

Degradation of paraquat from contaminated water using green TiO₂ nanoparticles synthesized from *Coffea arabica* L. in photocatalytic process

Patcharaporn Phuinthiang and Puangrat Kajitvichyanukul

ABSTRACT

The TiO₂ nanoparticles synthesized from the extract of *Coffea arabica* L. (or TiO₂/C) were used to remove paraquat from contaminated water in heterogeneous photocatalysis process. In this work, the sol-gel process using *Coffea arabica* L. as the solvent chemical were performed to obtain the TiO₂ nano-catalyst. The value of pH_{pzc} of TiO₂/C was 2.9 which caused a highly acidic surface of catalyst. The paraquat is effectively removed in alkaline medium due to the adsorption ability of paraquat on the surface of TiO₂/C. The paraquat degradation followed the pseudo-first-order model with the apparent rate constants of 5.84×10^{-2} , 4.08×10^{-2} , and $2.28 \times 10^{-2} \text{ min}^{-1}$ for TiO₂/C, TiO₂, and without TiO₂, respectively, under the presence of ultraviolet (UV) and H₂O₂. The combined TiO₂/C with UV and H₂O₂ was the most efficient process, exhibiting a maximum 66.3% degradation of 50 mg/L over 90 min at pH 10.

Key words | chemical oxidation, green chemistry, nanoparticles, paraquat, TiO₂, water treatment

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INTRODUCTION

Titanium dioxide (TiO₂) has proved to be a highly useful and active photocatalytic material to remove or degrade recalcitrant organic contaminants through the chemical oxidation reaction for water and air purification. Due to its physical and chemical properties, the application of TiO₂ with ultraviolet (UV) has been widely used, and it has been considered as one type of advanced oxidation processes (Chen *et al.* 2016). The organic pollutants can be degraded by photocatalytic oxidation in which photo-induced holes in TiO₂ oxidize OH⁻ or water molecules adsorbed on the surface of the particles to produce HO[•] and O₂^{-•} which subsequently attack adsorbed organic molecules (Hoffman *et al.* 1995). Photocatalytic reactions have been applied to degrade several pesticides including atrazine, bentazon, monuron, dichlorvos, propyzamide, dicloran and triadimefon (Pelizzetti *et al.* 1989; Pelizzetti *et al.* 1993; Pramuro *et al.* 1993; Minero *et al.* 1997).

The emerging of 'green chemistry' leads to the new synthesizing method of nanoparticles that can improve the physico-chemical properties of the materials. These green nanoparticles are expected to provide higher efficiency in contaminant removal (Humayun *et al.* 2017). However, few works reported in detail about the kinetics and degradation efficiency of the pollutant using those green nanomaterials,

especially the TiO₂. In this area, there has also been increasing interest in identifying environmentally friendly materials that are multifunctional and provide good properties of materials. In this work, coffee extract was chosen to be a solvent for TiO₂ formation following the green chemistry synthesis method. Caffeine/polyphenols from coffee extracts can form complexes with metal ions in solution and reduce them to the corresponding metals (Nadagouda *et al.* 2010). The caffeine/polyphenols contain molecules bearing alcoholic functional groups which can be exploited for reduction, as well as stabilization of the nanoparticles. Thus, these chemicals act as reducing agent and stabilizing agent in TiO₂ synthesis. The chemicals from coffee extracts are also the capping agent or dispersing agent of TiO₂ that can prevent the agglomeration of the nanoparticles and enhance the photocatalytic efficiency of the nanomaterials (Nadagouda *et al.* 2010; Varma 2012).

This work aims to synthesize the TiO₂ using green methods by applying the green solvent obtained from the extract of *Coffea arabica* L. (or TiO₂/C) and applying it in removal of paraquat from aqueous solution. Paraquat (1,1'-dimethyl-4,4'-bipyridinium dichloride) is a widely used commercial herbicide applied in many agricultural activities. This chemical has a high toxicity to mammals and is

recognized as a potent human poison. The U.S. EPA has classified paraquat as a possible carcinogen and has recommended the maximum concentration of paraquat in drinking water at 200 µg/L (Rossi 1997). The removal of paraquat using TiO₂ has been published previously (Zahedi *et al.* 2015). However, the application of green photocatalytic to remove paraquat is not reported elsewhere.

