36.6° correspond to the (210) and (211) crystallographic planes,[31] respectively. On the other hand, TiO_2 showed an intense peak at 25.5° which represents the (101) crystallographic plane and can be

indexed to the anatase phase (JCPDS no. 21-1272). With the "rectangles" representing the anatase phase present in TiO_2 and the circles representing the cubic structure of Ag_3PO_4, the prepared Ag_3PO_4–TiO_2 composite has all the crystallographic planes present in the crystalline cubic structure of Ag_3PO_4 and the (101) plane of the anatase phase of TiO_2. The as-prepared Ag_3PO_4–TiO_2 is therefore expected to exhibit high photocatalytic activity. Though the Ag_3PO_4–TiO_2 used for the analysis contained 50 wt% TiO_2, the diffraction peaks of the TiO_2 is weak. This can be ascribed to the relatively low crystallinity of TiO_2 when compared with that of Ag_3PO_4.

The morphology of the synthesized Ag_3PO_4 and Ag_3PO_4–TiO_2 photocatalyst were examined with SEM and the images presented in Fig. 3. The pristine Ag_3PO_4 is irregularly shaped spherical particles with diameter of *ca.* 100–400 nm. The P25 used for this study has a much smaller diameter of *ca.* 20 nm. The SEM images showed the agglomeration of the TiO_2 particles. The particle sizes of the Ag_3PO_4 and TiO_2 in the Ag_3PO_4–TiO_2 composite (Fig. 3 B–D) is similar to the pure Ag_3PO_4 and TiO_2. It can be seen from Fig. 3B to D that the TiO_2 covered the surface of the Ag_3PO_4 creating a heterojunction. The extent of the surface coverage is dependent on the wt% of the TiO_2 used for the synthesis. This coverage is expected to influence the photocatalytic activity. Positively charged ions adsorbs strongly to the surface of TiO_2.[29a,32] Since the P25 TiO_2 was first dispersed in $AgNO_3$, the Ag^+ ions adsorbed onto the surface of the TiO_2. The reaction between the Ag^+ and the PO_4^{3-} occurred on the surface of the TiO_2 when the Na_2HPO_4 was added, resulting in the formation of the TiO_2–Ag_3PO_4 composite. The SEM-EDX (Fig. 3E and F) spectrum confirms the presence of Ti, O, Ag and P. The elemental mapping showed that the elements Ti and O were evenly distributed on the surface of the Ag_3PO_4.

The UV-vis diffused reflectance spectra of the product with different wt% of TiO_2 are shown in Fig. 4. The P25 TiO_2 only absorbs light in the UV region of the electromagnetic spectrum with wavelength lower than approximately 390 nm. On the other hand, the pure Ag_3PO_4 has intense light absorption in the
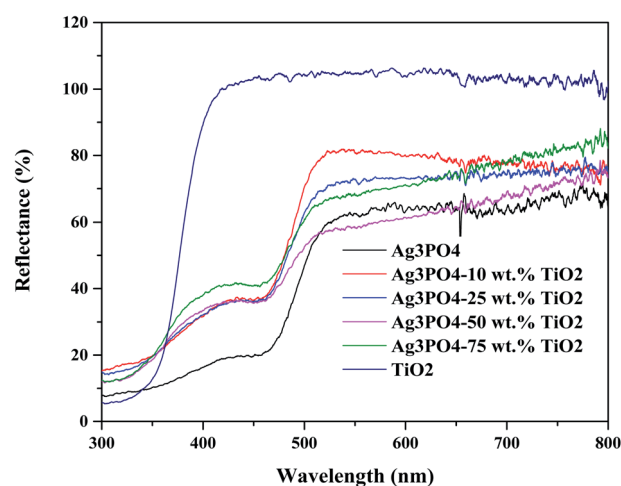

