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# Immobilizing a visible light-responsive photocatalyst on a recyclable polymeric composite for floating and suspended applications in water treatment†

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A visible light responsive  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  (10 : 1) nanocomposite was prepared and successfully immobilized (12 wt%) in a spherical polymeric matrix consisting of polysulfone and alginate (10 : 6). The resulted beads featured a sponge-like structure with interconnected macrovoids and micropores, and showed high adsorption and visible-light photocatalytic activity towards various wastewater pollutants, including the widely used dye – methylene blue ( $k = 0.0321 \text{ min}^{-1}$ ), and two emerging pharmaceutical contaminants – diclofenac ( $k = 0.018 \text{ min}^{-1}$ ) and triclosan ( $k = 0.052 \text{ min}^{-1}$ ). As determined, the  $\cdot\text{OH}$  radical and  $\text{h}^+$  are the primary reactive oxygen species responsible for the photodegradation. The composite photocatalytic beads are also effective in bacterial inactivation and degradation of acyl-homoserine lactones (AHLs), the bacterial quorum sensing autoinducers triggering biofilms, thus exhibiting a promising future in wastewater disinfection and biofilm retardation. Additionally, these beads could be used in inter-switchable suspended or buoyant forms, and be effectively regenerated by  $\text{H}_2\text{O}_2$  treatment, and used for multiple cycles without any significant loss in photoactivity. With these unique features, the prepared visible-light photocatalytic beads could be easily applied in large-scale water and wastewater treatment systems.

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## 1. Introduction

The  $\text{TiO}_2$ -based nanomaterials are still the most economical and efficient photocatalysts to degrade various water pollutants,<sup>1,2</sup> despite the efforts in searching for other metal oxides over the last few decades.  $\text{TiO}_2$  displays higher photoactivity than other semiconductors under UV irradiation, but its wide bandgap prevents the utilization of photons in the visible region. In contrast, photocatalysts with narrow bandgaps can utilize visible light, although their stability needs improvement.<sup>3</sup> Coupling  $\text{TiO}_2$  with narrow-bandgap semiconductors can extend the photo-response region to visible light and enhance the separation of photoinduced charges by forming well-matched heterogeneous junctions.

$\text{Ag}_3\text{PO}_4$ , with a narrow bandgap, is a potential candidate to separate the electron-hole pairs of  $\text{TiO}_2$  efficiently to improve

photocatalysis.  $\text{Ag}_3\text{PO}_4$  has been considered as an extremely promising auxiliary material for constructing visible light photocatalysts by forming heterojunction.<sup>4,5</sup> However, the efficiency of  $\text{Ag}_3\text{PO}_4$  decreases quickly after the initial use, due to the inherent fast charge recombination and its self-reduction to silver during photocatalysis.<sup>6</sup> The widely agreed strategy is to couple  $\text{Ag}_3\text{PO}_4$  with other semiconductors such as  $\text{AgCl}$ ,  $\text{In}(\text{OH})_3$ ,  $\text{SnO}_2$ ,  $\text{Bi}_2\text{WO}_6$ ,  $\text{CeO}_2$ , and other materials like graphene, PAN, *etc.*, to improve its photoactivity and stability.<sup>7</sup> The composite of  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$  photocatalyst has also been widely investigated and proved to be significantly better in photodegradation of various pollutants under visible light than the  $\text{Ag}_3\text{PO}_4$  itself.<sup>4,8,9</sup>

While significant progress has been made on increasing the visible light-harvesting efficiency of various photocatalysts, recovery and regeneration of them in large-scale applications remain a big challenge. Immobilization of photocatalysts in appropriate adsorptive material will facilitate the easy recovery of catalysts<sup>10,11</sup> and enhance photodegradation *via* bringing the pollutants near the active sites of catalysts. Moreover, buoyant immobilization material is highly desirable for applications with sunlight as the irradiation source.<sup>3,12–14</sup> Therefore, novel supporting materials with intensified adhesion of catalysts, super adsorption capacity, and controllable interconversion

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between buoyancy and suspension are needed for versatile applications of photocatalysis.

In our recent study, polysulfone (PSF) and alginate (Alg) were used together to immobilize  $\text{TiO}_2$  nanoparticles in macro beads (o.d.  $\sim 3$  mm), which showed a high photocatalytic activity under UV irradiation, thermal stability, long-term durability, and facile interconversion between buoyancy and suspension. The objective of this study was to develop immobilized visible light-responsive photocatalysts further. To this end,  $\text{Ag}_3\text{PO}_4$  was immobilized together with  $\text{TiO}_2$  in the PSF/Alg beads. The photocatalytic efficiency of these beads was further enhanced by improving the pore architecture and modifying the surface with the post-treatment. Performance and reusability of these beads for water purification were assessed using a dye methylene blue (MB) and two emerging pharmaceuticals (diclofenac and triclosan) as the target pollutants. The photocatalytic degradation mechanism was further examined with the reactive oxygen species (ROS) scavenging experiments. In addition, bacterial inactivation and degradation of acyl-homoserine lactones (AHLs), a type of bacterial signalling molecules promoting biofilm formation, were examined to evaluate its application for water disinfection and biofilm mitigation.

## 2. Experimental

### 2.1. Material

Granular PSF, sodium alginate (SA), *N*-methyl-2-pyrrolidone (NMP) with a purity of 99%, methylene blue (MB), diclofenac (DCF), triclosan (TCS), AHLs, and titanium tetra isopropoxide (TTIP) were obtained from local suppliers. Ultrapure (UP) water obtained from an OLABO system ( $\geq 18.2$  M $\Omega$ -cm) was used in all experiments. Other analytical grade chemicals like sodium hydroxide, hydrochloric acid, calcium chloride, sulfuric acid, sodium nitrate, silver sulphate, polyethylene glycol (PEG8000), and ethyl alcohol were purchased from Aladdin Industrial Corporation (Shanghai, China) and used without any further purification or pre-treatment.

### 2.2. Preparation of $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ photocatalyst

$\text{TiO}_2$  nanoparticles were prepared by a sol-gel method using TTIP as a precursor. The  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  photocatalyst was prepared using a simple precipitation method. Typically, a certain amount of the as-prepared  $\text{TiO}_2$  was added to a flask containing 100 mL of 1% PEG-8000 dissolved in UP water and stirred for 30 minutes, and 50 mL of  $\text{Na}_2\text{HPO}_4$  ( $0.1 \text{ mol L}^{-1}$ ) aqueous solution was added and stirred for additional 10 minutes. Then, under vigorous stirring, 50 mL of  $\text{AgNO}_3$  ( $0.3 \text{ mol L}^{-1}$ ) was added dropwise with a peristaltic pump at room temperature. After 3 h stirring, the yellow precipitate was allowed to settle for 12 h, filtered, washed, dried at  $105^\circ\text{C}$ , and calcined at  $400^\circ\text{C}$  for 4 h. The resulting  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  photocatalyst was stored in the dark prior to characterization and photocatalytic reactions. For comparison,  $\text{Ag}_3\text{PO}_4$  was prepared under the same condition without the addition of  $\text{TiO}_2$  nanoparticles.

### 2.3. Preparation of polymer beads and immobilization of $\text{TiO}_2/\text{Ag}_3\text{PO}_4$

To prepare the PSF/Alg beads, the desired amount (2, 4, 6, 8, 10%) of Alg was added slowly to a PSF (10% w/v) solution in NMP under vigorous stirring; then the mixture was dripped into a 4% (w/v)  $\text{CaCl}_2$  solution through a nozzle to form spherical beads with o.d. of  $\sim 3$  mm. The beads were gently stirred for 24 h to guarantee complete phase inversion, and then washed and stored separately prior to use. The adsorption capacity of the PSF/Alg beads was evaluated with MB, and the beads with 6% Alg (PA6) were selected as the immobilization material.  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  nanoparticles were added (12% w/v) to the PSF/Alg solution prior to dripping into the  $\text{CaCl}_2$  solution to form PSF/Alg/ $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  (PATAg) composite beads. For surface modification, the photocatalytic PATAg beads were gently stirred in acetone and NMP for a couple of minutes, respectively, and then sequentially rinsed with acetone, ethanol and UP water. The resulting beads were stored in a mild  $\text{AgNO}_3$  solution under dark.

### 2.4. Conversion of PATAg beads between floating and suspended forms

Controlled interconversion of the PATAg beads between suspended and floating forms was realized with a simple drying and wetting method. The water inside the beads could be removed by drying at  $50^\circ\text{C}$  for 1 h and added back again by boiling the beads for one minute and placing them in cold water, which resulted in buoyant and suspended beads, respectively.

