

Photocatalytic decomposition of 2-chlorophenol in aqueous solution by UV/TiO₂ process with applied external bias voltage

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Abstract

The decomposition of 2-chlorophenol by UV/TiO₂ process with the application of external bias voltage was examined in this study. Experiments were conducted in a batch reactor using TiO₂-coated titanium sheet as anode and platinum sheet as cathode. The anode photocatalysis of 2-chlorophenol was totally inhibited for experiments conducted with the application of external anodic bias voltage lower than the flat band potential of TiO₂. The decomposition rate of 2-chlorophenol was then increased with increasing external anodic bias voltage applied up to 0.0 V (versus SCE). The application of external bias voltage higher than 1.0 V did not markedly promote the photocatalysis of 2-chlorophenol possibly because the photocurrent induced was constant. Experimental results indicated that the decomposition of 2-chlorophenol was more effective for experiments conducted in acidic solutions due to the lower flat band potential of TiO₂ and the higher photocurrent induced. The presence of electron scavengers in aqueous solution, such as oxygen molecules, may increase the decomposition rate of 2-chlorophenol. However, the effect of dissolved oxygen was diminished for experiments conducted with applied external bias voltage. The photocatalytic decomposition rate of 2-chlorophenol was enhanced linearly with the increasing UV light intensity when the external bias voltage was applied.

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1. Introduction

Halogenated aromatics resulted from the improper discharge of industrial wastewater and the chlorination of naturally occurring aromatic matters during water purification are environmentally important pollutants because of their toxicity and possible accumulation in the environment [1]. Growing concerns on the contamination of organic pollutants to drinking water supplies and the aquatic environment has stimulated vigorous research activity on the development of various treatment technologies. Photocatalytic processes using semiconductor catalysts under appropriate illumination regarding water and wastewater treatment have attracted extensive attention [2]. TiO₂ in the anatase form is a promising photocatalyst because of its high chemical and photoelectrochemical durability, appropriate band-gap (~3.0 eV) to adsorb UV-A light at 365 nm and comparative cheapness. The photocatalytic properties of titanium

dioxide particles have been investigated extensively in slurry and immobilized-film reactors [3,4].

The recombination of photogenerated electrons and holes is often a seriously factor limiting the photocatalytic efficiency and obstructs the practical application of the photocatalytic process in the environmental areas [2]. Several endeavours have been made to modify titanium dioxide and increase the photocatalytic efficiency, such as ion doping [5], noble metal deposition [6,7], coupled photocatalysts [8] and the application of external bias voltage [9–14]. The application of external bias voltage to photocatalytic process (called electrochemically assisted photocatalytic process or photoelectrocatalytic process), the photocatalyst acts as photoanode and an external anodic bias is applied to drive the photogenerated electrons and holes in opposing directions so that the charge recombination is retarded.

The photoelectrocatalytic degradation rate of 4-chlorocatechol in aqueous solution using TiO₂ electrode operated at a constant current density was a function of 4-chlorocatechol concentration and solution pH. The initial degradation rates of 4-chlorocatechol exhibit a linear correlation with the concentration of 4-chlorocatechol. Both the highest photodegradation

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rate and the peak photocurrent were obtained for experiments conducted at pH 8 [15]. TiO_2 electrodes prepared by the electrophoretic immobilization of TiO_2 power on titanium alloy were used to investigate the photoelectrocatalytic oxidation of oxalate. Increases in the anodic photocurrent and the rate of oxalate degradation were observed with the presence of Fe^{3+} ion in the cathode compartment served as the electron acceptor [9]. The greatest performance of photoelectrocatalytic oxidation of rose Bengal in aqueous solution was achieved for experiments conducted with the TiO_2/Ti mesh electrode and the application of an electrical bias of 0.6 V [11]. Study on the photocatalytic degradation of aniline using TiO_2/Ni porous catalysts indicated that the external potential bias can noticeably improve the degradation efficiency of aniline [10]. The photocatalytic oxidation rate of nitrite ion in NaCl aqueous solutions using TiO_2/Ti as the working electrode was promoted by increasing solution pH, UV light intensity and bias potential; however, the oxidation rate was independent of nitrite ion concentration [13].