Fig. 4 UV-vis DRS spectra of Ag_3PO_4, TiO_2 and the various formulations of Ag_3PO_4–TiO_2.
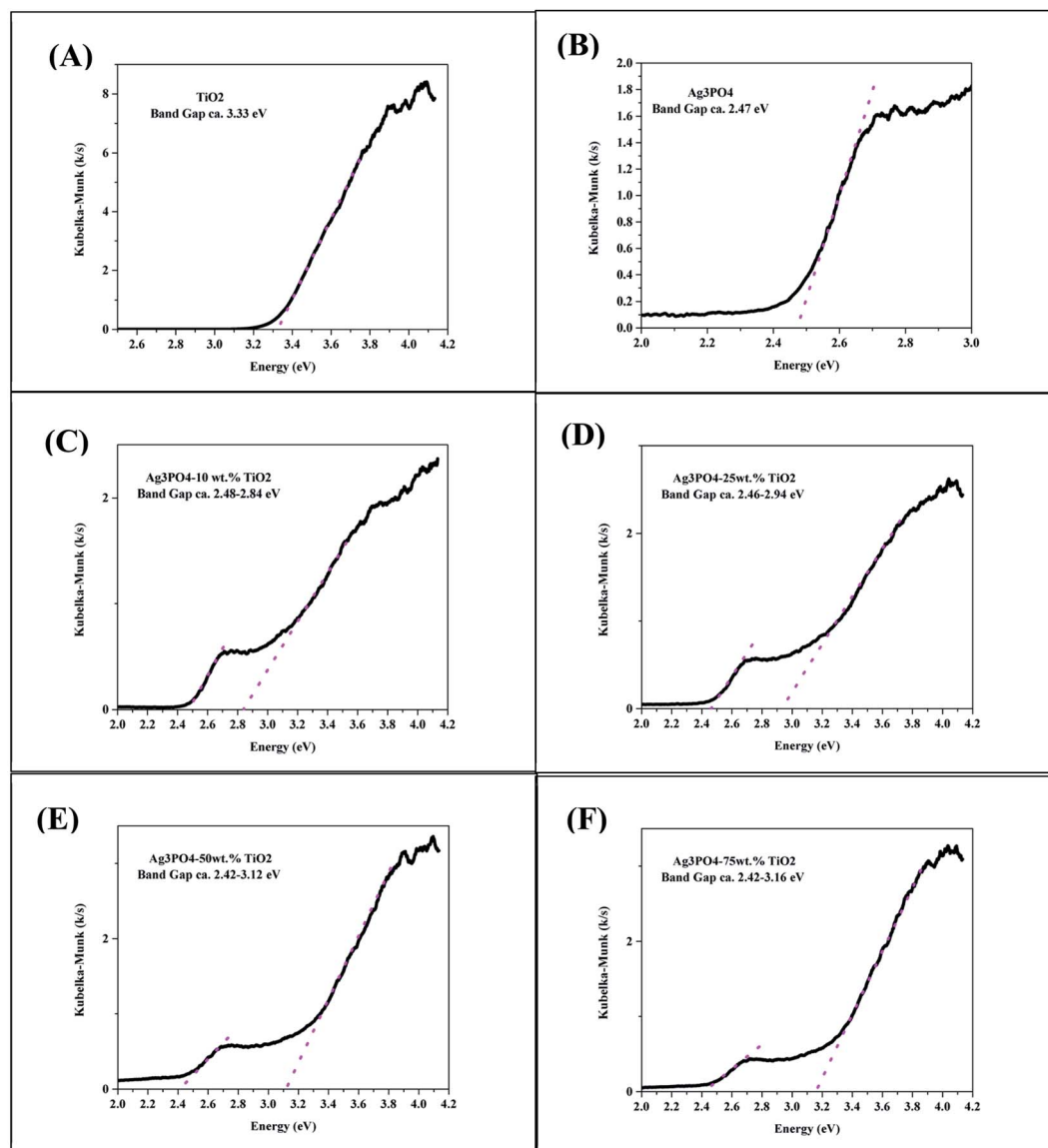
Fig. 5 Optical band gap estimation using Kubelka–Munk model for (A) TiO_2, (B) Ag_3PO_4, (C) Ag_3PO_4-10 wt% TiO_2, (D) Ag_3PO_4-25 wt% TiO_2, (E) Ag_3PO_4-50 wt% TiO_2 and (F) Ag_3PO_4-75 wt% TiO_2.

visible light region of the electromagnetic spectrum. The shape of the DRS spectra of the composite is a combination of that of Ag_3PO_4 and TiO_2 further proving the absence of any chemical interaction between TiO_2 and Ag_3PO_4. This agrees with observation made by Taheri et al.[33] The composite Ag_3PO_4–TiO_2 showed strong absorption in the visible light region due to the excellent visible light absorption by Ag_3PO_4. The composite Ag_3PO_4–TiO_2 can therefore harvest more visible light and result in an improved photocatalytic activity. The optical band gap of the photocatalysts synthesized were estimated from the DRS spectra using the Kubelka–Munk model[34] and are presented in Fig. 5. The optical band gap of the TiO_2 and Ag_3PO_4 were estimated to be 3.33 and 2.47 eV, respectively. The composite samples are characterized by two absorption thresholds, one corresponding to the TiO_2 and the other, Ag_3PO_4. A slight variation in the two absorption thresholds were observed upon

varying the weight percent of the TiO_2 used for the synthesis. The band gap for the absorption threshold corresponding to TiO_2 decreased with decreasing wt% of TiO_2 in the TiO_2–Ag_3PO_4 composite as can be seen in Fig. 5.

