

Non-thermal plasma-induced photocatalytic degradation of 4-chlorophenol in water

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Abstract

TiO₂ photocatalyst (P-25) (50 mg L⁻¹) was tentatively introduced into pulsed high-voltage discharge process for non-thermal plasma-induced photocatalytic degradation of the representative mode organic pollutant parachlorophenol (4-CP), including other compounds phenol and methyl red in water. The experimental results showed that rate constant of 4-CP degradation, energy efficiency for 4-CP removal and TOC removal with TiO₂ were obviously increased. Pulsed high-voltage discharge process with TiO₂ had a promoted effect for the degradation of these pollutants under a broad range of liquid conductivity. Furthermore, the apparent formation rates of chemically active species (e.g., ozone and hydrogen peroxide) were increased, the hydrogen peroxide formation rate from 1.10×10^{-6} to 1.50×10^{-6} M s⁻¹, the ozone formation rate from 1.99×10^{-8} to 2.35×10^{-8} M s⁻¹, respectively. In addition, this process had no influence on the photocatalytic properties of TiO₂. The introduction of TiO₂ photocatalyst into pulsed discharge plasma process in the utilizing of ultraviolet radiation and electric field in pulsed discharge plasma process enhanced the yields of chemically active species, which were available for highly efficient removal and mineralization of organic pollutants.

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1. Introduction

Non-thermal plasma in aqueous media (pulsed discharge plasma (PDP) in aqueous solution), namely, is the plasma produced from a fast rise-time (<200 ns) pulsed high-voltage electrical discharge in aqueous solution. The process accelerates free electrons, and the energized electrons ultimately collide with and ionize, dissociate or excite the ambient molecules, thus develops non-thermal plasma to produce chemically active species, i.e. high-energy electrons, •OH, •H, O•, O₃, H₂O₂, neutral molecules (excited state), and ionic species. Simultaneously some phenomena occur, which are quite similar to UV photolysis, ultrasonic cavitations, UV-radiation, shock waves and supercritical water conditions [1,2]. Non-thermal plasma process by pulse discharges introduced into water for the effective removal of organic compounds, especially toxic organic compounds, which are hardly efficiently degraded by conventional

technologies such as biotreatment, has attracted extensive attention [3,4–9].

Recently, to enhance the degradation efficiency of organic contaminant and energy efficiency of power supply, homogeneous catalysts (such as Fe²⁺ for Fenton's reactions) were introduced into the pulsed discharge plasma process to enhance the degradation of organic dye [8] and organic pollutant phenol [10], while homogeneous catalysts were difficult to separate from the treated solution and led to limit their practical application in wastewater treatment. Therefore heterogeneous catalysts, such as activated carbon [5], alumina, and silica gel [2] have been paid more attention to promoting the degradation of organic contaminants for their adsorptions and plasma-induced reactions, whereas these heterogeneous catalysts at high concentration would hinder the ultraviolet light radiation and plasma channels formation, resulting in poor degradation of organic pollutants.

For pulsed discharge plasma in aqueous solution exists positive electric field and ultraviolet light radiation (wavelength $\lambda = 75\text{--}185$ nm) [11], and TiO₂ is a semiconductor with a band gap of about 3.0 eV, UV light (with λ shorter than 400 nm) can excite pairs of electrons and holes [12]. When the TiO₂ photo-

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catalyst is introduced into this system, these conditions should excite the dissipation of electrons and holes in TiO_2 particle for its photochemical and photoelectrochemical properties, leading to more amounts of chemically active species, especially $\bullet\text{OH}$ radicals formed [13]. It was preliminarily reported by Lukes et al. that the phenol removal was enhanced in the presence of TiO_2 due to the increase of the yield of OH radicals [14]. However, there are few work reported in details about pulsed discharge plasma system in combination with TiO_2 catalyst for the decomposition of organic pollutants.

The objectives of this paper are to explore the enhancement of the decomposition rate and energy efficiency for the decomposition of organic pollutants, i.e., 4-CP, phenol and methyl red by the addition of TiO_2 photocatalyst into pulsed discharge plasma process, and compare the varieties of the primary intermediates and hydrogen peroxide formed between PDP with TiO_2 and without TiO_2 under different liquid conductivities during the degradation of 4-CP. Finally we present possible reasons of such enhancement by analyzing of the variances in the amounts of chemically active species (i.e. ozone and hydrogen peroxide).

2. Experimental section

2.1. Chemicals

TiO_2 powder (Degussa P-25, Germany) had a surface area ($49.6 \text{ m}^2 \text{ g}^{-1}$) and contained anatase and rutile phases in a ratio of about 3:1. The reused TiO_2 was recycled from the final treated solutions containing TiO_2 by filtering through the $0.22 \mu\text{m}$ membrane filters, then it was regenerated in distilled water, and finally it was dried at 333 K for next use. The organic pollutant 4-CP is analytic grade purchased from Hangzhou Huadong Medicine Group Co., Ltd.