### 2.5. Characterization of materials

The beads and photocatalysts were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), Brunauer, Emmett and Teller (BET) adsorption analyzer, thermogravimetric analyzer (TGA), and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). The surface roughness of the PATAg beads was measured using a scanning probe microscope (SPM). Detailed methods are provided in ESI (Text S1).†

### 2.6. Adsorption experiments

Adsorption capacities of the beads were investigated using MB solution ( $3.2 \text{ mg L}^{-1}$ ), which was added to a 15 mL quartz vial (effective volume of 10 mL) together with 0.5 g (approx. 50 beads) of the adsorbent and shaken at 150 rpm under darkness. The MB concentration was measured at a specific time interval using a UV-visible spectrophotometer (Lambda 950, PerkinElmer) at 664 nm.

### 2.7. Photocatalytic degradation experiments

Photocatalytic activity of the prepared powdered photocatalysts and photocatalytic beads in suspended and buoyant (only for the PATAg beads) form was first determined using MB as the target pollutant. Two pharmaceutically active compounds (PhACs), *i.e.*, diclofenac, an anti-inflammatory drug, and triclosan, a broad-spectrum antibiotic, both have been widely



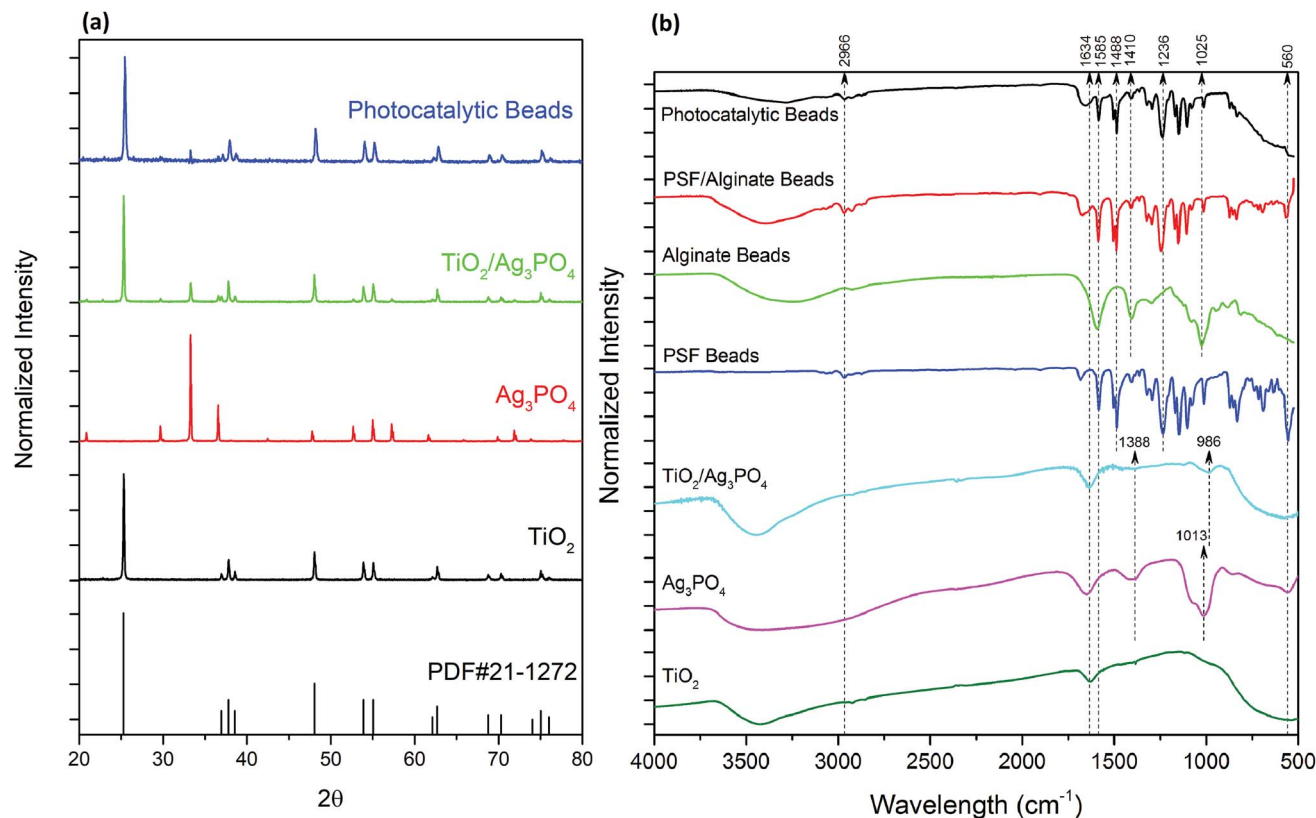


Fig. 1 XRD patterns (a) and ATR-FTIR spectrum (b) of photocatalytic powders and beads.

detected in aquatic environments, were selected as the target emerging contaminants further to evaluate the broad application potential of the PATAg beads.

**2.7.1. Batch degradation in suspended form.** All batch photocatalytic experiments were carried out in a 0.8 L laboratory-scale photocatalytic reactor equipped with a 15 W UV (Philips UV lamp, with an emission  $\lambda_{\text{max}}$  at 254 nm) or 15 W tubular LED light. The powdered catalysts ( $50 \text{ mg L}^{-1}$ ) were maintained in suspension *via* sparging air at a flow rate of  $1.5 \text{ L min}^{-1}$ . Before exposure to light, sparging was on for 30 min under darkness to reach adsorption/desorption equilibrium. The effects of beads dose ( $5, 10, 15 \text{ g L}^{-1}$ ), initial MB concentration ( $1.6, 3.2, 6.4 \text{ mg L}^{-1}$ ), pH ( $3, 7, 10$ ) and background ions (tap water, Table S1†) were examined. To evaluate the durability of the PATAg beads, we carried out the cyclic tests under the same condition, and the beads were washed and regenerated after each cycle.

Photocatalytic degradation of diclofenac and triclosan was evaluated using the same setup with an initial PhAC concentration of  $20 \text{ mg L}^{-1}$ . The concentrations of diclofenac and triclosan in filtered samples ( $0.22 \mu\text{m}$ ) were monitored using a UV-vis spectrophotometer at 275 and 280 nm, respectively.

**2.7.2. Photocatalytic degradation of MB in floating form.** Photodegradation of MB *via* the buoyant beads was carried out in a flat-bed photoreactor with an 0.8 L working volume, baffled and equipped with 3 air spargers. An overhead 200 W LED light was placed 15 cm above the water surface. Air was sparged at  $0.5$

$\text{L min}^{-1}$  to provide the oxygen required for the photooxidation process. The flat-bed photoreactor was operated at batch mode with continuous effluent recirculation during the operation.

**2.7.3. Regeneration of photocatalytic beads.** A very simple yet effective method was employed to regenerate the PATAg beads based on an earlier report<sup>15</sup> with some modifications. Typically, 5 g of used photocatalytic beads were added to 60 mL UP water containing 1 mL  $\text{H}_2\text{O}_2$  (30%) and stirred for 5 minutes; the beads were then washed with UP water for several times and

Table 1 FTIR peak assignments

Material	Peaks	Characteristic bands
Polysulfone	1148	O=S=O stretching (symmetric)
	1293	O=S=O stretching (asymmetric)
	2800–3000	Aliphatic and aromatic groups
	1236	C–O–C stretching (asymmetric)
Alginate	1488	Benzene (semi-ring stretch)
	1585	Benzene ring (quadrant stretch)
	3000–3600	O–H functional group
	1025	–C–O groups
TiO <sub>2</sub>	500–900	Ti–O stretching
Ag <sub>3</sub> PO <sub>4</sub>	3400	–OH stretching
	1650	–OH vibration
	1388	P=O stretching vibration
	1013	P–O–P stretching vibrations
	560	O=P–O bending vibration



employed for next use. Compared to the earlier report,<sup>15</sup> this method consumes a lower concentration of  $\text{H}_2\text{O}_2$  (1 mL in 60 mL vs. 1.8 mL in 60 mL), takes a much shorter period of time (5 min vs. 5 h), and is exempt from the need for extended drying (12 h at 65 °C).

**2.7.4. Scavenger experiments for reactive oxygen species (ROS).** To reveal the photodegradation mechanism of MB, we added ROS scavengers of ammonium oxalate (AO), 1,4-benzoquinone (*p*-BQ), and methanol (MeOH) separately to the MB solution during photodegradation. A borosilicate Petri plate was used as the photoreactor; 10 mM of a specific scavenger and the PATAg beads ( $100 \pm 5$ ) were added consecutively to 50 mL of a MB solution ( $6.4 \text{ mg L}^{-1}$ ) pre-sparged with air for 15 minutes. Then the reactor was illuminated with a 200 W LED lamp. Samples were taken at pre-set intervals and the MB concentration analyzed.