3.2 Photodegradation of rhodamine B, methylene blue and pesticides

Fig. 6A shows the photocatalytic performance of rhodamine B solution (200 mL, 6 mg L^{-1}) over Ag_3PO_4, TiO_2 and Ag_3PO_4–TiO_2 composites at a photocatalyst concentration of 0.5 g L^{-1} under UV-vis light irradiation. Before irradiation, the dye-photocatalyst solution was stirred in the dark for 30 minutes to achieve adsorption–desorption equilibrium. The percentages of rhodamine B adsorbed by Ag_3PO_4, TiO_2 and Ag_3PO_4–TiO_2 composite were 14.5, 18.8 and 12.0 wt%, respectively. The wt%
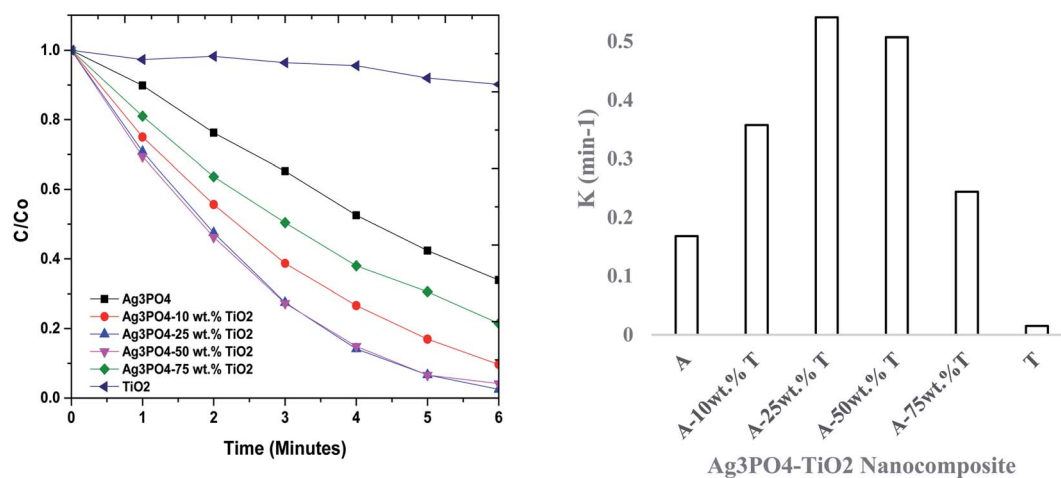
Fig. 6 (A) Photocatalytic activities of Ag_3PO_4, TiO_2 and $Ag_3PO_4-TiO_2$ (10, 25, 50, and 75 wt% of TiO_2) and (B) rate constants of Ag_3PO_4(A), TiO_2 (T) and $Ag_3PO_4-TiO_2$ (A-wt% T) on 6 mg L^{-1} rhodamine B dye.

of the rhodamine B adsorbed by the various formulations of the composite material was *ca.* 12%. The data obtained from the photocatalysis was fitted with a pseudo first order kinetics and the rate constants (k) calculated (Fig. 6B). Under UV-vis light irradiation, *ca.* 9.8% of rhodamine B ($k = 0.0153$ min^{-1}) was degraded by TiO_2 within the time (6 min) frame that the photocatalysis analysis was carried out. On the other hand, *ca.* 66% of the rhodamine concentration was degraded by Ag_3PO_4 within 6 min ($k = 0.168$ min^{-1}). The rate at which the concentration of the dye solution degraded by the composite ($Ag_3PO_4-TiO_2$) decreased was significantly higher than that of Ag_3PO_4 and TiO_2. For the same time period (6 min), the degradation efficiency obtained from the composites were 90, 98, 96 and 79% for Ag_3PO_4-10 wt% TiO_2 ($k = 0.3571$ min^{-1}), Ag_3PO_4-25 wt% TiO_2 ($K = 0.5406$ min^{-1}), Ag_3PO_4-50 wt% TiO_2 ($K = 0.5069$ min^{-1}) and Ag_3PO_4-75 wt% TiO_2 ($K = 0.2438$ min^{-1}), respectively. These values indicate that Ag_3PO_4 and TiO_2 act

synergistically to enhance photodegradation. This is so because the degradation efficiency and the rate constants of the composite $Ag_3PO_4-TiO_2$ were significantly higher than that of the individual components. The synergy was highest at 25 wt% TiO_2. A similar observation was reported by Taheri *et al.*[33] This observation can be attributed to the formation of a heterojunction between the TiO_2 and the Ag_3PO_4.[33] In addition, the photocatalytic activity is also affected by the extend of surface coverage. To obtain maximum photocatalytic activity, the extend at which the Ag_3PO_4 surface is covered by TiO_2 should be minimized. The uncovered surface of Ag_3PO_4 is utilized for maximum absorption of visible light.