2.2. Equipments and procedures

The pulsed high voltage power supply used in the present study is identical to that in previous work [9]. The scheme of experimental set-up is shown in Fig. 1. The needle-plate reactor that used in this work consisted of a glass-cylinder chamber ($\text{Ø}60 \text{ mm} \times 130 \text{ mm}$) with a water jacket to maintain the reactor at 298 K. The positive needle electrode was made from five stainless steel acupuncture needles ($\text{Ø}0.30 \text{ mm} \times 75 \text{ mm}$, come from Suzhou medical instruments Co., Ltd.), which were placed in the center of these microtubules protruded 1.0 mm from the top of them and located at the bottom of gas chamber. Each microtubule was made of stainless steel microtubule (4.0 mm in length and 1.0 mm at diameter), which was connected with gas chamber at bottom of the reactor. When the gas bubbled through the microtubules, the gas surrounded the needle tip to form bubbles to homogenize the solution, and resulted in the hybrid gas-liquid phase electrical discharge. The ground plate electrode was made from stainless steel plate of 45 mm at diameter and located at the Teflon cap with four holes for gas output. The electrode distance was varied by moving the ground plate electrode. The standard 1000 mg L^{-1} TiO_2 solution was sonicated to avoid the agglomeration of TiO_2 particles in the solution, then moved into 4-CP solution for treatment. The pH of mixed solution was adjusted by NaOH or HCl solution (0.01 M). Every sample is taken at interval of 6 min. Each series of samples had triplicates conducted. The experimental values were the averages of three samples, and reach over 95% confidence.

2.3. Analysis

The average output voltage and current were measured using an alternating current and voltage meter (Luguang instrument Group Co., Ltd., Shanghai). The applied voltage was 14 kV with a frequency of 150 Hz.

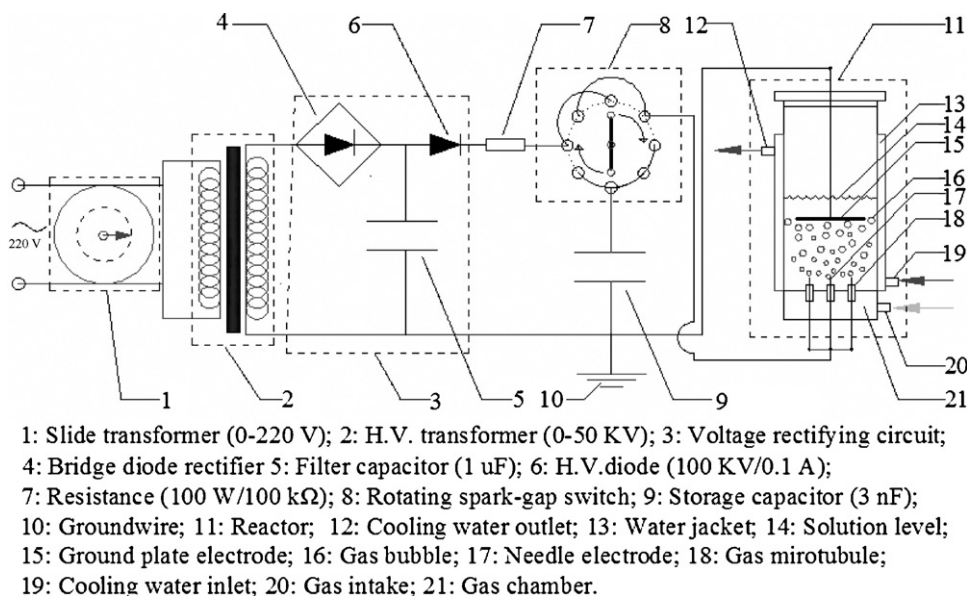


Fig. 1. Schematic diagram of experimental set-up.

The samples were analyzed by HPLC (Knauer-2005), equipped with a MS-2 C₁₈ column (Ø4.6 mm × 250 mm) and a UV detector set at 278 nm for 4-CP and 254 nm for phenol. The mobile phase was prepared by the H₃PO₄ solution (0.001, v/v) and methanol (chromatographically pure) at a flow rate of 1 mL min⁻¹, and the volumetric ratio between the H₃PO₄ solution and methanol was 50:50 (v/v). A total organic carbon (TOC) analyzer (Teledyne Tekmar Dohrmann Apollo 9000, USA) was used to analyze the treated water. The ozone concentration dissolved in liquid phase in distilled water was measured by UV absorption at 254 nm using UV-vis spectrophotometer (Techcomp 8500) [15]. The UV-vis spectrophotometer was set at a wavelength of 254 nm for analysis of methyl red. The H₂O₂ concentration was determined colourimetrically using the reaction of H₂O₂ with titanil ions by the analysis of the maximum absorbance of the yellow peroxotitanium (IV) complex at wavelength λ = 410 nm [16]. The conductivity of the solution was measured by a conductivity meter (DDS-11 A).

The crystal structure of TiO₂ was identified by XRD (Rigaku D/max 2550, Japan), performed over angular ranges of 2θ = 10–80°, scanned at a speed of 0.01°/s and steps of 0.01°. The equipment was operated at 40 kV and 50 mA. Used TiO₂ particles (marked as TiO_{2(used)}) was separated from the treated water by 0.22 μm cellulose membrane.