In this particular study, the primary research interests were in the effects of several operational factors, including solution pH, dissolved oxygen and UV intensity, on the photocatalytic reaction of 2-chlorophenol in aqueous solutions by UV/ TiO_2 process with applied external bias voltage was studied. The reaction rates and kinetic models were established based on the experimental results to understand the decomposition behaviour of 2-chlorophenol by photoelectrocatalytic process.

2. Experimental

The schematic diagram of experimental system employed in this research is shown in Fig. 1. The photoreactor used in this study consisted of a cylindrical reactor of 9.5 cm internal diameter and 30 cm long made entirely of Pyrex glass with an effective volume of 3 l. The cylindrical reactor contained a 5 cm diameter quartz tube to house a GTE F15T8/BLB lamp with approximately 15 W maximum output at about 365 nm. The output of the UV lamp was adjusted by a variable voltage transformer

and was detected by a Spectroline model DRC-100× digital radiometer combined with a DIX-365 radiation sensor. A magnetic stirrer was located at the bottom of the photoreactor.

Degussa P-25 TiO_2 power was employed in this study as received without further treatment. The TiO_2 particles were approximately spherical and non-porous with greater than 99.5% purity; the composition was reported to contain about 80% anatase and 20% of rutile. The anode was prepared by impregnating pieces of pre-cleaned titanium sheets in aqueous solution containing TiO_2 particles for about 10 min before it was heated in an oven for 2 h. The temperature of the oven was controlled to be 500 or 700 °C in order to obtain the desired morphological forms of TiO_2 (500 °C for anatase/700 °C for rutile determined by a Philips MP710 X-ray diffractometer). The titanium sheet was used as support for TiO_2 particles because of its good adhesion with TiO_2 and its resistance to corrosion. The impregnation process could be repeated for several times to increase the amount of TiO_2 coated on the sheets. The TiO_2/Ti anode was then fixed in the photoelectrochemical reactor. The anode was a platinum sheet of 1 cm × 4 cm and the reference electrode was a saturated calomel electrode (SCE). The applied external bias voltage was supplied by an EG & G Model 273A galvanostat/potentiostat.

Predetermined amount of experimental solution containing known concentrations of 2-chlorophenol and NaClO_4 (served as electrolyte) was taken into the photoelectrocatalytic reactor and then aerated continuously with various type of gases (O_2 , air or N_2) during the course of the reaction. Solution pH value was kept at desired levels, ranging from pH 3.0 to 9.0, by the additions of sodium hydroxide (NaOH) and/or sulfuric acid (H_2SO_4) solutions using an automatic potentiometric titrator (Kyoto Electronic AT-200). The solution temperature was maintained by a thermostat circulator and all experiments were conducted isothermally at 25 °C. A dissolved oxygen detector (Orion Model 810) was used to measure the dissolved oxygen concentration in the solution. The operating time required for the photoelectrochemical reactor system to establish the dissolved gas equilibrium in the bubbling of various gases was usually