The degradation of methylene blue (200 mL, 8 mg L^{-1}, 0.5 g L^{-1} catalyst concentration) was also examined under UV-vis light irradiation and the results shown in Fig. 7. After the adsorption–desorption equilibrium was attained, 8.9 (Ag_3PO_4), 16.7 (TiO_2), 31.0 (Ag_3PO_4-10 wt% TiO_2), 66.4 (Ag_3PO_4-25 wt%
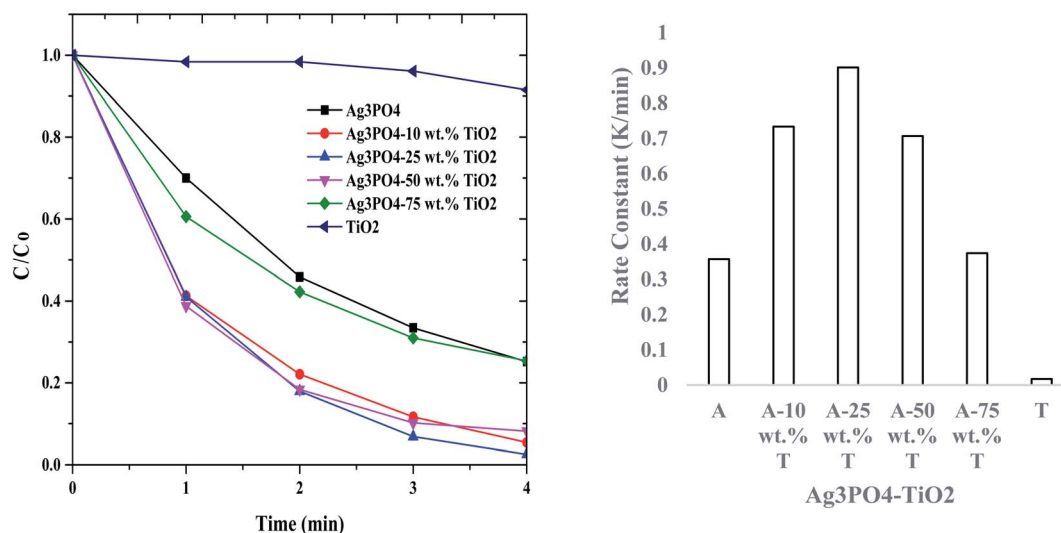

Fig. 7 (A) Photocatalytic activities of Ag_3PO_4, TiO_2 and $Ag_3PO_4-TiO_2$ (10, 25, 50, and 75 wt% of TiO_2) and (B) rate constants of Ag_3PO_4 (A), TiO_2 (T) and $Ag_3PO_4-TiO_2$ (A-wt% T) on 8 mg L^{-1} methylene blue dye.

Fig. 8 The reusability of Ag_3PO_4–TiO_2 nanocomposite.

TiO_2), 71.8 (Ag_3PO_4-50 wt% TiO_2) and 79.6% (Ag_3PO_4-75 wt% TiO_2) of the methylene blue dye was removed by adsorption. This informed the authors to conduct a detailed adsorption kinetics and equilibrium test. The photocatalytic activity of TiO_2 on methylene blue was low (16.7%, $k = 0.0175$ min^{-1} within 4 min). Within the same time frame, Ag_3PO_4 recorded a photocatalytic efficiency of 79% with a rate constant of 0.3573 min^{-1}. From Fig. 7, it is observed that the Ag_3PO_4–TiO_2 composite is much more active photocatalytically than Ag_3PO_4 and TiO_2. The photocatalytic efficiency and the rate constants were 96.3% and

0.7338 min^{-1}, 99.1% and 0.9010 min^{-1}, 97.7% and 0.7069 min^{-1} and, 94.8% and 0.3743 min^{-1}, for Ag_3PO_4-10 wt% TiO_2, Ag_3PO_4-25 wt% TiO_2, Ag_3PO_4-50 wt% TiO_2 and Ag_3PO_4-75 wt% TiO_2, respectively. Again, the Ag_3PO_4-25 wt% TiO_2 recorded the highest photocatalytic efficiency and rate constant.

The stability of the synthesized nanocomposite was examine using Ag_3PO_4-50 wt% TiO_2 and rhodamine B. The results for the stability/reusability of the nanocomposite is presented in Fig. 8. After five cycles of the photodegradation test, the degradation efficiency decreased from 96% to 85%. The developed Ag_3PO_4–TiO_2 nanocomposite is therefore fairly stable under the experimental conditions used in this study.