In this work, the details in kinetics and paraquat degradation efficiency were calculated and reported. The paraquat degradation performance using this new type of TiO₂/C in comparison with that using the conventional TiO₂ was also discussed. This approach addresses several factors that play an important role in paraquat removal enhancement by this new type of green TiO₂ nanomaterial.

MATERIALS AND METHODS

Materials

Titanium tetraisopropoxide (TTiP), paraquat, and glacial acetic acid (CH₃COOH) were purchased from Aldrich Chemicals, Thailand. Nitric acid (HNO₃), sulphuric acid (H₂SO₄) and sodium hydroxide (NaOH) were obtained from Merck Chemicals, Thailand. All chemicals were used as received for preparing the nanocatalysts and conducting photocatalytic experiments. The 18 MΩ deionised water (H₂O) was used for the preparation of all the solutions. All reagents used were of analytical grade and employed as received.

TiO₂ catalyst synthesis

All experiments were conducted at the Center of Excellence on Environmental Research and Innovation, Naresuan University. The typical sol-gel synthesis of TiO₂-loaded nanoparticles was used in this work. The method is as follows: TTiP (4.83 mL), glacial acetic acid (15.35 mL) and water were used in the molar ratio of 1:10:300.16 TTiP was mixed with glacial acetic acid in an ice bath. When this mixture turned to a sol, it was stirred at room temperature to form a gel before undergoing the drying process. After drying at 100 °C for 90 min, the powder was collected and calcined at 600 °C. The nanoparticles obtained from this process were shortly denoted as 'TiO₂'.

For the green TiO₂ nanoparticles synthesized from *Coffea arabica* L., 1 g of coffee was boiled in 50 mL of water and filtered through a filter paper (Whatman, No. 41). Then 5 mL of coffee extract was added to the mixture solution of TTiP and glacial acetic acid. The drying process

was the same procedure as above. The obtained TiO₂ nanoparticles were denoted as 'TiO₂/C'.

Adsorption and photocatalytic of paraquat

Photocatalysis experiments were performed in a batch reactor. The reactor was cylindrical with a volume of 1.1 L made from quartz glass (ACE Glass Co. 7841-06; Vineland, NJ, USA). The UV light source was a 10 W (Philips) with 254 nm wavelength. The initial concentration of paraquat was in the range of 5–50 mg/L, and the catalyst was 0.6 g/L. In this photocatalytic experiment, the paraquat solution was injected into the reactor and treated in batch operation mode with a steady temperature maintained at 25 ± 2 °C throughout the test in an oxygen atmosphere. The liquid was allowed to equilibrate in the dark for 30 min. The paraquat adsorption data were collected. After reaching equilibrium, the reaction was started by switching on the light at t = 0, and the initial concentration of paraquat was designated as C₀. The initial pH of solution was 7. It was adjusted to pH 3 by adding 36.8 N H₂SO₄ and to pH 10 by adding NaOH before the photoreaction experiment unless otherwise specified. At a chosen interval of irradiation time, aliquots of the reaction mixture were withdrawn and filtered through a membrane filter (0.1 µm). Paraquat concentration was detected by a colorimetric method using UV-Vis spectrophotometer (Model Lambda 650, Perkin Elmer, USA) by reducing paraquat to its blue radical. A solution sample in the test tube was added with 0.1% sodium dithionite in 0.1 M sodium hydroxide. The mixture was gently mixed and measured for light absorbance within 1 min. The detection was done at 600 nm wavelength using a spectrophotometer. The paraquat concentrations in the final solution for each experiment were also confirmed by liquid chromatography-mass spectrometry (Model Single Quadrupole LC/MS, Agilent, USA). Total organic carbon (TOC) analysis was done by TOC carbon analyzers (Model TOC-L, Shimadzu, Japan). The Brunauer-Emmett-Teller (BET) surface area for all nanoparticles were done by BET surface area analyzer (Model SA-9600, Horiba, Japan). Analysis of pH at point of zero charge (pH_{pzc}) for all nanoparticles was measured by Zetasizer (Model ZS90, Malvern, UK).