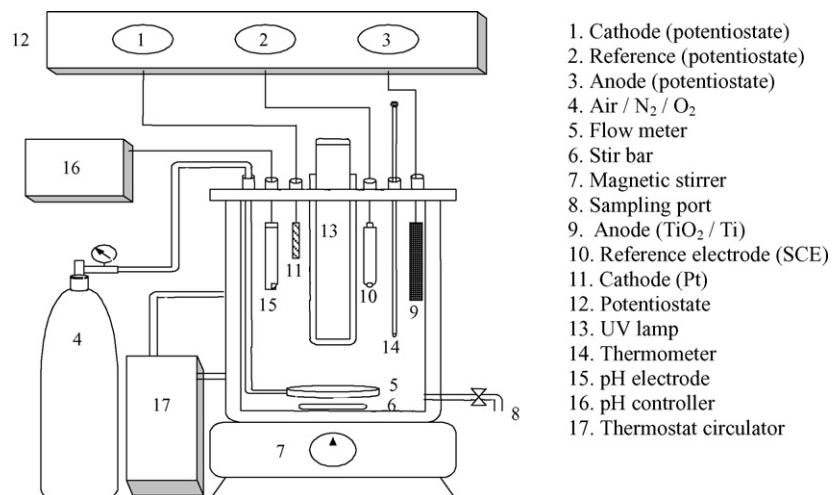


Fig. 1. Schematic of reactor set-up.

about 30 min. For experiments conducted under different conditions, aliquots of 10 ml solution were sampled at predetermined time intervals from the reactor for further analyses. The total sample volume throughout an experiment was kept below 5% of the initial volume of solution. Concentration of 2-chlorophenol in the sample solution was measured with a Spectra System HPLC equipped with an Inerstil ODS-3 5 μm column and a Spectra System UV1000 detector. The chloride ion and TOC were determined by a Dionex DX-100 ionic chromatograph and an OIC Model 700 analyzer, respectively.

3. Result and discussion

There was no indication of 2-chlorophenol electrolysis occurred for background experiments conducted with applied bias voltage between 0.0 and 3.0 V, which implied that the amount of electrons flow through the external circuits was the same for experiments conducted within the applied bias voltage range. The comparisons of 2-chlorophenol decomposition for experiments conducted with anatase and rutile catalysts are depicted in Fig. 2. The 2-chlorophenol decompositions were always superior for experiments using anatase than those using rutile, which was more evident with applied external bias potential for experiments using anatase. Other reporter also indicated that anatase appears to be the more active and be probably due to differences in the extent and nature of the surface hydroxyl groups present in the low temperature anatase structure [16].

Comparing photocatalytic with photoelectrocatalytic reactions, the charge recombination was inhibited under photoelectrocatalytic condition. More holes were available on the TiO_2 particle for 2-chlorophenol decomposition under photoelectrocatalytic condition than that under photocatalytic condition. For

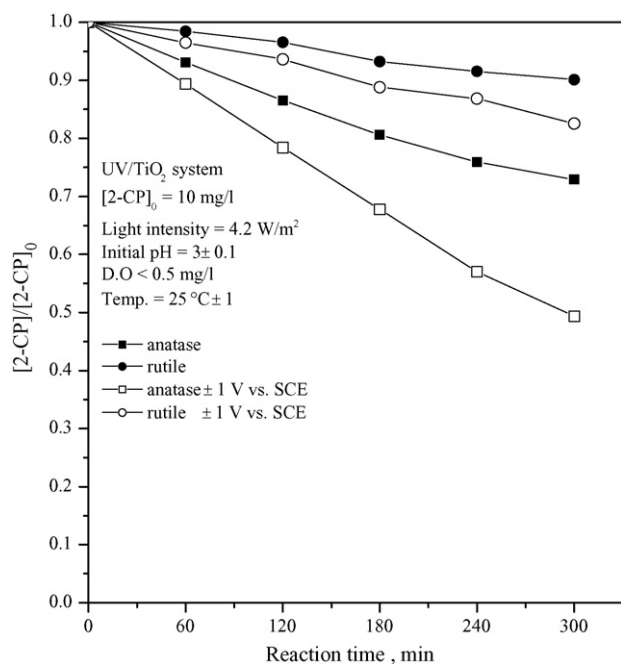


Fig. 2. Decomposition of 2-chlorophenol in aqueous solution by UV/TiO₂ process with and without 1 V applied external bias voltage and various crystal forms of TiO₂.