The degradation reactions of 4-CP obeyed the apparent first order law. The kinetic pathway of 4-CP degradation could be expressed as follows:

$$\ln \left(\frac{C_0}{C_t} \right) = k_{cp} t \quad (1)$$

where C_t , C_0 , k_{cp} and t are the concentration of 4-CP at a given reaction time, the initial concentration, the rate constant (s⁻¹) and reaction time (s), respectively.

In order to compare the discharge energy efficiency of 4-CP removal under different conditions, $G_{50\%}$ yield values (g (kWh)⁻¹) were evaluated by the weight amount of 4-CP converted divided by energy input of the reactor required as follows [17]:

$$G_{50\%} = \frac{0.5 C_0 V_{sol.}}{1/2(CV^2 f t_{50\%})} \quad (2)$$

where C_0 is the initial 4-CP concentration at $t=0$ (g L⁻¹), $V_{sol.}$ the solution volume (L), C capacitance of pulse forming capacitor (F), V its charging voltage (V), f the pulse frequency (Hz), and $t_{50\%}$ is the treatment time when 50% of 4-CP is removed (s).

Since the reactions of the formation of H₂O₂ and O₃ in distilled water are assumed to be of zero order [18]. The apparent formation rates of hydrogen peroxide and ozone ($K_{H_2O_2}$, K_{O_3}) are determined from the slope of the plots of their concentrations over time.

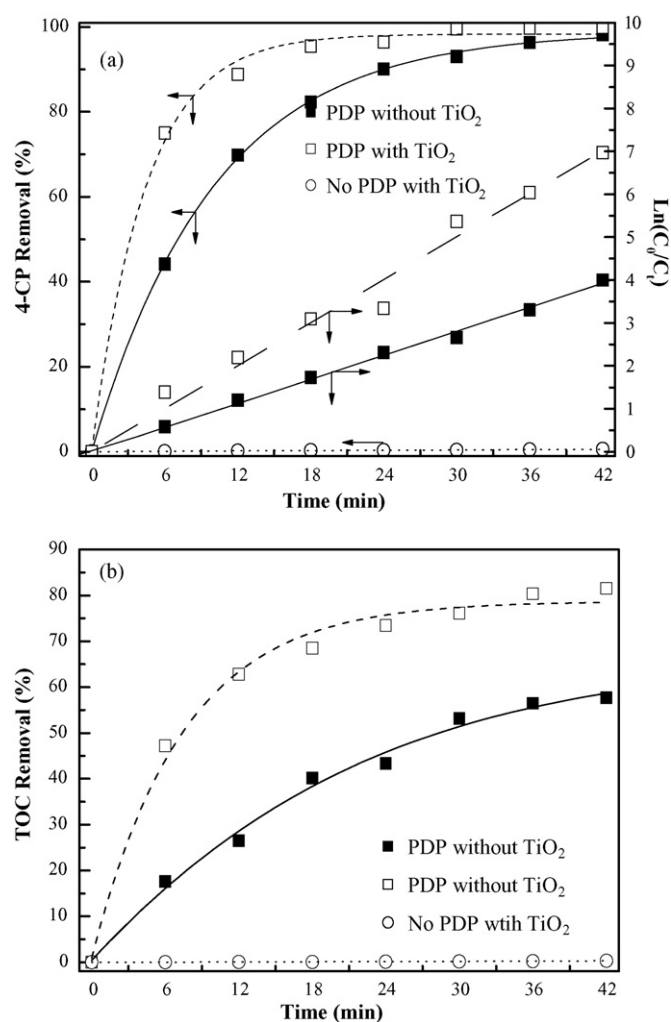


Fig. 2. 4-CP degradation (a) and TOC removal (b) in the PDP process with/without TiO₂ under low liquid conductivity. (Experimental conditions: applied voltage: 14 kV; electrode distance: 2 cm; TiO₂ concentration: 50 mg L⁻¹; O₂ flow rate: 100 L h⁻¹; pH 6.5; liquid conductivity: 1.50–4.0 μS cm⁻¹.)

3. Results and discussion

3.1. Degradation and mineralization of various organic pollutants in the PDP process with/without TiO₂

In order to investigate the effect of the presence of TiO₂ power (50 mg L⁻¹) in 4-CP solution (100 ppm) on the degradation and mineralization of organic contaminant 4-CP, 4-CP removal and TOC removal were evaluated. As shown in Fig. 2(a), the adsorption of TiO₂ for 4-CP hardly contributes to the removal of 4-CP. The removal of 4-CP in the pulsed discharge plasma process with TiO₂ is faster than that without TiO₂, and the 4-CP removal is obtained at 90% in approximately 12 min. The treated time is about one time shorter than that without TiO₂ in about 25 min. In addition, energy efficiency for 4-CP removal with TiO₂ (2.15 g kWh⁻¹) is over two times as great as without TiO₂ (0.95 g kWh⁻¹). Table 1 summarizes rate constants and energy efficiencies of the degradation of different organic compounds (4-CP, phenol and dyes) reported in previous literatures compared with in our works. It is found that our results for the PDP

Table 1
Comparison of our experimental results with other results reported in previous literatures