## 2.8. Bacterial disinfection and AHLs degradation

The utilization of these beads for bacterial disinfection and quorum quenching (AHLs degradation) was also assessed. The

overnight-culture of a bacterial strain (*Pseudomonas fluorescens*), maintained in the LB broth, was used to evaluate the capability of the PATAg beads for bacterial inactivation. The PATAg beads ( $50 \pm 3$ ) were dispersed in 50 mL of PBS solution containing bacterial strain, and then illuminated with a 200 W LED lamps for a certain time. Samples were taken regularly, and 100  $\mu\text{L}$  of 10-fold serially diluted samples were spread on LB Agar plates and incubated at 37 °C for 24 h; the colony-forming units (CFUs) were determined as the bacterial content in each sample. All experiments were repeated three times, and the average values were presented.

AHLs are crucial quorum sensing autoinducers for biofilm formation. Quorum Quenching (QQ), which reduces or depletes the AHL levels *via* microbial or enzymatic measures, has been used for biofouling control in wastewater treatment membrane bioreactors; however, utilization in the field is difficult or too costly.<sup>16</sup> Hence, use of the PATAg beads as an alternative QQ technology was evaluated. Fifty milliliters (50 mL) of 6-AHLs mixture (0.5 mM each) were placed in a borosilicate Petri plate;

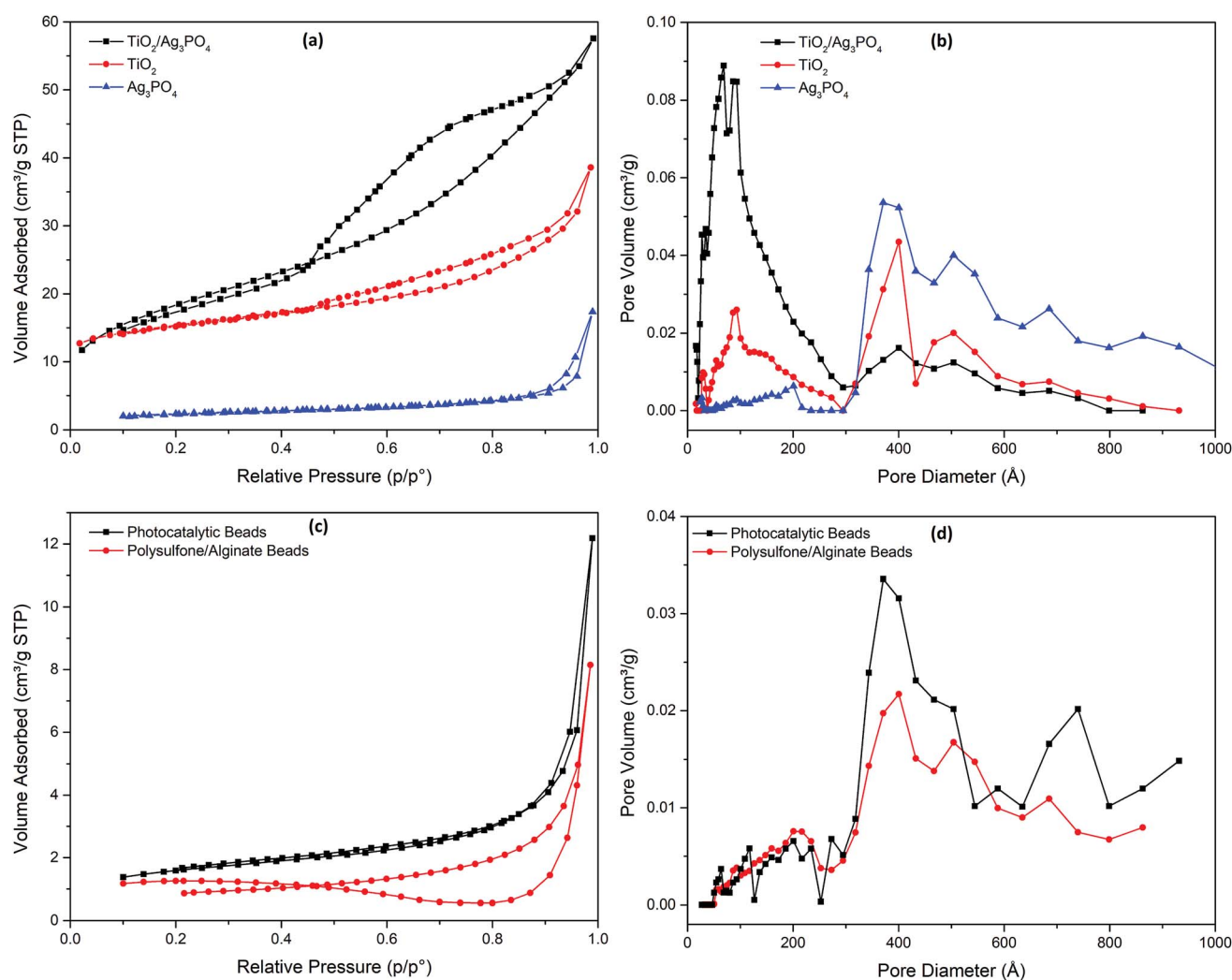


Fig. 2 Nitrogen adsorption–desorption isotherms and pore size distribution curves of (a and b) photocatalyst powders and (c and d) polymer (PSF/Alg) and photocatalytic (PATAg) beads.





50 PATAg beads were added and exposed to visible light (200 W LED lamp) for a certain time. Samples were taken and filtered through 0.22  $\mu\text{m}$  syringe filters; the AHL concentration was determined by a LC/MS/MS (LCMS-TSQ-Endura, Thermo Fisher, China).

### 3. Results and discussion

#### 3.1. Characterization of materials

The XRD patterns of the prepared photocatalysts are shown in Fig. 1a. All diffraction peaks of pure  $\text{TiO}_2$  could be indexed to the anatase phase of  $\text{TiO}_2$ , according to PDF card no. 21-1272, which shows peaks at 25.3°, 36.9°, 37.8°, 38.6°, 48.0°. The XRD pattern of  $\text{Ag}_3\text{PO}_4$  is in good agreement with the standard

$\text{Ag}_3\text{PO}_4$  (JCPDS no. 06-0505), and the dominant peaks at 33.3° and 36.6° correspond to the (2 1 0) and (2 1 1) planes, respectively. All the peaks that appeared in pure  $\text{TiO}_2$  were also found in the  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composite indicating the stability of the  $\text{TiO}_2$  crystallinity. In contrast, the intensity of diffraction peaks for  $\text{Ag}_3\text{PO}_4$  was significantly reduced owing to its lower concentration.

ATR-FTIR was used for the evaluation of functional groups (Fig. 1b). The absorbance peaks of the  $\text{TiO}_2$  sample between 900 and 500  $\text{cm}^{-1}$  could be assigned to the Ti-O stretching bands, which agrees with XRD results for rutile  $\text{TiO}_2$ .  $\text{Ag}_3\text{PO}_4$  showed a broad peak around 3400  $\text{cm}^{-1}$  and a sharp peak at 1650  $\text{cm}^{-1}$ , which corresponds to the -OH stretching and bending vibrations of surface anchored  $\text{H}_2\text{O}$  molecules, respectively.<sup>17</sup> The