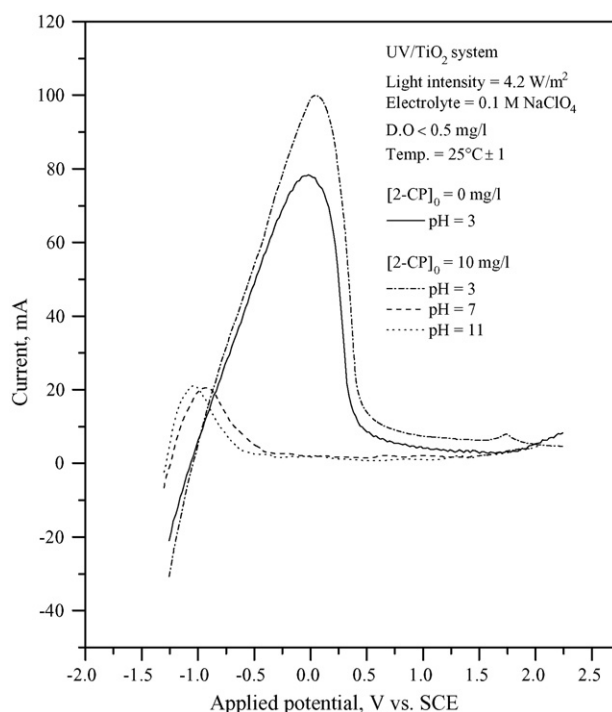


Fig. 3. Photocurrent as a function of applied external bias voltage by UV/TiO₂ process after addition of 2-chlorophenol and photocurrent at various solutions pH.

photoelectrocatalytic reactions, the reaction threshold is controlled by the flat-band potential of the photocatalyst used. Fig. 3 shows the induced photocurrent for the UV/TiO₂ process in aqueous solution as a function of applied external bias voltage with and without the addition of 2-chlorophenol. For both cases, the applying external bias voltage at zero photocurrent was about -1 V (versus SCE), implied that the flat-band potential for the UV/TiO₂ process was approximately -1 V. These results suggest that an external bias potential greater than -1 V is sufficient to provide enough driving force to withdraw electrons to the counter-electrode. Also as shown in Fig. 3, the photocurrent induced was peaked for experiments conducted at applied bias potential of about 0 V.

Results of the photoelectrocatalytic decomposition of 2-chlorophenol in aqueous solution for experiments conducted with various applied external bias voltages are shown in Fig. 4. The decomposition of 2-chlorophenol was determined to be only about 8% for experiments conducted with external bias voltage of -1.5 V, because the reverse bias voltage suppressed the separation of electrons and holes at the TiO₂/Ti anode. 2-Chlorophenol decompositions were increased with increasing applied external bias voltage for experiments conducted with an external bias voltage greater than -1.5 V. However, the decomposition rate of 2-chlorophenol was almost same for experiments conducted with an external bias voltage greater than 1 V. These results suggest that the application of -1.0 V potential is enough to withdraw the flow of electrons to the counter electrode, which also agrees with that flat-band potential of TiO₂ determined in this experiment (approximately -1.0 V as showed in Fig. 3). Also as shown in Fig. 4, about 27% of 2-chlorophenol was