Experimental conditions	Pollutants	Initial treatment conditions	k_{cp}	$G_{50\%}$ (g kWh ⁻¹)	Reference
Without TiO ₂	4-Chlorophenol	(100 mg L ⁻¹ , pH 6.5, 1.50–4.0 μS cm ⁻¹)	$1.56 \times 10^{-3} \text{ s}^{-1}$	0.95	In our works
	Phenol		$1.19 \times 10^{-3} \text{ s}^{-1}$	0.89	
With TiO ₂ (50 mg L ⁻¹)	4-Chlorophenol	(100 mg L ⁻¹ , pH 6.5, 380–390 μS cm ⁻¹)	$1.44 \times 10^{-3} \text{ s}^{-1}$	0.58	
	Methyl red	(100 mg L ⁻¹ , pH 5.5, 3.0–5.0 μS cm ⁻¹)	$1.05 \times 10^{-3} \text{ s}^{-1}$	0.71	
	4-Chlorophenol	(100 mg L ⁻¹ , pH 6.5, 1.50–4.0 μS cm ⁻¹)	$2.79 \times 10^{-3} \text{ s}^{-1}$	2.15	
	Phenol		$2.42 \times 10^{-3} \text{ s}^{-1}$	1.97	
	4-Chlorophenol	(100 mg L ⁻¹ , pH 6.5, 380–390 μS cm ⁻¹)	$2.36 \times 10^{-3} \text{ s}^{-1}$	1.64	
	Methyl red	(100 mg L ⁻¹ , pH 5.5, 3.0–5.0 μS cm ⁻¹)	$1.42 \times 10^{-3} \text{ s}^{-1}$	1.12	
PCDs ^a with ozone and silica gel	Phenol	(25 mg L ⁻¹ at 3.3 mL min ⁻¹)		1.93	[2]
PCDs	Methylene blue	(13.25 mg L ⁻¹ at 10 mL min ⁻¹)		0.67	
PNR ^b with O ₂ (dissolved 250 μM)	Phenol	(100 mg L ⁻¹ , KCl (150 μS cm ⁻¹))	–	1.2	[5]
HGLR ^c with O ₂ (150 SCCM)		(100 mg L ⁻¹ , pH 5.0, 150 μS cm ⁻¹)		0.7	[6]
HGLR ^d with O ₂ (150 SCCM)				1.7	
EHD ^e reactor (3.5 L/7-kJ)	4-Chlorophenol	(25.7 mg L ⁻¹ , pH 5.0 (0.015 NaH ₂ PO ₄))	$(9.40 \pm 1.4) \times 10^{-4}$ (discharge ⁻¹)	0.20	[19]
EHD reactor (1.0 L/7-kJ)			$(2.43 \pm 1.5) \times 10^{-4}$ (discharge ⁻¹)	0.07	

^a Pulsed corona discharges.

^b Plate-needle reactor with a hollow tube high voltage electrode.

^c Hybrid gas–liquid phase reactor with stainless steel ground electrode.

^d Hybrid gas–liquid phase reactor with RVC ground electrode.

^e Electrohydraulic reactor.

process in combination with TiO₂ catalyst exhibits higher values of rate constants and energy efficiencies of organic compounds degradation than those in other reports. In the meantime, the enhanced effect of TiO₂ for non-colour compounds, i.e., 4-CP and phenol is greater than that of coloured compound methyl red, due to the hinder of ultraviolet light emitted from plasma channels to TiO₂ surface by coloured pollutant. This substantiates that this hybrid technique performs higher potentiality for the degradation of organic pollutant. Meantime, Fig. 2(a) demonstrates that rate constant k_{cp} is increased to more than one and half times with TiO₂ in pulsed discharge plasma process compared with that without TiO₂, from $1.56 \times 10^{-3} \text{ s}^{-1}$ ($R^2 = 0.9969$) without TiO₂ to $2.79 \times 10^{-3} \text{ s}^{-1}$ ($R^2 = 0.9823$) with TiO₂.

On the other hand, Fig. 2(b) illustrates the mineralization of organic pollution 4-CP in the presence of TiO₂ in water. The adsorption of TiO₂ for 4-CP also barely contributes to the TOC removal. The TOC removal of 4-CP solution with TiO₂ is obvious increased by approximately 24%, from 58% without TiO₂ to 82% with TiO₂.

3.2. Higher initial liquid conductivity for 4-CP degradation in the PDP process with/without TiO₂

To evaluate the catalytic effect of TiO₂ for 4-CP degradation under a broad range of experimental conditions, our work was performed at a greater initial liquid conductivity (380–390 μS cm⁻¹), and other experimental conditions were similar to those mentioned above.

The degradation of 4-CP under higher liquid conductivity is shown in Fig. 3(a). The speed of 4-CP degradation under higher liquid conductivity is lower than that under low liquid conductivity, as shown in Fig. 2(a), whether TiO₂ catalyst is present in the PDP process or not. The rate constant (k_{CP}) for 4-CP degra-

ation at 380–390 μS cm⁻¹ without TiO₂ is $1.44 \times 10^{-3} \text{ s}^{-1}$, which is less than $1.56 \times 10^{-3} \text{ s}^{-1}$ for low liquid conductivity (1.5–4.0 μS cm⁻¹). Similarly, the rate constant (k_{cp}) for 4-CP degradation under higher liquid conductivity in the case of with TiO₂ ($2.36 \times 10^{-3} \text{ s}^{-1}$) is lower than that for low liquid conductivity ($2.79 \times 10^{-3} \text{ s}^{-1}$). It was indicated that the high liquid conductivity had adverse effect on the degradation of 4-CP with/without TiO₂, however, TiO₂ catalyst had a promoted effect for rate constant of 4-CP degradation, which was increased by 63.9% compared with the absence of TiO₂.