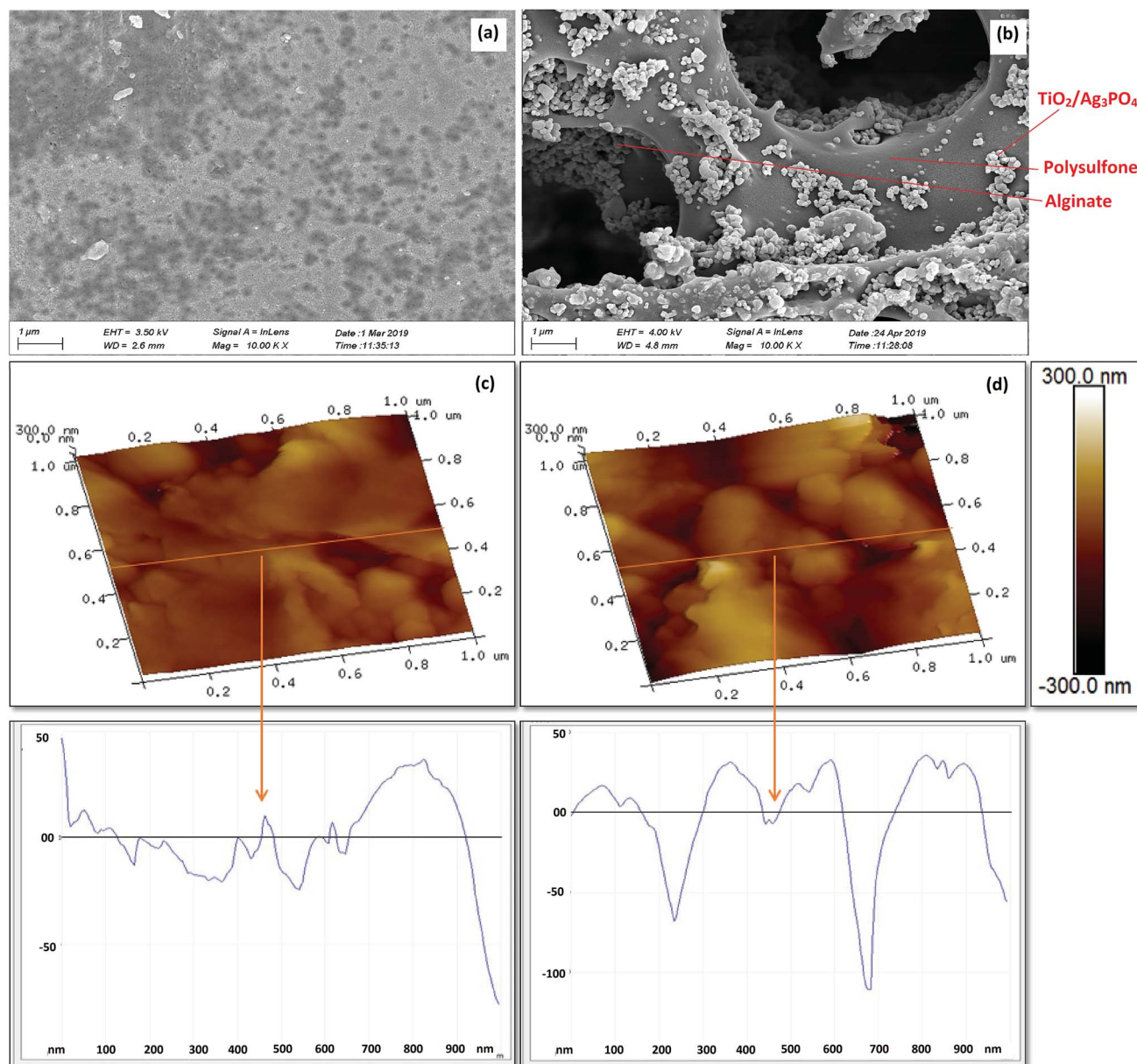


Fig. 3 SEM images of PSF/Alg beads (a) and photocatalytic beads (b), and 3D surface profilometry of PSF/Alg beads (c) and photocatalytic (PATAg) beads (d).

peaks at 560, 1013, and 1388  $\text{cm}^{-1}$  are attributed to the O=P-O bending vibration, asymmetric stretching vibrations of P-O-P rings, and P=O stretching vibration, respectively. The peak for stretching vibrations of P-O-P has shifted to 986  $\text{cm}^{-1}$  in  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composite, indicating strong interaction within the composite, which ensures the stability of the composite material.

Fig. 1b also shows the characteristic absorption bands of polymers (Table 1). All the PSF peaks are visible in both PSF/Alg and PATag composite beads. However, the absorption peaks of alginate were masked by PSF and  $\text{TiO}_2$  owing to their higher concentrations. No additional peaks appeared in the PATag composite beads, which indicates that the entrapped  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  nanoparticles did not disrupt the polymer structure. Meanwhile, the wide peak around 3450  $\text{cm}^{-1}$ , corresponding to

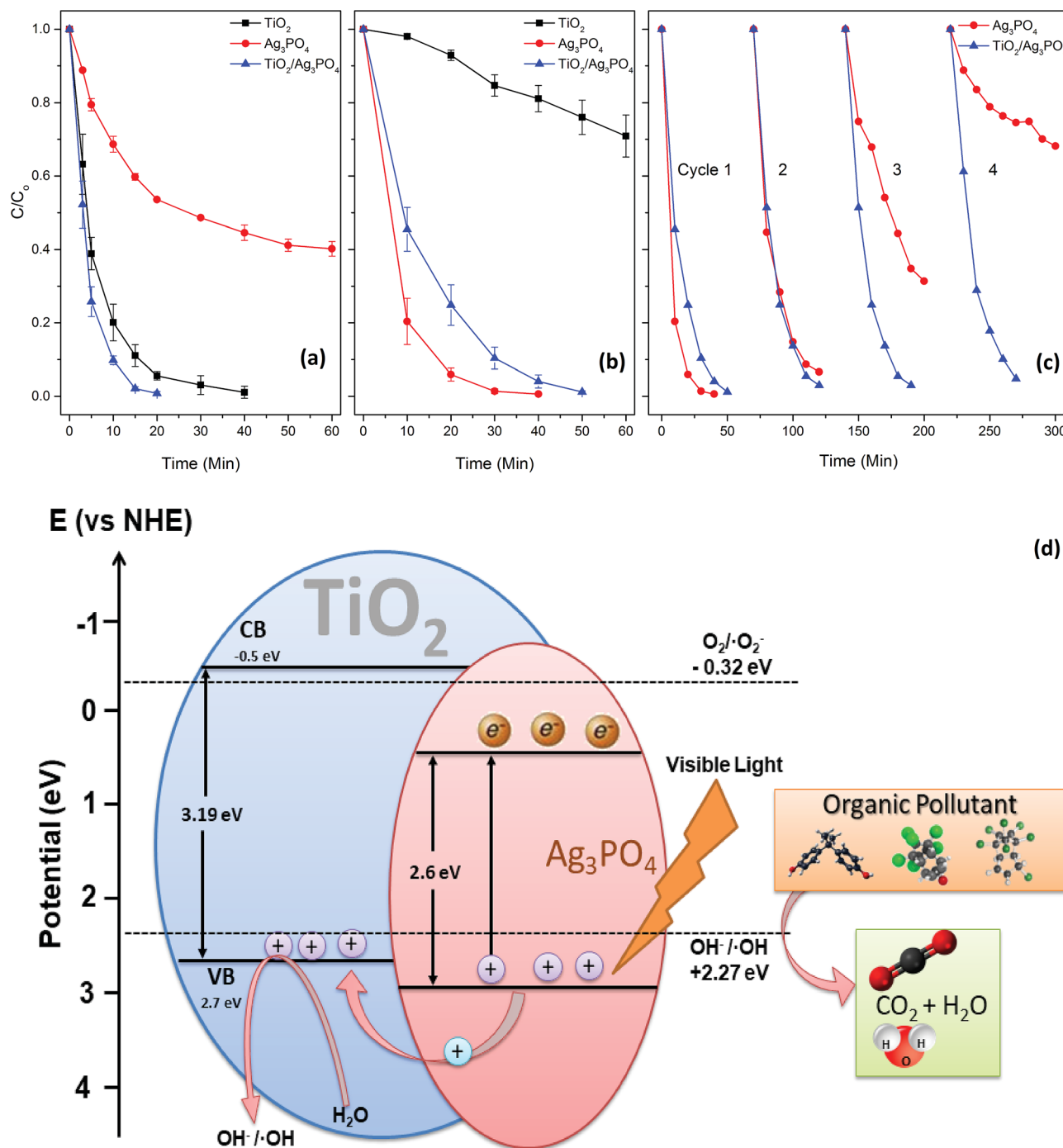


Fig. 4 Photocatalytic degradation of MB over various powdered photocatalysts under (a) UV and (b) visible light; (c) repeated use of powdered  $\text{TiO}_2$  and  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  under visible light; (d) schematic diagram showing the mechanism of photocatalytic degradation. ([MB] $_0$  = 3.2  $\text{mg L}^{-1}$ ; pH = 7; reaction volume = 0.8 L; catalyst dose (powdered) = 50  $\text{mg L}^{-1}$ ).



the stretching vibration of hydroxyl groups, became weaker in PATAg beads, indicating the strong interaction between these groups and  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ .