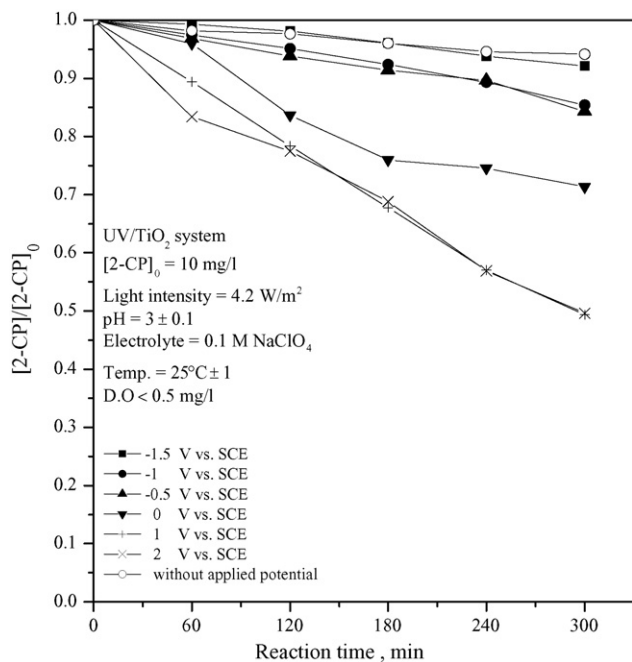


Fig. 4. Decomposition of 2-chlorophenol in aqueous solution by UV/TiO₂ process with various applied external bias voltages.

decomposed after 5 h of operating time for experiment conducted with 0 V applied bias potential. Similar experimental results of the photoelectrocatalytic degradation of formic acid and nitrite using TiO₂ electrode indicated that the application of bias potentials significantly promoted the reaction rates. However, a limiting bias potential existed [13,17]. Similar to the decomposition of 2-chlorophenol shown in Fig. 4, the formation of chloride ions and the decomposition of total organic carbon (TOC) illustrated in Fig. 5 were also increased with increasing applied external bias voltage for experiments conducted with an external bias voltage greater than -1.5 V.

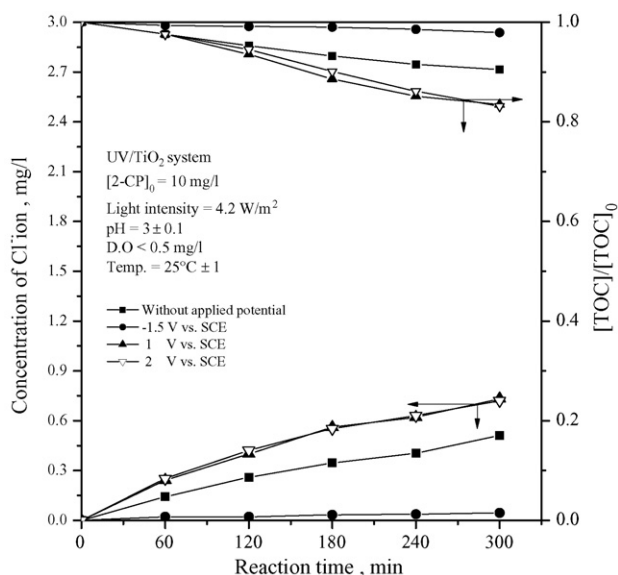


Fig. 5. Cl⁻ ion generation and TOC decomposition in aqueous solution by UV/TiO₂ process with various applied external bias voltages at pH 3.

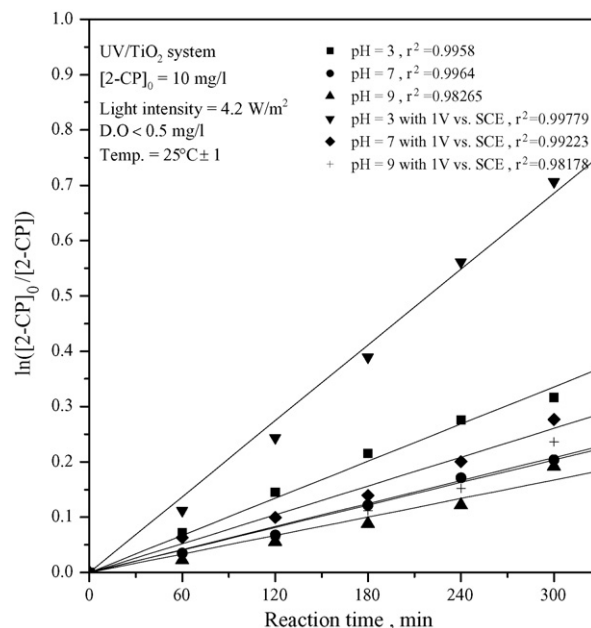


Fig. 6. Determination of global pseudo first-order rate constant of 2-chlorophenol with and without applied external bias voltage by UV/TiO₂ Process at various solutions pH.