RESULTS AND DISCUSSION

Adsorption of paraquat onto TiO₂ surface

Preliminary adsorption experiments revealed that in the absence of TiO₂, no noticeable change in paraquat

concentration occurred during a 60-min experimental period. Adsorption of paraquat using TiO₂/C at different pH was evaluated as shown in Figure 1. The adsorption was rapid in the first few minutes and reached equilibrium within 20 min for all pH conditions. The paraquat adsorption was highest at pH 10 with the maximum adsorption capacity of 20 mg/g. At pH 3 and pH 7, the maximum adsorption capacities were 16.8 and 12.2 mg/g, respectively. Our results are in good agreement with previous work. Florencio *et al.* (2004) reported that the degradation of diquat and paraquat did not take place in acid medium but was pronounced in an alkaline solution. Less adsorption of paraquat on the surface of TiO₂ resulted in low degradation of the chemicals in acidic and moderate degradation in neutral pH medium (Florencio *et al.* 2004).

The paraquat adsorption of TiO₂/C was compared with that of TiO₂ from chemical-based process as shown in Figure 2. The BET surface areas of TiO₂/C (75.8 m²/g) was slightly changed when compared with TiO₂ (73.2 m²/g). While the values of pH_{zpc} were 2.9 and 4.6 for TiO₂/C, and TiO₂, respectively. The lower the pH_{zpc} causes the higher affinity for cations to adsorb on the surface of nanoparticles. Thus, using the *Coffea Arabica* L. for TiO₂ synthesis mainly affected

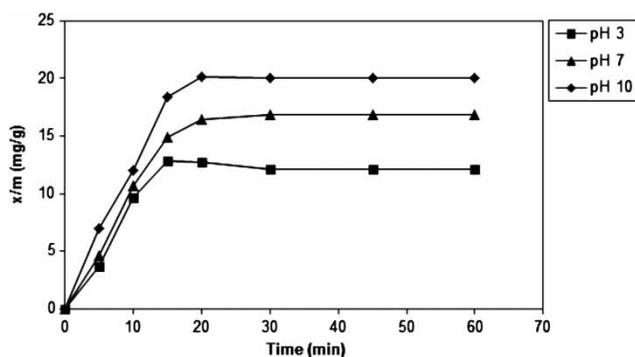


Figure 1 | Adsorption of paraquat using TiO₂/C at different pHs. Experimental condition: [TiO₂] = 0.6 g/L, and [PQ] = 50 ppm.

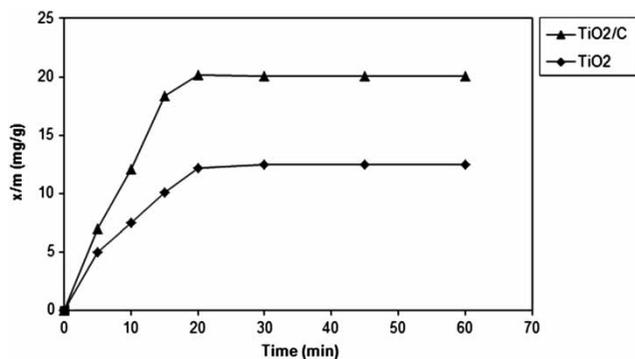


Figure 2 | Comparison of paraquat adsorption using TiO₂/C, and TiO₂ at pH 10. Experimental condition: [TiO₂] = 0.6 g/L, [PQ] = 50 ppm and pH 10.

on the surface charge rather than the surface area and, consequently, resulting in higher adsorption ability of TiO₂/C over TiO₂. At pH 10, the surface charges of the catalyst were negative, favouring the adsorption of cations like paraquat. This finding also occurred for other types of catalyst such as TiO₂/SBA-15 and Cu-TiO₂/SBA-15 (Sorolla II *et al.* 2012).