Nitrogen adsorption-desorption isotherm is a widely used technique to investigate porous structure and BET surface area of a material. As shown in Fig. 2a, the as-prepared photocatalysts exhibited type IV isotherms according to BDDT (Brunauer-Deming-Deming-Teller) classification with hysteresis loops at the relative pressure from 0.5 to 0.9 for  $\text{TiO}_2$  and  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  and from 0.8 to 1.0 for  $\text{Ag}_3\text{PO}_4$ , which indicates the mesoporous structure of the catalysts.<sup>2</sup> The corresponding pore

sizes of  $\text{TiO}_2$  and  $\text{Ag}_3\text{PO}_4$  overlapped from 30–60 nm, while a peak at approximately 10 nm was only shown for  $\text{TiO}_2$  (Fig. 2b and S2†). The  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composites displayed a different pore size distribution with a dominant peak around 10 nm. The BET specific surface area of  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  ( $65.2 \text{ m}^2 \text{ g}^{-1}$ ) was higher than  $\text{TiO}_2$  ( $49.5 \text{ m}^2 \text{ g}^{-1}$ ) and  $\text{Ag}_3\text{PO}_4$  ( $7.9 \text{ m}^2 \text{ g}^{-1}$ ). The least surface area of  $\text{Ag}_3\text{PO}_4$  can be attributed to the greatest pore size of the  $\text{Ag}_3\text{PO}_4$ , as observed in a previous report<sup>2</sup> and discussed in a recent review.<sup>18</sup> With the immobilization of  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composite in the PATAg beads, the pores at approximately 10 nm vanished and pores from 30–90 nm of the PSF/Alg

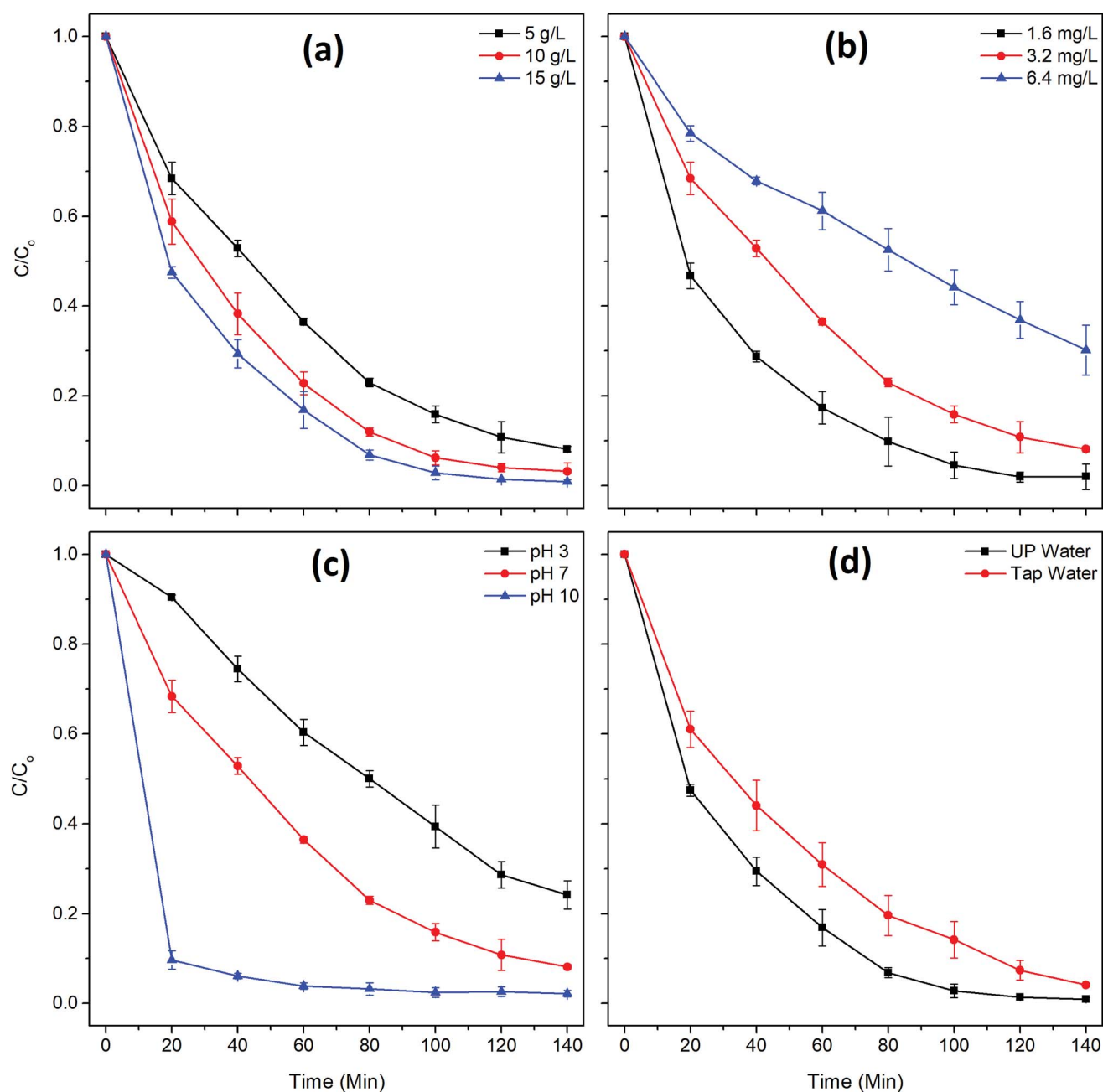


Fig. 5 Effects of various treatments on photocatalytic degradation of MB using photocatalytic beads under visible light irradiation; (a) catalyst dose; (b) initial dye concentration; (c) pH; and (d) background ions.

**Table 2** Comparison of rate constants for MB (3.2 mg L<sup>-1</sup>), DCF (20 mg L<sup>-1</sup>), TCS (20 mg L<sup>-1</sup>) degradation and *Pseudomonas fluorescens* (~10<sup>6</sup> CFU mL<sup>-1</sup>) inactivation using powdered and immobilized photocatalysts

Solution	Light source	Pseudo-1 <sup>st</sup> order rate constant $k$ (min <sup>-1</sup> )			
		Dose (powder): 50 mg L <sup>-1</sup>			
		TiO <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	TiO <sub>2</sub> /Ag <sub>3</sub> PO <sub>4</sub>	PATAg beads
MB	UV	0.1218	0.0191	0.2457	
	Visible	0.0054	0.1344	0.0826	0.0344 (15 g L <sup>-1</sup> ) 0.0262 (10 g L <sup>-1</sup> ) 0.0182 (5 g L <sup>-1</sup> )
DCF	Visible			0.0813	0.0184 (10 g L <sup>-1</sup> )
TCS	Visible			0.3003	0.0520 (10 g L <sup>-1</sup> )
<i>Pseudomonas fluorescens</i>	Visible				0.0274 (10 g L <sup>-1</sup> )

composite dominated (Fig. 2c, d and S2†). Meanwhile, the addition of the TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite doubled the BET surface area of the PSF/Alg beads (2.7 m<sup>2</sup> g<sup>-1</sup> to 5.4 m<sup>2</sup> g<sup>-1</sup>).

The UV-vis absorption spectra of TiO<sub>2</sub>, Ag<sub>3</sub>PO<sub>4</sub> and TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite are shown in Fig. S1a† and corresponding bandgap energies were calculated using Tauc plot (Fig. S1b†). Ag<sub>3</sub>PO<sub>4</sub> can effectively absorb visible light less than 700 nm, while pure TiO<sub>2</sub> can only absorb light less than 380 nm. The TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite extended the light absorbance of TiO<sub>2</sub> to 550 nm, suggesting that the composite can harvest much more visible light than the pure TiO<sub>2</sub> and thus suitable for visible light photocatalytic reactions (Fig. S1a†). The emission spectra of UV and visible (LED) light sources used in this study were examined and shown in Fig. S1c.† UV lamp emits at 254 nm, whereas the LED lamp emits in a broad spectrum from 400 to 700 nm with two peaks at ca. 450 and 540 nm. These peaks coincide with the absorbance spectrum of TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite, suggesting suitable excitation with the light sources.

The SEM analyses show a very smooth outer surface of PSF/Alg beads (Fig. 3a) contrary to the PATAg beads (Fig. 3b). Most importantly, macropores (4 to 8 μm) appeared uniformly throughout the surface of PATAg beads. It was also observed that TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> formed randomly scattered agglomerates on the surface and inside the pores. All of these resulted in significantly higher surface roughness of the PATAg beads ( $R_a = 45 \pm 9$ ) compared to PSF/Alg beads ( $R_a = 20 \pm 5$ ), as indicated by the scanning probe microscopy (SMP) analysis (Fig. 3c and d). These results suggest that the addition of TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> significantly improved the advanced pore structure of the photocatalytic beads.

Thermo-Gravimetric Analysis (TGA) was performed to characterize the temperature-induced degradation of different beads (Fig. S3†). The profile of the PSF/Alg beads showed a continuous weight loss from 100–800 °C, while the PSF beads were stable at a temperature of less than 450 °C and started decomposition at higher temperatures (~500 °C). The addition of TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite to the PSF/Alg beads significantly reduced the weight loss rate at a temperature below 450 °C. The prominent decomposition of PATAg beads was observed at the higher temperature (~500 °C). This improvement in thermal stability can be ascribed to the dispersion of the naturally

thermally stable TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite in the PSF/Alg matrix, which also indicates favorable compatibility between TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> and PSF/Alg matrix.<sup>19</sup> Heat-treatment significantly altered the size and shape of the beads (Fig. S4†). However, the PATAg beads suffered a minimum loss in size and retained their shape, which can be attributed to the strong interaction between alginate and TiO<sub>2</sub> nanoparticles.