Fig. 6 and Table 1 illustrate the global pseudo first-order rate constants for 2-chlorophenol decomposition by UV/TiO₂ process with and without applied external bias voltage for experiments conducted in aqueous solutions of various pH levels under N₂ atmosphere. The global pseudo first-order rate constant is defined as the lump-sum rate constant with respect to the concentration of 2-chlorophenol regardless of other factors affecting reaction kinetics, such as light intensity, TiO₂ dosage, etc. The experimental results of the pH effect revealed that the residual 2-chlorophenol concentrations varied substantially throughout the solution pH range studied. Higher decomposition rates were obtained for experiments conducted in aqueous solutions of pH 3, the decomposition of 2-chlorophenol decreased for higher pH conditions. Fig. 3 reveals that higher photocurrents were induced for experiments conducted in acidic solutions of various pH levels under various applied bias potentials. The flat-band potentials of TiO₂ electrode shifted to more negative for experiments conducted in neutral and alkaline solutions. On the contrary, Barakat et al. [18] observed the photocatalytic decomposition rates of

Table 1

Pseudo first-order decomposition rate constant of 2-chlorophenol with and without applied external bias voltage by UV/TiO₂ Process at various solutions pH

	Solution pH value		
	3	7	9
Without applied external bias voltage	0.00112	6.78 × 10 ⁻⁴	5.57 × 10 ⁻⁴
With applied external bias voltage 1 V vs. SCE	0.00229	8.68 × 10 ⁻⁴	6.92 × 10 ⁻⁴

The initial concentration of 2-chlorophenol was 10 mg/l and the light intensity was 4.2 W/m². The unit of the pseudo first-order decomposition rate constant was min⁻¹.

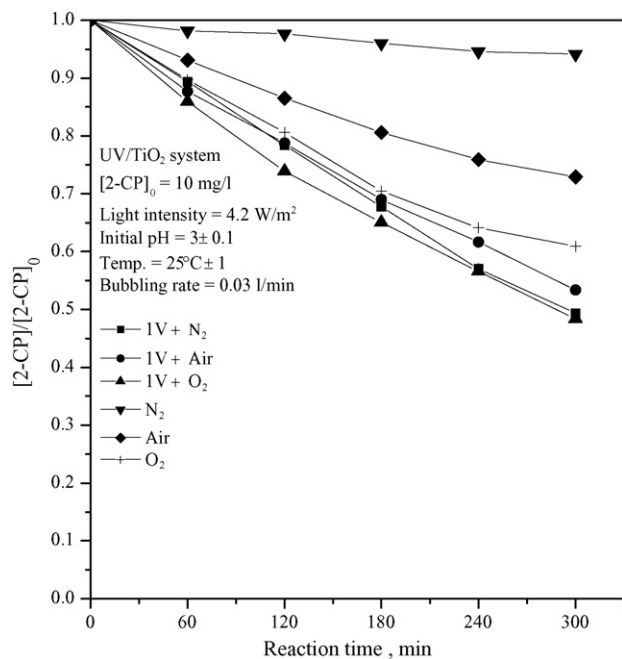


Fig. 7. Decomposition of 2-chlorophenol in aqueous solution by UV/TiO₂ process with 1 V applied external bias voltage and various gas atmospheres.

2-chlorophenol increased with increase of the pH when the pH decreased during the photocatalytic decomposition runs and was adjusted by using 0.1 M NaOH. Tseng and Huang [19] observed the photocatalytic decomposition rates of 2-chlorophenol were independent of initial pH with no attempt was made to maintain pH constant during the course of experiment by any buffer.