Paraquat removal by TiO₂/C photocatalytic reaction

Paraquat degradation using TiO₂/C with UV in different concentrations of paraquat is shown in Figure 3. The removal percentages of paraquat with initial concentrations of 5, 10, 20, 35, and 50 mg/L were 76.3, 52.1, 31.7, 27.9, and 4.3%, respectively. These results clearly indicate that low concentration paraquat solutions were easily degraded by photocatalytic reactions. However, as the initial concentration of paraquat increased (higher than 35 ppm), the TiO₂/C with UV hardly degraded paraquat within 1 h. It was previously reported that the paraquat removal using TiO₂ was feasible for the concentration lower than 30 mg/L since it is chemically stable in nature (Moctezuma *et al.* 1999). The paraquat solutions remained stable in the temperature range of 20–40 °C and after standing for 23 days (Florencio *et al.* 2004).

To enhance the paraquat degradation, H₂O₂ was added to the experiment. Solutions of 50 ppm paraquat were irradiated under four different conditions: H₂O₂/UV, TiO₂/C with UV (without H₂O₂), TiO₂/C with UV + H₂O₂, TiO₂ with UV (without H₂O₂), and TiO₂ with UV + H₂O₂ systems. Figure 4 shows the changes in the degree of degradation of aqueous paraquat versus irradiation time. It is noted that there was no paraquat degradation by the direct photolysis with a 10 W UV lamp during 90 min. As shown previously in Figure 3, the 50 mg/L of paraquat was hardly decreased using TiO₂/C with UV irradiation and the removal efficiency was only 4.3%. The paraquat removal increased up to 36.2%

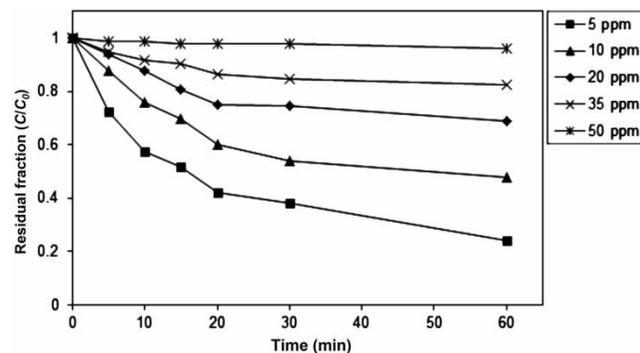


Figure 3 | Paraquat degradation by photocatalytic process using different concentration of TiO₂/C. Experimental condition: [TiO₂] = 0.6 g/L, UV 10 watt and pH 10.

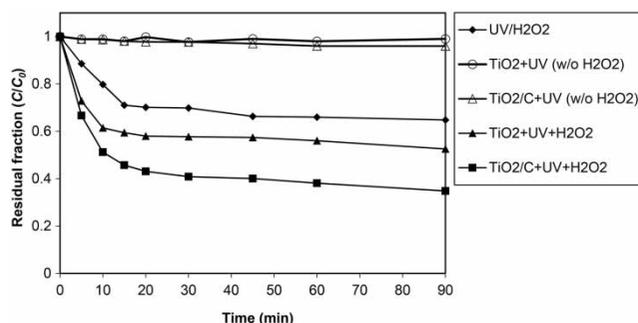
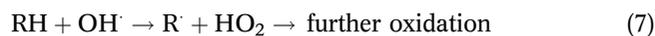
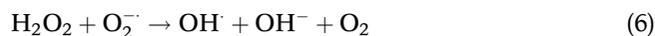


Figure 4 | Paraquat degradation using different processes, (a) UV/H₂O₂, (b) TiO₂+ UV (without H₂O₂), (c) TiO₂/C+ UV (without H₂O₂), (d) TiO₂/C + UV + H₂O₂, and (e) TiO₂ + UV + H₂O₂, Experimental condition: [TiO₂] = 0.6 g/L, [PQ] = 50 ppm, [H₂O₂] = 10 mM, UV = 10 W, and pH 10.

in the presence of 10 mM of H₂O₂ under UV irradiation (without TiO₂/C). Approximately 66.3% of paraquat was degraded within 90 min when 0.6 g/L TiO₂/C was added with UV and 10 mM H₂O₂.