Alginate beads have been previously reported for the immobilization of TiO<sub>2</sub> and subsequent removal of different organic dyes.<sup>20,21</sup> However, the alginate beads are relatively soft, which can be easily damaged during real application. The use of PSF as the backbone of the immobilization material has significantly improved the durability and mechanical stability of the prepared PATAg beads. Moreover, PSF shaped the macrovoids, while Alg contributed to the formation of micropores inside the beads. This unique sponge-like structure with interconnected macrovoids and micropores would greatly facilitate the adsorption and photocatalytic capacity of the beads.

### 3.2. Photocatalytic degradation of MB by powdered photocatalysts

The as-prepared powdered photocatalysts were employed to degrade MB under both UV and visible light irradiation in the annular photoreactor. Under UV irradiation, the photocatalytic activity is in the order of TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> > TiO<sub>2</sub> >> Ag<sub>3</sub>PO<sub>4</sub> (Fig. 4a), while it is Ag<sub>3</sub>PO<sub>4</sub> > TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> >> TiO<sub>2</sub> under visible light irradiation (Fig. 4b). The photocatalytic activity of materials under UV irradiation can be explained based on the fact that TiO<sub>2</sub> has a more negative potential of the conduction band (CB) and valence band (VB) than that of Ag<sub>3</sub>PO<sub>4</sub>; therefore, the photo-induced holes in the VB of Ag<sub>3</sub>PO<sub>4</sub> can transfer to the VB of TiO<sub>2</sub> (Fig. 4d), thus contributing to efficient separation of electron-hole pairs.<sup>2</sup> The lower band gap energy of the TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite (3.12 eV) than that of TiO<sub>2</sub> (3.19 eV) also plays an important role in deciding photocatalytic efficiency (Fig. S1b†). The pure TiO<sub>2</sub> photocatalyst showed a very low visible-light photocatalytic activity for MB degradation ( $k = 0.0054$  min<sup>-1</sup>). This is attributed to the weak visible light absorption of TiO<sub>2</sub>. The pronounced enhancement of the photocatalytic activity of TiO<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> is attributable to the





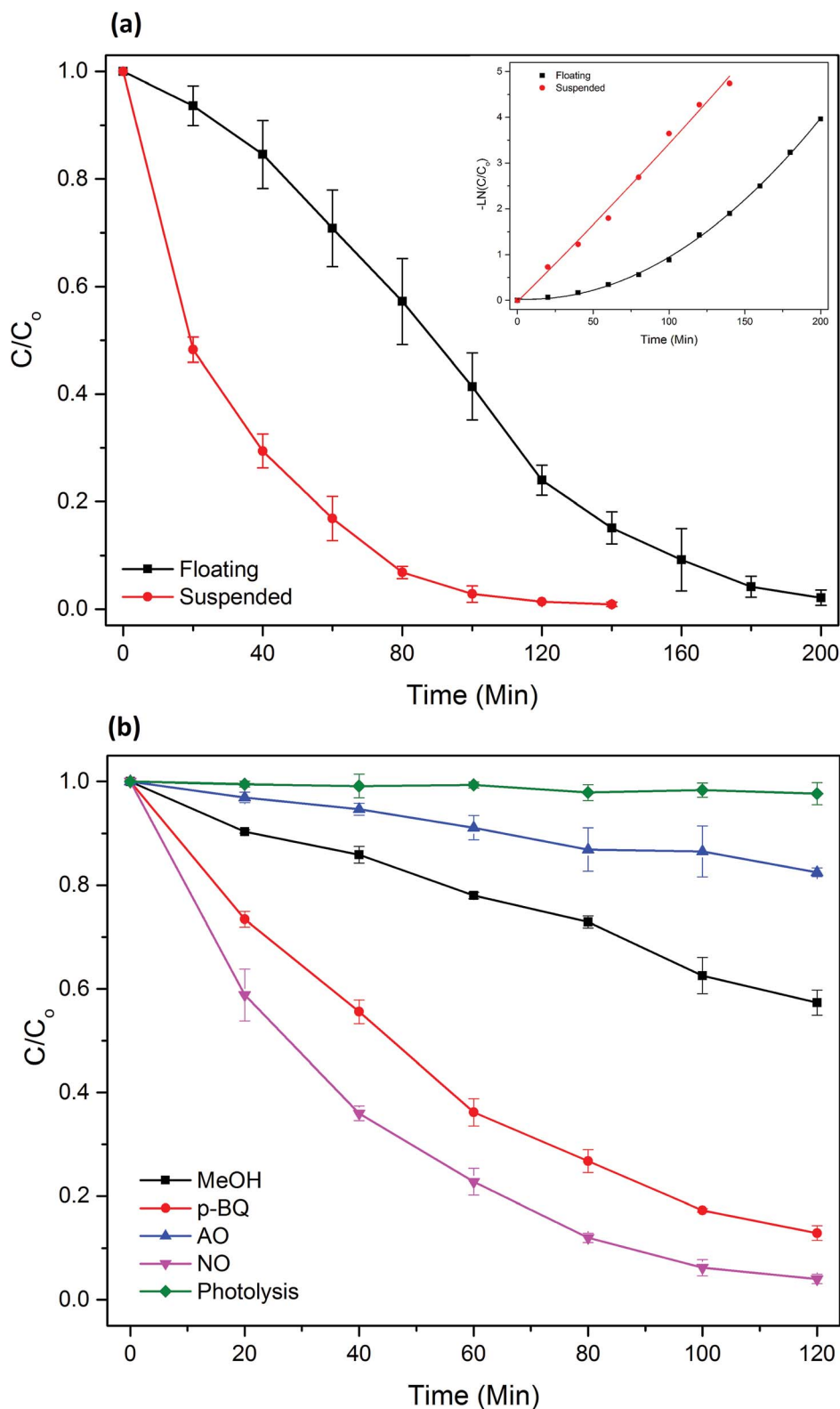


Fig. 6 Photocatalytic degradation of MB (3.2 mg L<sup>-1</sup>) with suspended (15 g L<sup>-1</sup>) and floating (15 g L<sup>-1</sup>) form of photocatalyst beads under visible light irradiation (a) [inset:  $-\ln(C/C_0)$  vs. time]; effect of ROS scavengers during MB degradation by PATAg beads (b). (MeOH – methanol; p-BQ – 1,4-benzoquinone; AO – ammonium oxalate; NO – without scavenger; error bars represent standard deviation of the mean,  $n = 2$ ).

heterojunction of Ag<sub>3</sub>PO<sub>4</sub> and TiO<sub>2</sub>. The enhancement effect of Ag<sub>3</sub>PO<sub>4</sub> is a function of the weight percent (wt%) of Ag<sub>3</sub>PO<sub>4</sub> to TiO<sub>2</sub>. It is noteworthy that the rate of MB degradation quickly

increases to 0.1576 min<sup>-1</sup> when 10% (weight percentage) of Ag<sub>3</sub>PO<sub>4</sub> is loaded to the TiO<sub>2</sub>. Ag<sub>3</sub>PO<sub>4</sub> plays an important role in the photocatalytic activity of the Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> composite

(Fig. S5†). Whereas, the pure silver phosphate showed higher photocatalytic degradation of MB than that of  $\text{TiO}_2$  and  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composite. This is mainly due to the quantity of silver phosphate, which is highly diluted in the  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composite, and titania – a larger constituent – is photoactive only under UV radiation. Thus, the amount of  $\text{Ag}_3\text{PO}_4$  in  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composite determines the photocatalytic activities under visible light irradiation. The lower photocatalytic activity of  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  compared to  $\text{Ag}_3\text{PO}_4$  under visible light is probably due to the much less (10%) content of  $\text{Ag}_3\text{PO}_4$  in the composite.

These photocatalytic beads and powdered photocatalyst could be easily regenerated by stirring in an aqueous solution of  $\text{H}_2\text{O}_2$  (0.5%) for 5 minutes (Fig. S6†). Repeated regeneration and visible light illumination (Fig. 4c) revealed that the  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composite retained its photocatalytic activity for 4 cycles. Simultaneously,  $\text{Ag}_3\text{PO}_4$  quickly lost its photoactivity and achieved only 35% MB degradation during the fourth cycle. The effect of catalyst dose on MB degradation was also investigated. The MB degradation rate increased with the increase in the photocatalyst dose until  $0.8 \text{ mg mL}^{-1}$ , where the highest degradation rate ( $k = 0.124 \text{ min}^{-1}$ ) was achieved. In contrast, a further increase in the photocatalyst dose slightly declined the MB degradation rate (Fig. S7†). Too much photocatalyst dose made the MB solution turbid and hindered light penetration, resulting in a declined photoactivity.