For experiments conducted without applied external bias voltage, the decomposition rate of 2-chlorophenol at pH 3 was found to be increased with the presence of dissolved oxygen, as illustrated in Fig. 7 and Table 2. The decomposition of 2-chlorophenol was faster for experiments conducted with oxygen bubbling than nitrogen bubbling. The decomposition of 2-chlorophenol was close to 40% in high dissolved oxygen 37.2 mg/l (oxygen bubbling through the solution) with no applied external bias voltage. It is clear that oxygen molecules dissolved in aqueous solution scavenged the conduction band electrons on TiO₂ particles and promoted the decomposition reaction. Nevertheless, the photoelectrocatalytic decomposition

Table 2

Pseudo first-order decomposition rate constant of 2-chlorophenol by UV/TiO₂ process with and without applied external bias voltage and various gas purging

	Dissolved oxygen (mg/l)		
	N ₂ purging <0.5	Air purging 8.3	O ₂ purging 37.2
Without applied external bias voltage	0.00022	0.00112	0.00177
With applied external bias voltage 1 V vs. SCE	0.00229	0.00206	0.00241

The initial concentration of 2-chlorophenol was 10 mg/l and the light intensity was 4.2 W/m². The unit of the pseudo first-order decomposition rate constant was min⁻¹.

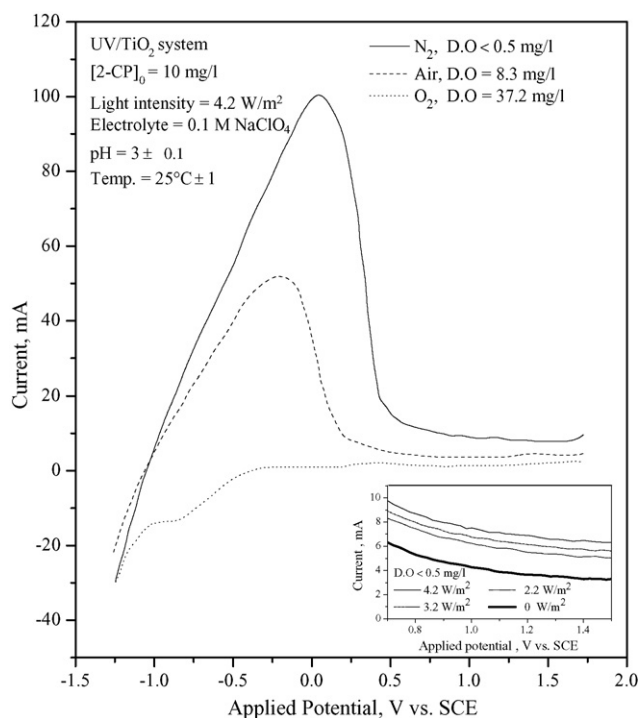


Fig. 8. Photocurrent as a function of applied external bias voltage by UV/TiO₂ Process at various gas atmospheres (inset: photocurrent under various light intensities at D.O. < 0.5 mg/l).

of 2-chlorophenol at pH 3 was not noticeably affected by the presence of dissolved oxygen for experiments conducted with applied external bias voltage of 1 V because both the external bias voltage and dissolved oxygen molecules might act as acceptors for electrons for a photoelectrocatalytic reaction. About 50% of 2-chlorophenol was decomposed for experiments conducted even with the presence of low dissolved oxygen 0.5 mg/l (nitrogen bubbling through the solution) with applied external bias voltage of 1 V. Similar results on the photoelectrocatalytic degradation of formic acid using a porous TiO₂ thin-film electrode were observed [17]. However, another experimental result indicated that the presence of dissolving oxygen imposed an adverse effect on the decomposition of oxalate on electrodes prepared by the electrophoretic immobilization of Degussa P25 TiO₂ power on titanium alloy [9]. Fig. 8 reveals the photocurrent induced under various applied bias potentials for experiments conducted in aqueous solutions of pH 3 with different dissolved oxygen levels. The photocurrent was significantly decreased with increasing dissolved oxygen levels indicating the competition for electrons by both dissolving oxygen molecules and applied external bias potential. Considering that the flat-band shifted positively, the reaction threshold in the presence of dissolved oxygen was higher than dissolved nitrogen or air. Dissolved oxygen acted as electrons acceptor to generate super oxide ions and hydrogen oxide free radicals to promote the photoelectrocatalytic reaction. Furthermore, hydrogen oxide free radicals generated around anode with an external bias were tough on backward reaction to oxygen.