The photocatalytic activity of Ag_3PO_4-25 wt% TiO_2 on three pesticides (pyrimethanil, atrazine and imidacloprid) was examined (Fig. 9). The Uv-vis absorption spectrum in Fig. 9 indicated a reduction in the concentration of the pesticides after photocatalysis. Though the concentration of the three pesticides are the same, the rate of degradation differed from one pesticide to the other. The pseudo first order rate constants were calculated to be 1.319, 0.013 and 0.011 min^{-1} for pyrimethanil, imidacloprid and atrazine, respectively. The variation in the calculated rate constants can be attributed to the different stabilities of the pesticides used for this study. The photoproducts formed from the photodegradation of pyrimethanil were identified with LC-MS.
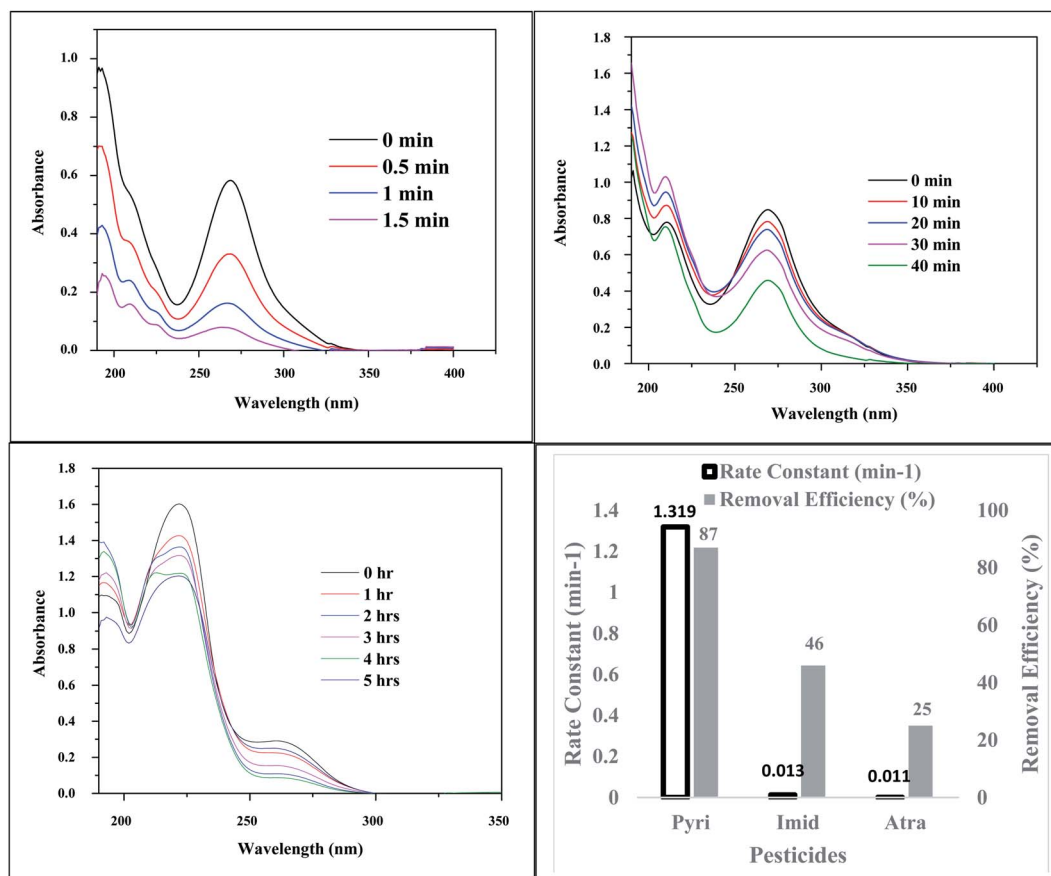

Fig. 9 Ag_3PO_4-25 wt% TiO_2 photodegradation of (A) 10 mg L^{-1} pyrimethanil, (B) 10 mg L^{-1} imidacloprid, (C) 10 mg L^{-1} atrazine; (D) calculated rate constants and removal efficiencies.

The first step in the photocatalytic degradation of pyrimethanil is the electrophilic substitution of one or two hydrogen atom in the pyrimethanil structure by hydroxyl radical.[35] Electrophilic substitution will form compounds **2** (m/z = 231, t_R = 1.944 min), **3** (m/z = 215, t_R = 2.034), **4** (m/z 215, t_R = 2.156 min), **5** (m/z = 213, t_R = 1.653 min), **6** (m/z = 177, t_R = 1.852 min) and **7** (m/z = 198, t_R = 3.195 min). Mono-hydroxylation of pyrimethanil will result in the formation of compound **4** with m/z 215 (t_R = 2.034 min). Compound **8** (t_R = 1.354 min) was formed by the hydrolysis of pyrimethanil molecule with the loss of benzene ring. Aliphatic intermediate such as compound **9** (t_R = 5.049 min) was also identified. Most of the intermediate compounds identified in this study were also identified by other researchers after photocatalytically

degrading pyrimethanil.[36] The structure of the compounds identified by LC-MS after the photocatalytic degradation of pyrimethanil are presented in Fig. 10.