### 3.3. Adsorption and photocatalytic degradation of MB by immobilized photocatalysts

**3.3.1. Adsorption of MB over prepared beads.** The adsorption capacity of PSF, PSF/Alg, and PATAg beads was evaluated firstly, as photocatalytic activity of these beads largely depends on the ability of the catalysts to adsorb target pollutants.<sup>22</sup> As expected, addition of alginate in the PSF matrix significantly enhanced the adsorption capacity of the beads (Fig. S8†), which was further improved with the addition of  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ . After 6 h, the maximum MB adsorption achieved by the beads was 28, 45, and 59% for PSF, PSF/Alg, and PATAg beads, respectively.

**3.3.2. Photocatalytic degradation of MB with suspended PATAg beads.** The effect of photocatalytic beads dose (5, 10,  $15 \text{ g L}^{-1}$ ) on MB degradation efficiency was determined in the concurrent adsorption-photodegradation process. Under the tested condition, consecutive increments in MB degradation efficiency were observed with the increase in the beads dose (Fig. 5a), and the degradation rate constant ( $k$ ) was almost linearly increased, *i.e.*, 0.0182, 0.0262 and  $0.0344 \text{ min}^{-1}$  for 5, 10 and  $15 \text{ g L}^{-1}$ , respectively (Table 2).

Three different initial dye concentrations ( $1.6$ ,  $3.2$ ,  $6.4 \text{ mg L}^{-1}$ ) were tested at a fixed-dose ( $5 \text{ g L}^{-1}$ ) of the bead photocatalyst (Fig. 5b). The diluted dye solution ( $1.6 \text{ mg L}^{-1}$ ) was degraded much faster ( $k = 0.0321 \text{ min}^{-1}$ ) compared to the concentrated ( $6.4 \text{ mg L}^{-1}$ ) dye solution ( $k = 0.0084 \text{ min}^{-1}$ ). Photocatalytic degradation of dye molecules primarily depends on the formation of reactive species on the surface of catalyst under light irradiation and their reaction with the adsorbed dye molecules. Therefore, the MB degradation rate of the tests was

catalyst limited. Nevertheless, at a higher initial dye concentration, the photocatalyst may be shielded by dye molecules, thus decreasing the number of photons reaching the catalyst surface.<sup>23</sup>

The  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composite can have different surface charges, bearing with positive charges under acidic conditions and negative charges under alkaline conditions. This can be explained based on the point of zero charge (pH 6.3) of  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ . On the other hand, MB is cationic in aqueous solution.<sup>24</sup> Therefore, the alkaline conditions are more favorable for MB adsorption due to the electrostatic attraction; on the contrary, degradation of MB decreases in acidic conditions because of the coulombic repulsion. The results in Fig. 5c show the highest MB degradation efficiency at pH 10 and the lowest at pH 3, which corresponds well with the theory. It should be noted that the interaction of  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composite with the PSF/Alg matrix also affects the surface properties of catalysts, and thus influencing the adsorption and degradation of pollutants on catalysts. The interfering effect of other ions (Table S1†) on MB degradation was evaluated with tap water as the working solution (Fig. 5d). The degradation rate was higher in UP water ( $k = 0.0344 \text{ min}^{-1}$ ) compared to tap water ( $k = 0.0215 \text{ min}^{-1}$ ), which could be explained by the competition of other ions present in the tap water for active sites.<sup>25</sup>

**3.3.3. Photocatalytic degradation of MB with buoyant PATAg beads.** Buoyant photocatalytic beads are very attractive for environmental applications, as they are localized at the air/water interface, thus receiving the highest solar/visible light intensity. The PATAg beads can be switched to either suspended or floating form by a simple drying or wetting procedure. To compare the photocatalytic activity of the two forms, we used an equal number of photocatalytic beads (wet weight  $\sim 15 \text{ g L}^{-1}$ ) in two photoreactors with a  $0.8 \text{ L}$  working volume to treat  $3.2 \text{ mg L}^{-1}$  MB solution. The results show that in suspended form, complete degradation of MB was achieved within 120 minutes. However, this was extended to 200 minutes in floating

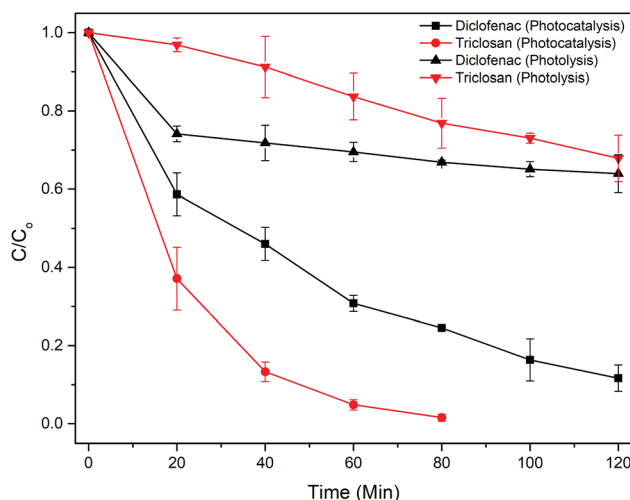


Fig. 7 Photocatalytic degradation of pharmaceutical compounds by the PATAg beads under visible light (initial drug concentration =  $20 \text{ mg L}^{-1}$ ; beads loading =  $10 \text{ g L}^{-1}$ ; reaction volume  $0.8 \text{ L}$ ).



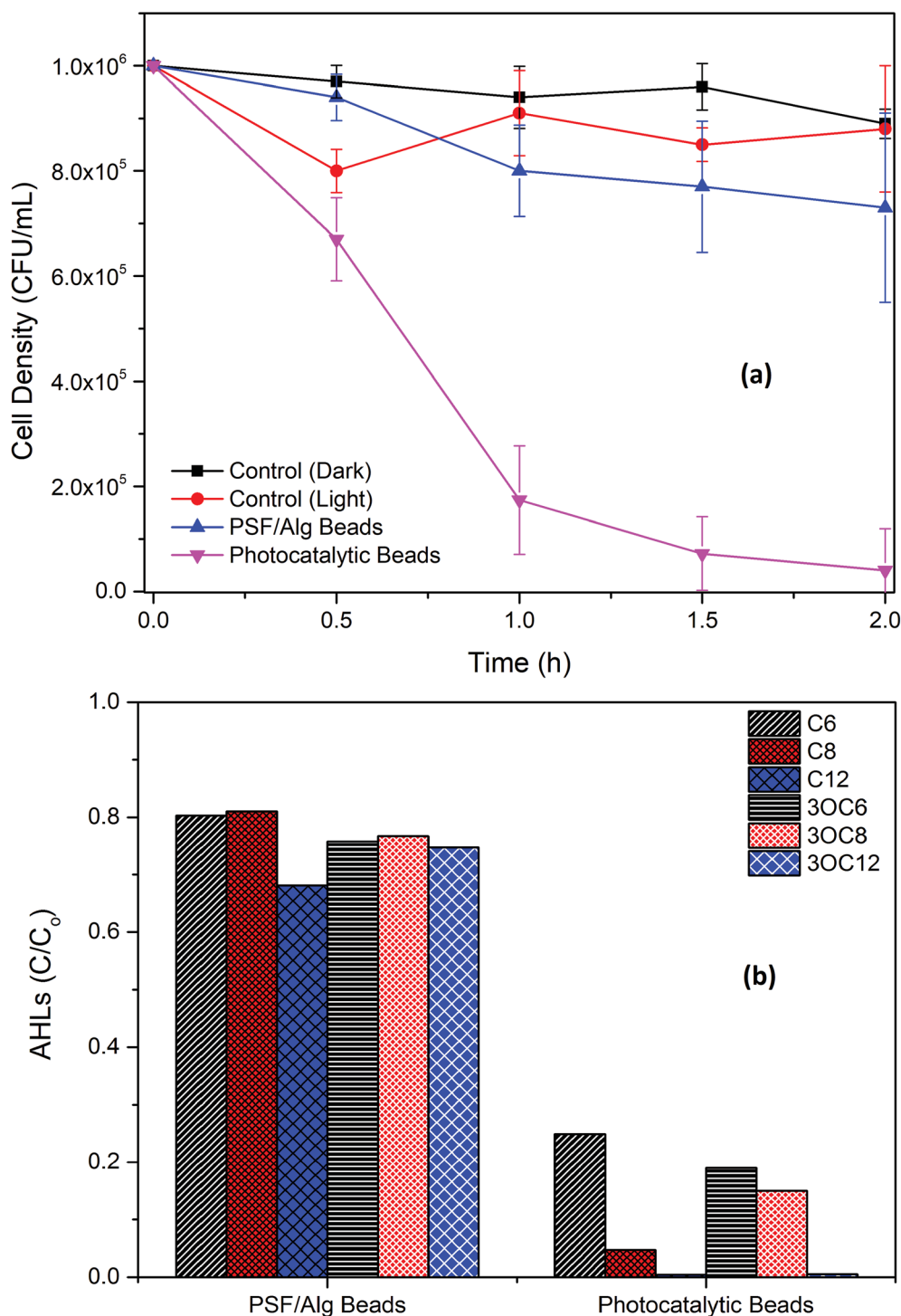


Fig. 8 Photocatalytic inactivation of bacterial strain (a); and photocatalytic degradation of AHLs (b).