In comparison, the paraquat degradation using TiO₂/C was compared with TiO₂ in the presence of H₂O₂ under UV irradiation as shown in the same figure. The TiO₂/C provided the higher photocatalytic efficiency for paraquat degradation than the TiO₂. The high efficiency in paraquat removal using TiO₂/C partially due to the high adsorption of paraquat onto its surface as explained earlier, enhancing more paraquat to react with OH radicals. The least amount of degradation was observed for chemical based TiO₂, which has slightly lower surface area, higher value of pH_{pzc} and the lower adsorption of paraquat on its surface as seen in Figure 2. The overall percentages of degradation for paraquat after 90 min of irradiation were 66.3, 48.7, 36.2, and 4% for TiO₂/C with UV + H₂O₂, TiO₂ with UV + H₂O₂, UV/H₂O₂, and TiO₂/C +UV (without H₂O₂), respectively.

The reaction mechanisms during the TiO₂ in the presence of H₂O₂ under UV irradiation are summarized as follows (Barakat *et al.* 2005; Gao *et al.* 2015):



where RH refers to the paraquat compound.

In the system that contained only TiO₂, the electron (e⁻) and hole (h⁺) on the TiO₂ surface were generated upon UV irradiation (Equation (1)). Equations (3), (4), and (7) express that the hydroxyl radicals were formed under light excitation when the positive holes reacted with OH⁻ on the TiO₂ surface. When the H₂O₂ was presented in the system, the UV/H₂O₂ reaction can generate OH[·] (Equation (2)), enhancing the rate of photocatalytic reaction. H₂O₂ was a better electron acceptor than oxygen in other mechanisms (Equation (5)). Thus, the amount of electron recombination decreased, and the paraquat degradation using this photocatalytic process was enhanced as shown in Figure 4.

To describe the kinetics of this paraquat degradation, the Langmuir–Hinshelwood model (or L–H model) was selected as it demonstrated a good fit in photocatalysis process in many previous works (Rajeshwar *et al.* 2008). The development of this model to obtain a kinetic equation depends on the limiting step (adsorption, surface reaction, or desorption). The L–H model relates the degradation rate (*r*) to the concentration of the organic reactant (*C*), as shown in Equation (8).

$$r = -\frac{dC}{dt} = \frac{k_r K_{ad} C}{1 + K_{ad} C} \quad (8)$$

where *k_r* is the rate constant, and *K_{ad}* is the adsorption equilibrium constant. When the adsorption is relatively weak, or the concentration of the reactant is low, Equation (8) can be simplified to be the first-order kinetics with an apparent rate constant *k_{app}* (Equation (9)):

$$\ln\left(\frac{C}{C_0}\right) = -k_r K_{ad} t = -k_{app} t \quad (9)$$

Plotting $-\ln(C/C_0)$ vs. reaction time (*t*) generates a straight line with a slope equal to *k_{app}* (Chiou *et al.* 2008). The apparent rate constants (*k_{app}*), initial degradation rates (*r*), and correlation coefficients (*R*²) for paraquat degradation using different types of TiO₂ are shown in Table 1.

Table 1 | Apparent rate constants (*k_{app}*), initial degradation rates (*r*), and correlation coefficients (*R*²) for paraquat degradation using different types of TiO₂

TiO ₂	Photocatalytic condition	<i>k_{app}</i> (min ⁻¹)	<i>r</i> (mM/min)	<i>R</i> ²
-	UV + 10 mM H ₂ O ₂	0.0228	0.0044	0.9990
TiO ₂	UV + 10 mM H ₂ O ₂	0.0408	0.0106	0.8391
TiO ₂ /C	UV only	0.0014	0.0004	0.9080
TiO ₂ /C	UV + 10 mM H ₂ O ₂	0.0584	0.0130	0.9203