It is obvious from the present study that the Ag_3PO_4–TiO_2 composite has an enhanced photocatalytic activity when compared to pure Ag_3PO_4 and TiO_2. The photocatalytic activity of TiO_2 can be enhanced by coupling it with other semiconductors. Recently published work on Ag_3PO_4–TiO_2 has suggested that the enhanced photocatalytic activity can be attributed to the unique band matching between TiO_2 and Ag_3PO_4, inhibition of the electron hole recombination by TiO_2, and the inter semiconductor hole transfer between the valence bands of TiO_2 and Ag_3PO_4.[29a,33,37]
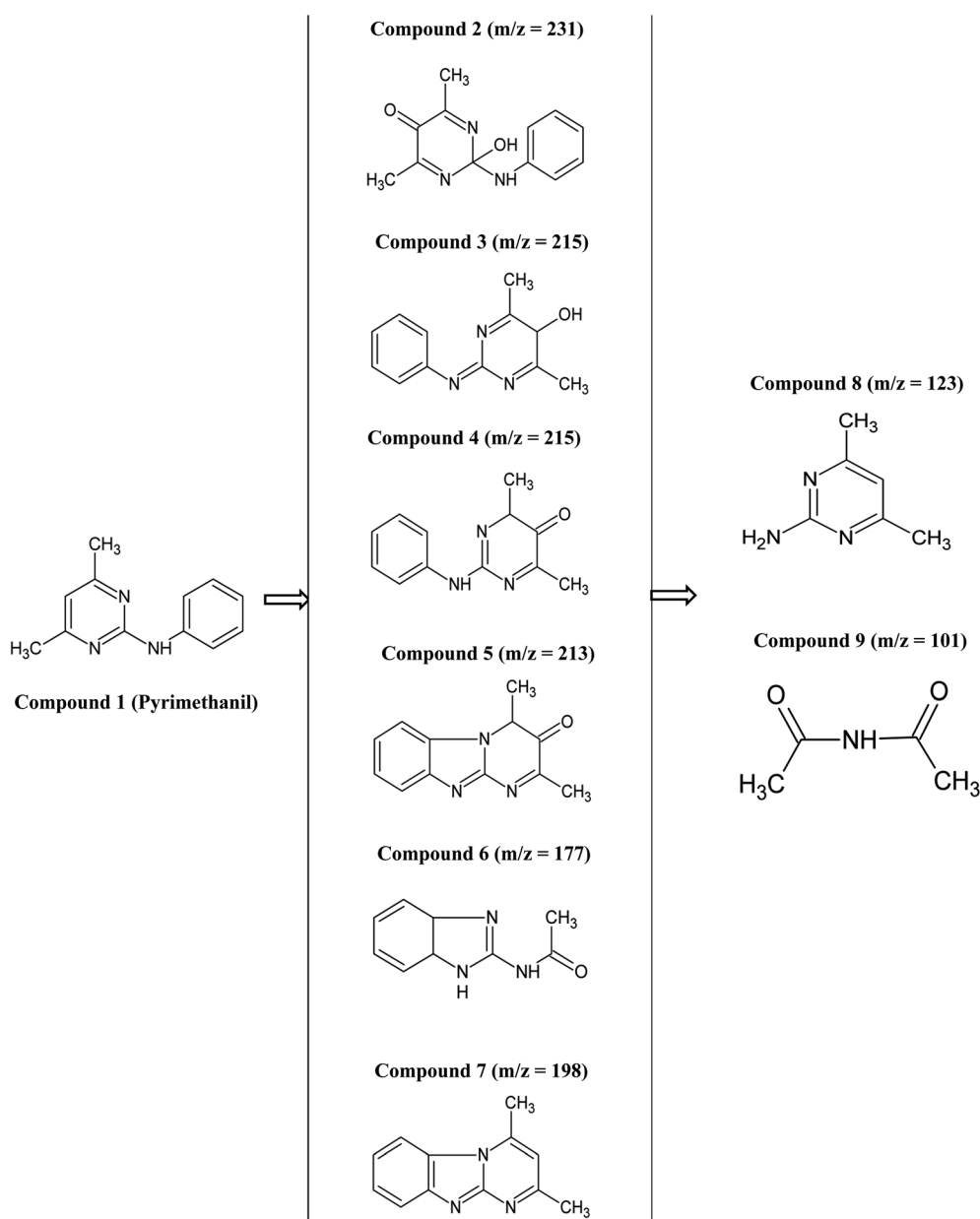

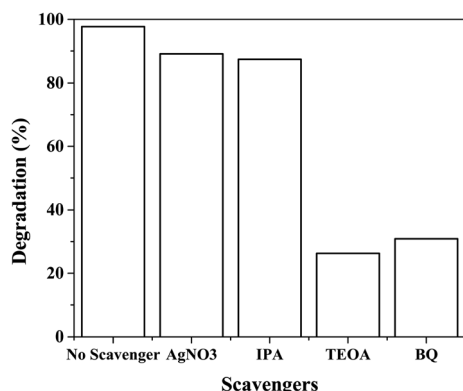**Fig. 10** The intermediate photoproducts identified by LC-MS after photodegrading pyrimethanil.