Fig. 3(b) illustrates that the mineralization extent for 4-CP pollutant under higher liquid conductivity with/without TiO₂. In the case of higher liquid conductivity, the mineralization extent of 4-CP was decreased by approximately 10% compared with the condition of low liquid conductivity, in spite of the addition of TiO₂ or not. However, under higher liquid conductivity TiO₂ catalyst still kept remarkable enhanced effect for 4-CP mineralization, which promoted 22.6% in contrast with the PDP process without TiO₂.

As determined from the above results, the higher liquid conductivity would compensate the space charge electric field on the streamer head to shorten streamer channel length, and decrease the production rate of chemically active species [18]. Thereby the higher liquid conductivity had adverse effect on 4-CP removal, however, it hardly influenced enhanced effect of TiO₂ catalyst for 4-CP degradation.

3.3. Comparison of residual H₂O₂ concentrations in low and high liquid conductivity

Curves of the concentration of hydrogen peroxide over treatment time during 4-CP degradation are displayed in Fig. 4. At low initial liquid conductivity, the residual H₂O₂ concentration

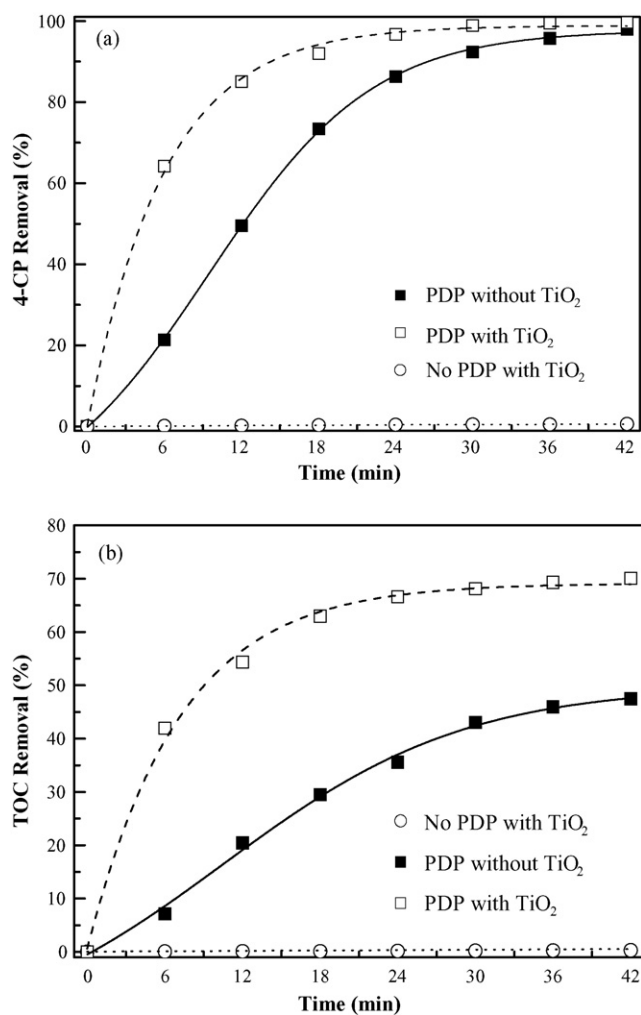


Fig. 3. 4-CP degradation (a) and TOC removal (b) in the PDP process with/without TiO₂ under high liquid conductivity. (Experimental conditions: applied voltage: 14 kV; electrode distance: 2 cm; TiO₂ concentration: 50 mg L⁻¹; O₂ flow rate: 100 L h⁻¹; pH 6.5; liquid conductivity: 380–390 μS cm⁻¹.)

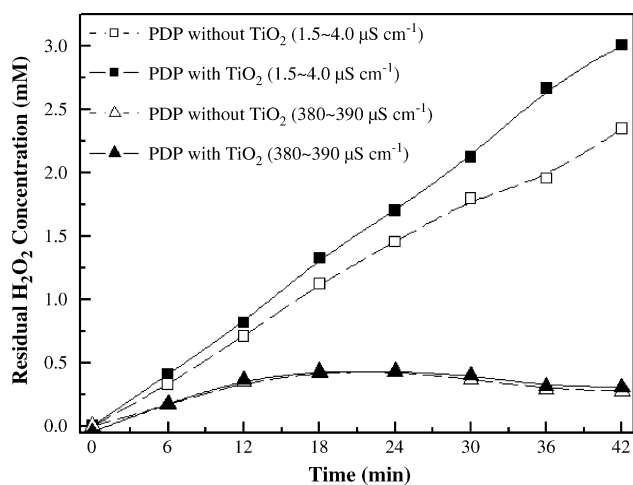


Fig. 4. Hydrogen peroxide formed during the degradation of 4-CP in the PDP process with/without TiO₂ under different liquid conductivities. (Experimental conditions: applied voltage: 14 kV; electrode distance: 2 cm; TiO₂ concentration: 50 mg L⁻¹; O₂ flow rate: 100 L h⁻¹; pH 6.5.)