The decomposition of 2-chlorophenol and the induced photocurrent for experiments conducted at pH 3 was found to be

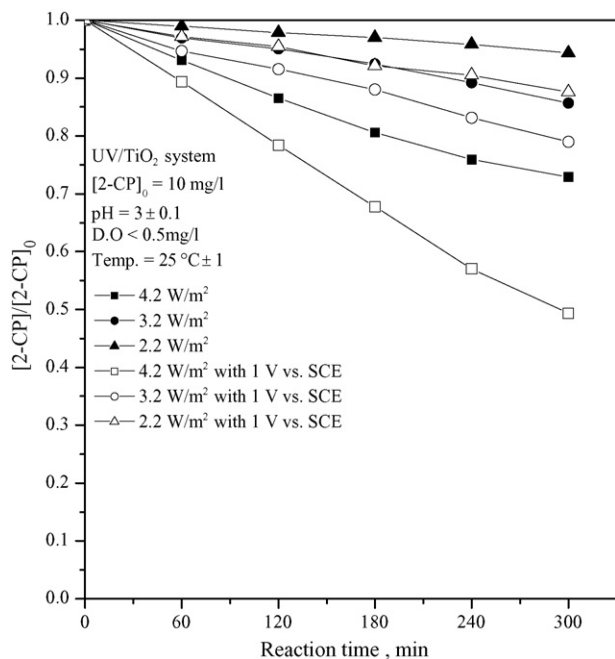


Fig. 9. Decomposition of 2-chlorophenol in aqueous solution by UV/TiO₂ process with and without 1 V applied external bias voltage and under various light intensities.

increased with applied light intensity, as illustrated in Fig. 9 and the inset of Fig. 8, respectively. These results are in agreement with the observations reported by several researchers. The experimental results of the photocatalytic decomposition of gaseous toluene with TiO₂ coated-alumina reticulate indicated that the oxidation rate dependence on UV intensity followed a power law with an exponent of 0.55 ± 0.03 [20]. Study on the photocatalytic decomposition of 2- and 3-chlorophenol in titanium dioxide aqueous suspensions noticed that reaction rate increased linearly with UV intensity for experiments conducted with light intensity less than 200 W/m², whereas the reaction rate increased linearly with square root of UV intensity for experiments conducted with light intensity greater than 200 W/m² [21].

4. Conclusion

For the application of photoelectrocatalytic reactions, the flat-band potential of catalyst used must be considered. With applied external bias voltage greater than the flat-band potential of TiO₂, the decomposition of 2-chlorophenol in aqueous solution by UV/TiO₂ process was demonstrated to be effectively promoted in this study. The optimum decomposition rate constant of 2-chlorophenol by UV/TiO₂ process is 0.00241 min^{-1} with 1 V versus SCE applied external bias voltage and O₂ gas purging at pH 3 with 4.2 W/m² light intensity. Experimental results also revealed that the decomposition rate of 2-chlorophenol was elevated with greater induced photocurrents. Dissolved oxygen molecules in aqueous solution played as electron capturer to improve the separation of electron-hole pairs and 2-chlorophenol decomposition. However, the decomposition of 2-chlorophenol was not obviously improved with the presence of dissolved oxygen molecules for experiments conducted with

applied external bias potential because of the competition for electrons between the dissolving oxygen molecules and applied external bias potential.

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