Fig. 13 (A) Langmuir and Freundlich adsorption isotherms, (B) pseudo second order (C) pseudo first order kinetics and (D) interparticle diffusion model for the adsorption of methylene blue by Ag_3PO_4-50 wt% TiO_2.

3.3 Adsorption equilibrium and kinetic studies

The adsorption equilibrium and kinetic studies were conducted using 200 mL of 5 mg L^{-1} methylene blue solution and 100 mg of Ag_3PO_4-50 wt% TiO_2. Fig. 13 and Table 2 contain the plots and data obtained from the adsorption studies. From Fig. 13A the amount of dye adsorbed at equilibrium (Q_e) increased with increasing equilibrium concentration of the dye (C_e). To obtain a better understanding of the adsorption process, the experimental data was fitted with the Langmuir and Freundlich equilibrium isotherms. The Langmuir isotherm is given as;

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \qquad (1)$$

In this equation, C_e (mg L^{-1}) is the equilibrium concentration of the dye, Q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, Q_m (mg g^{-1}) is the maximum adsorption capacity corresponding to a monolayer coverage and K_L (L mg^{-1}) is the Langmuir constant. The plot of Q_e vs. C_e is presented in Fig. 13A. Q_m and K_L can be estimated from the slope and intercept of linearized Langmuir isotherm expression. The estimated Q_m and K_L are presented in Table 2. To examine the favorability or otherwise of the adsorption process, an equilibrium parameter R_L was calculated from the equation below and the values presented in Table 2.

$$R_L = \frac{1}{1 + K_L C_O} \qquad (2)$$

K_L (L mg^{-1}) is the Langmuir constant and C_o (mg L^{-1}) is the initial dye concentration. The R_L value indicates adsorption process is irreversible when R_L is 0; favorable when R_L is

Table 2 Calculated adsorption isotherm and equilibrium kinetics parameters for the adsorption of methylene blue by Ag_3PO_4-50 wt% TiO_2

Adsorption kinetic models	Adsorption kinetic parameters
Langmuir	$Q_m = 17.112$ (mg g^{-1})
	$K_L = 0.3324$ (L mg^{-1})
	$R^2 = 0.9920$
	$R_L = 0.231$–0.6 (L mg^{-1})
Freundlich	$K_F = 4.4181$ (mg g^{-1} (mg L^{-1})$^{1/n}$)
	$n = 1.7531$
	$R^2 = 0.9888$
Pseudo first order	$Q_e = 3.9886$ (mg g^{-1})
	$K_1 = 0.00341$ (min^{-1})
	$R^2 = 0.3639$
Pseudo second order	$Q_e = 3.5804$ (mg g^{-1})
	$K_2 = 2.2036$ (g mg^{-1} min^{-1})
	$R^2 = 0.9995$
Interparticle diffusion model	$K_P = 2.5812$ (mg g^{-1} min$^{-1\frac{1}{2}}$)
	$R^2 = 0.9189$

between 0 and 1; linear when R_L is 1 and unfavourable when R_L is greater than 1. The maximum monolayer adsorption capacity (Q_m) and the equilibrium parameter (R_L) of the Ag$_3$PO$_4$-50 wt% TiO$_2$ were calculated to be 17.112 mg g^{-1} and 0.231–0.600, respectively. These values imply that the surface of the Ag$_3$PO$_4$-50 wt% TiO$_2$ is homogenous and was covered with a monolayer methylene blue dye. In addition, the adsorption of methylene blue by Ag$_3$PO$_4$-50 wt% TiO$_2$ was favorable.

In addition to the Langmuir equilibrium model, the adsorption data was fitted with the Freundlich equation. The Freundlich equation is presented below;

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

Q_e (mg g^{-1}) is the amount of dye adsorbed on Ag$_3$PO$_4$-50 wt% TiO$_2$ at equilibrium, C_e is the equilibrium concentration of the dye in solution, K_F (mg g^{-1}(mg L^{-1})$^{1/n}$) and $1/n$ are the Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively. Higher values of K_F indicate higher affinity for adsorption and the values of $1/n$ lie between $0.1 < 1/n < 1$, indicating favorable adsorption.[44] The Freundlich constants were calculated from the linearized Freundlich isotherm expression and presented in Table 2. The value of $1/n$ is less than 1 indicating favorable adsorption process. The K_F and a correlation coefficient were estimated as 4.4181 mg g^{-1} (mg L^{-1})$^{1/n}$ and 0.9888, respectively. Since the correlation coefficient for both the Langmuir and Freundlich model were greater than 0.95, the adsorption process may have followed both models. It is however likely the adsorption process followed the Langmuir isotherm model since it had a relatively higher correlation coefficient when compared to Freundlich isotherm.