increases approximately linearly with the elapse of treatment time. Its concentration with TiO₂ is higher than that of without TiO₂, as observed in other work [14], owing to more amount of hydrogen peroxide produced by the photocatalytic effect of TiO₂ catalyst. However, in the case of higher liquid conductivity, the residual H₂O₂ concentration exponentially increases with increasing treatment time in the first 18 min and then drops slowly. The trend of the concentration of hydrogen peroxide present with TiO₂ in the period of 4-CP removal is identical to that of without TiO₂, because more free electron in high intensity of ions at high liquid conductivity can recombine of photo-generated holes (h_{vb}⁺) in the valence band on the surface of TiO₂ particle to weaken the photocatalytic effect of TiO₂. Furthermore, the concentration of residual hydrogen peroxide is evidently greater at low liquid conductivity than that of high liquid conductivity, regardless of the presence of TiO₂ in such a process or not.

3.4. Variation of the primary intermediates under a broad range of liquid conductivity

The primary intermediates were identified by GC/MS (Trace 2000 series), including 4-chloro-1,4-benzoquinone (Cl-BQ), hydroquinone (HQ), 1,4-benzoquinone (BQ) and the small molecule organic acids (formic, acetic and oxalic acid). These primary byproducts were also detected by Knauer-2005 HPLC from their calibration standards. The degradation pathway without TiO₂ was similar to with TiO₂, and the 4-CP was converted to the intermediates, and then the intermediates were mineralized to H₂O, CO₂, including inorganic ions Cl⁻ [20].

To investigate the catalytic effect of TiO₂ on the changes of the concentrations of the primary intermediate products under different initial liquid conductivities, the curves of the primary intermediates, such as Cl-BQ, HQ and BQ, as a function of treatment time under low liquid conductivity are shown in Fig. 5(a), and those for higher liquid conductivity are shown in Fig. 5(b).

In Fig. 4(a), it is found that the concentrations of Cl-BQ, BQ and HQ at the presence of TiO₂ catalyst are lower than those at the absence of TiO₂. Moreover, the disappearance of Cl-BQ with TiO₂ addition is faster than that of BQ or HQ. The peak of the intermediate Cl-BQ at approximately 15 mg L⁻¹ without TiO₂ (or 3 mg L⁻¹ with TiO₂) is higher than that of BQ or HQ (less than 2 mg L⁻¹), because the first-step intermediate product Cl-BQ is generated through hydroxylation by the attack of hydroxyl radicals, which is subsequently converted into BQ and HQ. In our work, it was found that the final pH values of treated solution were close to 3.0, due to the oxidation of these intermediates into large amounts of small-molecule organic acids [21].

Fig. 4(b) illustrates that under higher liquid conductivity, the concentrations of Cl-BQ, BQ and HQ at the presence of TiO₂ catalyst are also lower than those at the absence of TiO₂, except for minor difference of residence time of the peak of BQ. The enhanced effect of TiO₂ for the conversion of Cl-BQ with TiO₂ is greater than that of BQ or HQ. The residence times of the peak of Cl-BQ and HQ are delayed for 6 min from 12 to 18 min, from 18 to 24 min, respectively. In addition, it is found that the

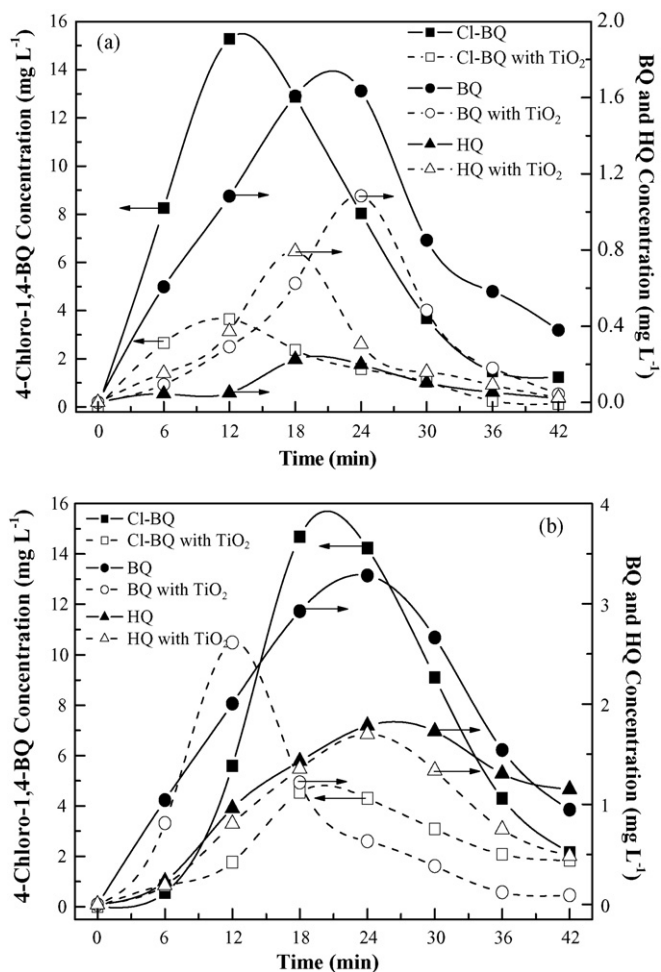


Fig. 5. The concentrations of the primary intermediates in the PDP process with/without TiO₂ under low liquid conductivity (a) and high liquid conductivity (b). (Experimental conditions: applied voltage: 14 KV; electrode distance: 2 cm; TiO₂ concentration: 50 mg L⁻¹; O₂ flow rate: 100 L h⁻¹; pH 6.5.)