form (Fig. 6a). The lower photodegradation in the floating form could be explained by its less quantum yield, lower oxygen mass transfer, and MB mass transfer limitation.<sup>3</sup> Even though the photoactivity of the as-prepared PATAg beads in floating form was lower than that in suspended form, it is still very promising to utilize them under visible light and constrained conditions, *e.g.*, no stirring and aeration, with almost no energy input. The

floating PATAg beads can be reused for several consecutive times without any significant decrease in photocatalytic activity. The form of these beads can also be inter-switched multiple times without any significant deterioration to the beads.

**3.3.4. Mechanism of photocatalytic degradation of MB.** AO, MeOH, and *p*-BQ, the typical h<sup>+</sup>, <sup>•</sup>OH and O<sub>2</sub><sup>•-</sup> scavengers,<sup>26,27</sup> respectively, were used to determine the role of ROS

during MB degradation under visible light by PATAg beads. The degradation rate constant of MB (Fig. 6b) was reduced by 37%, 81% and 93% in presence of *p*-BQ ( $k = 0.017 \text{ min}^{-1}$ ), MeOH ( $k = 0.005 \text{ min}^{-1}$ ) and AO ( $k = 0.002 \text{ min}^{-1}$ ), respectively, as compared to without a scavenger ( $k = 0.027 \text{ min}^{-1}$ ), suggesting the primary role of  $\text{h}^+$  and  $\cdot\text{OH}$  radicals in the MB photodegradation among all ROS. The  $\cdot\text{OH}$  radicals can attack the  $\text{C}=\text{S}^+=\text{C}$  functional group in MB, which is the initial step of MB degradation.<sup>28</sup>

The primary route of  $\cdot\text{OH}$  formation is well reported as the oxidation of  $\text{OH}^-$  or water at the  $\text{TiO}_2$  surface through the highly oxidizing  $\text{h}^+$ ;<sup>26,29</sup> hence, scavenging of  $\text{h}^+$  almost completely stopped  $\cdot\text{OH}$  formation, and thus MB photodegradation. Importantly, none of the ROS completely stopped the MB degradation, which implies that not a single ROS is solely responsible for the process. Additionally, MB is not prone to photodegradation under visible light ( $k = 0.0002 \text{ min}^{-1}$ ).

Comparing with the ROS scavenging experiments of photocatalytic  $\text{TiO}_2$  beads under UV, where quenching the  $\text{h}^+$  with the addition of AO only resulted in a 33% reduction in the reaction rate constant, the  $\text{h}^+$  radicals played a significantly greater role in MB degradation by the  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  beads. This observation indicates that, under visible light, the ROS are generated primarily through valence band holes on  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composite, while a lot of ROS were generated through conduction band electrons on  $\text{TiO}_2$  nanoparticles. Therefore, these excited electrons were mostly trapped by  $\text{Ag}_3\text{PO}_4$ , suggesting the effective heterojunction between  $\text{TiO}_2$  and  $\text{Ag}_3\text{PO}_4$ .<sup>7,8</sup>

### 3.4. Photocatalytic degradation of pharmaceuticals

The Fig. 7 shows that triclosan was completely degraded ( $k = 0.052 \text{ min}^{-1}$ ) within 80 min of photocatalysis, while it took 120 min for diclofenac ( $k = 0.018 \text{ min}^{-1}$ ). Powdered  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  composite was also tested for drugs degradation, and showed higher rate constants compared to immobilized photocatalyst (Fig. S9†) due to larger surface area and more efficient utilization of light. However, powdered photocatalysts are difficult to recycle and reuse. New peaks at 235, 256, 279, 289 nm and a broad peak from 320 to 340 nm emerged in the UV-vis scan of diclofenac (Fig. S10†) after 5 minutes of reaction, indicating the appearance of intermediate compounds. As indicated by the peaks of 275–280 nm in the UV spectra, the aromatic intermediates were probably more resistant to photocatalysis than the diclofenac residual, as reported earlier.<sup>30</sup> Photocatalytic degradation of diclofenac using the  $\text{ZnO}-\text{WO}_3$  catalysts, prepared with different molar ratios, was carried out by Mugunthan *et al.*,<sup>31</sup> and an apparent rate constant for first-order kinetics of  $\sim 0.0131 \text{ min}^{-1}$  was reported. Chen *et al.*,<sup>32</sup> reported a similar degradation rate constant of  $0.013 \text{ min}^{-1}$  for diclofenac with  $\text{WS}_2$  nanosheets. These rate constants are significantly less than the present study despite a higher visible light intensity.

As emerging contaminants, triclosan and diclofenac have attracted a lot of interest due to their adverse impacts on human health and environments. Especially, diclofenac has been listed on the watch list of water contaminants by the EU Water Framework Directive (Decision 2015/495) since 2015. The

environmentally relative concentrations of these two PhACs are typically in the range of  $<1 \mu\text{g L}^{-1}$ ; hence, photocatalysis is a promising technology to polish the water contaminated with trace amounts of PhACs.

### 3.5. Photocatalytic disinfection and quorum quenching (AHLs degradation)

Bacterial disinfection was carried out in Petri dishes with the bacterial strain (*Pseudomonas fluorescens*). After exposure to visible light for 90 min, the PATAg beads effectively disinfected the strain, while the controls (light and dark) and PSF/Alg beads presented negligible inactivation (Fig. 8a). As leaching of Ti and Ag ions from the PATAg beads was not observed (Table S2†), this bacterial inactivation was majorly attributed to the ROS generated under visible light. This highly effective disinfection capability of PATAg beads can be utilized as an alternative to UV disinfection for posttreatment of effluents in decentralized wastewater treatment facilities.

Prominent AHL compounds were also tested for their degradation under visible light using PATAg beads in floating form (Fig. 8b). It can be seen that C6-, 3OC6-, and 3OC6-AHLs were removed over 80% after 90 min, while C8-AHL was removed over 95%, and C12- and 3OC12-AHLs were almost completely removed. It is also noticed that the adsorption of all AHLs to the PSF/Alg matrix was less than 25–30%. The AHL degradation efficiencies of these PATAg beads were much higher than that of a typical QQ strain (data not shown), which indicates that the photocatalytic QQ with PATAg beads can be used as a very efficient technology for biofilm control.

## 4. Conclusions

In this study, we have successfully prepared  $\text{TiO}_2/\text{Ag}_3\text{PO}_4$  nanoparticles and immobilized them onto the polysulfone-alginate matrix to form visible light-active photocatalytic polymer beads, termed as PATAg beads. The major conclusions are as follows.

(1) The addition of  $\text{Ag}_3\text{PO}_4$  does not have any negative impacts on the sponge-like structure of the photocatalytic polymer beads. The macrovoids of 30–90 nm dominate the beads, and provide a BET surface area of  $5.4 \text{ m}^2 \text{ g}^{-1}$ . The synergistic interactions between the catalysts and the immobilization material provide exceptional thermal stability of the beads.

(2) The PATAg beads show a very high visible light photocatalytic activity towards MB, TCS and DCF in the suspended form with a 100% removal time of 120, 80 and 120 min, respectively. The  $\cdot\text{OH}$  radicals are determined to be the primary ROS responsible for the photocatalytic reactions.

(3) The PATAg beads can be easily switched between the suspended and the buoyant form. The PATAg beads remained its high visible light photocatalytic activity in the buoyant form, removing MB completely within 200 minutes under stagnant condition.





(4) The PATAg beads can be effectively regenerated by  $\text{H}_2\text{O}_2$  treatment and used for multiple cycles without any significant loss in photoactivity.

With these features, it is believed that this hybrid system is pragmatic for applications in engineered and natural (waste) water treatment systems at larger scales.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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