The mechanism and rate controlling step of the entire adsorption process was examined using the following adsorption kinetic models; pseudo-first order, pseudo-second order and intra-particle diffusion models. The pseudo-first order equation is presented below;

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303} t \quad (4)$$

Q_e and Q_t (mg g^{-1}) are the amount of the dye adsorbed at equilibrium and at time t (min), respectively. K_1 (min^{-1}) is the pseudo-first order rate constant. The parameters K_1 and Q_e were estimated from Fig. 13C and presented in Table 2. The correlation coefficient obtained is low ($R^2 = 0.3639$). This suggests that the pseudo-first order kinetic model is not suitable to describe the adsorption process.

The adsorption kinetics was also investigated using pseudo-second order kinetic model presented below;

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (5)$$

K_2 (g mg^{-1} min^{-1}) is the pseudo-second order rate constant. Q_e and Q_t (mg g^{-1}) are the amount of dye adsorbed at equilibrium and at time t (min), respectively. Q_e and K_2 were calculated from Fig. 13B. The high correlation coefficient of 0.9995 suggests that the adsorption process follows a pseudo-second order adsorption kinetics process.

The Langmuir adsorption isotherm confirm the monolayer adsorption of methylene blue onto the surface of the Ag$_3$PO$_4$-50 wt% TiO$_2$. The dye molecules were probably transported from the dye solution to the Ag$_3$PO$_4$-50 wt% TiO$_2$. The possibility of intra-particle diffusion was therefore examined using the intra-particle diffusion model[45] presented below;

$$Q_t = K_p t^{1/2} + C \quad (6)$$

Q_t (mg g^{-1}) is the amount of methylene blue dye adsorbed at time t (min), C is the intercept and K_p (mg g^{-1} min^{-1}) is the intra-particle diffusion rate constant. K_p was estimated from Fig. 13D and presented in Table 2. The plot in Fig. 13D shows a double straight line. The initial stage represents the transportation of methylene blue to the external surface of the Ag$_3$PO$_4$-50 wt% TiO$_2$ through film diffusion within a very short time. The first linear part can be due to the entry of methylene blue molecules into the Ag$_3$PO$_4$-50 wt% TiO$_2$ by intra-particle diffusion.[46] The final equilibrium stage is represented by the second linear portion of Fig. 13D.

The results presented in this article revealed that TiO$_2$–Ag$_3$PO$_4$ has the potential of removing water pollutants through adsorption and photocatalysis. TiO$_2$–Ag$_3$PO$_4$ therefore has a potential application in the development of water treatment technologies.

4 Conclusion

In this study, TiO$_2$ semiconductor was coupled with Ag$_3$PO$_4$. SEM images of the as-prepared TiO$_2$–Ag$_3$PO$_4$ showed a covering of the Ag$_3$PO$_4$ surface by TiO$_2$ creating a heterojunction between coupled semiconductors. DRS analysis and optical band gap estimation revealed two absorption thresholds corresponding to TiO$_2$ and Ag$_3$PO$_4$. TiO$_2$–Ag$_3$PO$_4$ showed strong photocatalytic activity for rhodamine B, methylene blue, pyrimethanil, imidacloprid and atrazine. LC-MS analysis of the photodegraded pyrimethanil resulted in the identification of hydroxylated and aliphatic derivatives of pyrimethanil. The photocatalytic activity was dependent on the weight percent of the TiO$_2$ used in the synthesis with 25 wt% TiO$_2$ recording the highest photocatalytic removal efficiency and rate constant. The synergy between the TiO$_2$ and Ag$_3$PO$_4$ semiconductors was attributed to the good band gap matching that resulted in the efficient separation of charges which in turn led to a suppression of the electron–hole recombination. The TiO$_2$–Ag$_3$PO$_4$ showed strong adsorption towards methylene blue dye and the adsorption equilibrium isotherm and kinetics followed the Freundlich and Langmuir isotherms, and pseudo second order rate kinetics, respectively. TiO$_2$–Ag$_3$PO$_4$ therefore removes the pollutants by both photocatalytic and adsorption process. The results from this study showed the potential application of TiO$_2$–Ag$_3$PO$_4$ in water treatment technologies.

Conflicts of interest

There is no conflict to declare.

Acknowledgements

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