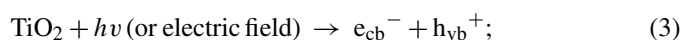
concentrations of these intermediate products kept in lower values under low liquid conductivity than those under higher liquid conductivity.

We summarize the conclusions that the intermediates disappeared faster with TiO₂ than those without TiO₂, and higher liquid conductivity had adverse effect on the conversion of the primary intermediate products. In addition, TiO₂ catalyst well favors the conversion of CI-BQ. This revealed that TiO₂ catalyst in the PDP process obviously demonstrated catalytically enhanced effect.

3.5. Apparent formation rates of chemically active species in the PDP process with/without TiO₂

To investigate the effect of TiO₂ addition in pulsed discharge plasma system on the yields of chemically active species, the apparent formation rates of chemically active species in distilled water without any pollutant were measured. As illustrated in Table 2, $K_{\text{H}_2\text{O}_2}$ is $1.10 \times 10^{-6} \text{ M s}^{-1}$ without TiO₂, which is greatly less than that with TiO₂ ($K_{\text{H}_2\text{O}_2} = 1.50 \times 10^{-6} \text{ M s}^{-1}$).

In the meantime, energy efficiencies for H₂O₂ and O₃ formation were enhanced by the introduction of TiO₂ photocatalyst, from 3.28×10^{-1} to $4.16 \times 10^{-1} \text{ g kWh}^{-1}$ for hydrogen peroxide formation, from 8.19×10^{-3} to $9.05 \times 10^{-3} \text{ g kWh}^{-1}$ for dissolved ozone, respectively. Energy efficiency for dissolved ozone formation (only aqueous-phase ozone) is rather less than that referred in the literature [22], which were overall ozone generation efficiency including in gas-liquid two phases, due to different operational parameters, such as reactor configuration (little solution volume (0.1 L) in our work), electrode types (including electrode material, electrode distance (only 2 cm in our work) and electrode curvature radius) and ozone-transfer (the shorter contact time of gas-discharge generated ozone with aqueous solution, resulting in a large amount of gaseous ozone escaping out through the gas-bubbling channels at a larger gas flow velocity in our work), and the fast ozone destruction reactions, especially hydrogen peroxide present in PDP system via a peroxone process [22,23]. However, under our experimental conditions, TiO₂ catalyst demonstrated the promoted effect for aqueous phase ozone generation efficiency. Additionally, more numerous hydrogen peroxide is formed in the presence of TiO₂ through the following possible reactions [1,13]:



From reaction (4), it indicates a large number of hydroxyl radicals ($\bullet\text{OH}$) produced in the presence of TiO₂ is available to form more hydrogen peroxide in water [1].

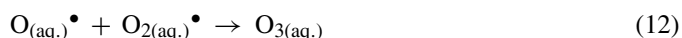
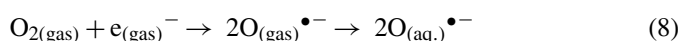
On the other hand, The dissolved ozone in water was measured by UV absorption in several seconds. The dissolved ozone concentration increased linearly with the elapse of treated time, and its concentration in water solution with TiO₂ catalyst was higher than that without TiO₂ catalyst, as observed in our experiments. The apparent formation rate of dissolved ozone with TiO₂ is evidently higher than that without TiO₂ as listed in Table 2. K_{O_3} is $1.99 \times 10^{-8} \text{ M s}^{-1}$ without TiO₂, which is much less than that with TiO₂ ($K_{\text{O}_3} = 2.35 \times 10^{-8} \text{ M s}^{-1}$). When oxygen gas bubbled through the microtubules, the molecular oxygen was transferred into aqueous phase in solution by the effects of over-pressure shock waves and electrohydraulic cavitation. Simultaneously molecular oxygen (O₂) was cleaved into single atomic oxygen radical (O \bullet) by gas phase electrical pulses, and then entered aqueous solution. Oxygen molecule dissolved in aqueous phase was converted to negative oxygen radicals (O_{2(aq.)} \bullet^-) by the effect of highly-energized electrons (e⁻) and photogenerated electrons (e_{cb}⁻) in the conduction band on the surface of TiO₂ particle by UV light illumination from pulsed discharge plasma. Subsequently, negative oxygen radicals (O_(aq.) \bullet^- and O_{2(aq.)} \bullet^-) was transformed into more chemically active species (i.e. O_(aq.) \bullet , O_{2(aq.)} \bullet) by electron acceptor of holes (h_{vb}⁺) in the valence band on the surface of TiO₂ particle, thus results in more amount of ozone production through the following possible reaction path-