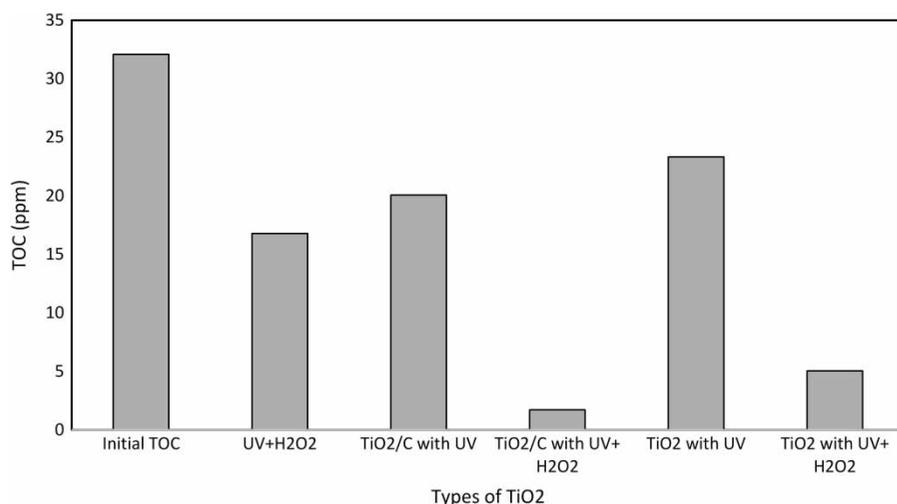


Figure 5 | TOC concentration of paraquat in photocatalytic process using different processes. Experimental condition: [TiO₂] = 0.6 g/L, [PQ] = 50 ppm, [H₂O₂] = 10 mM, UV = 10 W, and pH 10.

The initial reaction rate of the TiO₂/C with UV + H₂O₂ (5.84×10^{-2} mM/min) in paraquat removal was nearly forty-two fold that of the TiO₂/C with UV but without the H₂O₂ system (1.4×10^{-3} mM/min). This difference is attributed to the contributions of the hydroxyl radicals produced by H₂O₂ during the TiO₂/C with the UV + H₂O₂ process.

The degradation percentage of paraquat regarding mineralization of TOC in the presence of UV + H₂O₂, TiO₂ with UV and TiO₂ with UV + H₂O₂ was also investigated. The initial concentration of paraquat was 50 ppm with an initial TOC value of 32.08 ppm. The degradation percentage and mineralization to the TOC of paraquat using different processes are shown in Figure 5. All cases were expressed as mean \pm standard deviation. An analysis of variance (ANOVA) was used to test the significance of the results with $p < 0.05$ and $F = 4.34$ was statistically significant. From the results, mineralization of paraquat for TiO₂/C in the presence of UV with H₂O₂ showed the highest yield. By contrast, the TiO₂ from chemical-based synthesis provided lowest TOC percentage removal.

CONCLUSIONS

In this work, a green, low-cost, and reproducible of TiO₂ nanoparticles were used to remove paraquat from contaminated water in heterogeneous photocatalysis process. The novel 'green' nanoparticles were obtained by the sol-gel process using coffee as the solvent chemical. The paraquat degradation using the TiO₂/C was conducted in comparison with the TiO₂ from chemical-based synthesis. Both TiO₂ with UV and TiO₂ with UV/H₂O₂ have been investigated.

From overall experiments, the combined TiO₂/C with UV and H₂O₂ was the most effective photocatalyst, exhibiting a maximum 66.3% degradation of 50 mg/L over 90 min at pH 10. The paraquat removal depended on the pH of the medium. The TiO₂/C provided the highest adsorption percentage of paraquat due to its dominated negative charge on the surface. The BET surface areas of TiO₂/C (75.8 m²/g) was slightly changed when compared with TiO₂ (73.2 m²/g); however, the values of pH_{pzc} of both materials were pronouncedly different. The pH_{pzc} of TiO₂ were 2.9, and 4.6 for TiO₂/C, and TiO₂, respectively. Thus, the surface charge of particles played a major role for the adsorption of positive ions of paraquat in this work. The high adsorption of paraquat on TiO₂/C led to high efficiency in paraquat removal. The Langmuir–Hinshelwood model could well describe the photodegradation of paraquat during all three catalytic oxidation processes. The apparent first-order rate constants were 5.84×10^{-2} , 4.08×10^{-2} , and 2.28×10^{-2} min⁻¹ for TiO₂/C, TiO₂, and UV, respectively, under the presence of UV and H₂O₂. Results from this work offer the benefit of using the green nanoparticles (such as TiO₂/C) in pollutant removal for water and wastewater treatment.

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