Table 2
Apparent formation rates of ozone and hydrogen peroxide in distilled water

Apparent formation rate ($M s^{-1}$)	H_2O_2 ($\times 10^{-6}$)	O_3 ($\times 10^{-8}$)	$G_{50\%}$ ($g kWh^{-1}$)	H_2O_2 ($\times 10^{-1}$)	O_3 ($\times 10^{-3}$)
Without TiO_2	1.10	1.99	Without TiO_2	3.28	8.19
R^2	0.9872	0.9889	–	–	–
With TiO_2	1.50	2.35	With TiO_2	4.16	9.05
R^2	0.9927	0.9850	–	–	–

Experimental conditions: applied voltage: 14 kV; electrode distance: 2 cm; TiO_2 concentration: $50 mg L^{-1}$; O_2 flow rate: $100 L h^{-1}$; pH 6.5; liquid conductivity: $1.50\text{--}4.0 \mu S cm^{-1}$.

ways [13,24,25]:



$e_{(gas)}^-$: highly-energized electron in gas phase and $e_{(aq.)}^-$: highly-energized electron in aqueous phase.

3.6. Comparison of original TiO_2 and used TiO_2 for 4-CP removal

Fig. 6(a) illustrates that TiO_2 repeatedly used thrice (marked as $TiO_{2(used\ thrice)}$) has no negative effect on the 4-CP removal, and the promoting effect of $TiO_{2(used\ thrice)}$ on 4-CP removal is the same as original TiO_2 (marked as $TiO_{2(original)}$). It is revealed that the rigorous ambience conditions in pulsed discharge plasma process hardly influences the physical and chemical properties of TiO_2 . This also is supported by the XRD patterns of $TiO_{2(original)}$ and $TiO_{2(used\ thrice)}$. As shown in Fig. 6(b), the peaks of anatase and rutile phases have not obvious differences between $TiO_{2(original)}$ and $TiO_{2(used\ thrice)}$ in such system.

4. Conclusion

The results of the present work clearly demonstrate that pulsed discharge plasma in combination with TiO_2 catalyst is very effective to generate more amounts of chemically active species (i.e. ozone and hydrogen peroxide), and leads to synergistic removal and higher energy efficiency of organic pollutants in water, and this process have no influence on the crystal structure of TiO_2 , therefore it reminds us to further study on this new promising TiO_2 -aqueous phase pulsed discharge plasma process for the elimination of organic pollutants.

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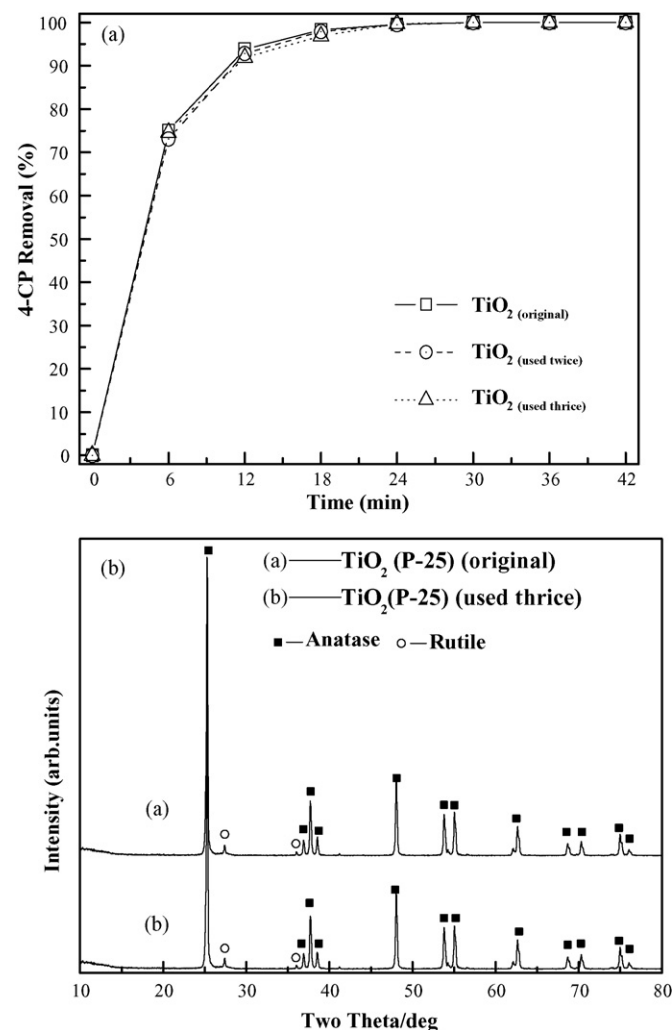


Fig. 6. Comparison of 4-CP removals between original TiO_2 and $TiO_{2(used\ thrice)}$ (a) and XRD patterns of original TiO_2 and $TiO_{2(used\ thrice)}$ (b). (Experimental conditions: applied voltage: 14 kV; electrode distance: 2 cm; TiO_2 concentration: $50 mg L^{-1}$; O_2 flow rate: $100 L h^{-1}$; pH 6.5; liquid conductivity: $1.50\text{--}4.0 \mu S cm^{-1}$.)

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