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Evaluation of bias potential enhanced photocatalytic degradation of 4-chlorophenol with TiO_2 nanotube fabricated by anodic oxidation method

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ABSTRACT

TiO_2 nanotube was fabricated using anodic oxidation method. The samples were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET). The obtained TiO_2 nanotube exhibited increased photoelectrocatalytic (PEC) activities compared to TiO_2 film for 4-chlorophenol (4-CP) degradation in aqueous solution. Comparing with electrochemical process (EP), direct photolysis (DP) and photocatalytic (PC), a significant PEC synergetic effect was observed. The factors influencing the degradation of 4-CP by the PEC process including bias potential, pH, initial concentration of 4-CP, UV light intensity and electrolyte concentration were examined. The results revealed that the bias potential played an important role in the degradation of 4-CP and the most efficient degradation of 4-CP was achieved in highly acidic and alkaline medium. Initial concentration of 4-CP was also a significant factor affecting the degradation of 4-CP. Moreover, the degradation rate increased with both UV light intensity and electrolyte concentration increasing.

1. Introduction

4-Chlorophenol (4-CP) is an important organic chemical for environmental studies because of its widespread application in the natural chlorination of organic material or the large-scale disinfection of drinking water [1–6]. It can accumulate in living organisms and result in negative effects including carcinogenicity and acute toxicity. Degradation of this important problematic environmental contaminant has been studied extensively by a wide variety of methods, including biological treatment, chlorination and adsorption. However, the biological treatment usually requires considerably long treatment period and leads to unacceptable level in the final effluent [7–9]. Chlorination poses another problem since it often generates carcinogenic by re-products. Activated carbon adsorption is the other commercialized process but the spent carbon needs to be disposed safely [10]. Therefore, it has been necessary to develop more effective process for the destruction of such contaminants.

Semiconductor mediated photocatalytic (PC) oxidation as one of the advanced oxidation technologies has been accepted as a promising alternative to the conventional methods because most of the pollutants can be completely mineralized to carbon dioxide with suitable catalysts in the presence of UV light illumination [11,12]. Among the semiconductors employed, TiO_2 is proved to be a good photocatalyst because of its high photosensitivity, non-toxicity, strong oxidizing power and long-term stability [13–16]. Recently, many researchers attracted wide attention in TiO_2 nanotube structure [17–20]. It is because that comparing with various nanostructure of titania, TiO_2 nanotube has higher specific surface area. It can improve the efficiency of PC treatment of chlorophenol. However, the recombination of photo-generated electrons and holes is often a seriously factor limiting the PC efficiency and obstructs the practical application of the PC process in the environmental areas [21]. The application of external bias potential [22–27] has been made to increase the PC efficiency which is called electrochemically assisted photocatalytic or photoelectrocatalytic (PEC) process. The photocatalyst acts as photoanode and an external anodic bias is applied to drive the photo-generated electrons and holes in opposing directions so that the charge recombination is retarded.

Xie [28] fabricated TiO_2/Ti nanotube electrode by galvanostatic–potentiostatic anodization process and found that 2,2-bis(4-hydroxyphenyl) propane (BPA) degradation efficiency was evidently improved in either PC or PEC by using nanotubular TiO_2/Ti electrode instead of TiO_2/Ti film electrode. Yang et al. [29] reported that the PEC degradation of pentachlorophenol using a

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rutile nanotube-like TiO_2/Ti film electrode was higher than those of the rutile TiO_2/Ti film electrode. Moreover, the effects of various operating factors such as bias potential, the initial concentrations of organic pollutants, pH, electrolyte concentration and UV light intensity had been investigated [30–32], but the improvement of degradation efficiency is still worthy of particular attention for practical applications.

In this work, therefore, we focused on the PEC degradation of 4-CP with TiO_2 nanotube electrode fabricated in anodic oxidation method. A comparison was made between the as-prepared TiO_2 nanotube and TiO_2 film under identical conditions. Different degradation processes of 4-CP were also studied. Meantime, effects of several factors, including bias potential, solution pH, the initial concentration of organic pollution, electrolyte concentration and UV light intensity, was investigated on the PEC reaction of 4-CP in aqueous solutions by TiO_2 nanotube electrode.

2. Experimental

2.1. Fabrication of TiO_2 nanotube

Titanium (Ti) sheet (purity 99.6%, thickness 1.0 mm) was obtained from Beijing Academy of Steel Service, China. All the other chemicals were of analytical grade and were used as received without further purification.

Prior to any electrochemical treatment, the titanium foil was first mechanically polished with different abrasive papers (400#, 600#, 800#, 1000#, 1500#, 2000#) and cleaned in an ultrasonic bath containing cold distilled water for 20 min, then chemically etched in strong acidic mixture solution of HF and HNO_3 ($HF/HNO_3/H_2O = 1:4:5$ v/v/v) for 30 s to form a fresh smooth surface. The last step of pretreatment was rinsing with acetone and deionized water. The substrate was then dried in air at room temperature.

Electrochemical experiments were carried out at room temperature using a DC power source. The pretreated Ti foil served as anode and Pt foil as cathode in the anodic oxidation experimental set-up. The distance between Ti foil and Pt foil is fixed at 2 cm. The electrolyte was 1 M $(NH_4)_2SO_4$ with the addition of small amounts of 0.1 M NH_4F and continuously stirred using a magnetic stirrer. Initially the potential of the Ti sample was ramped from 0 to 20 V at a rate of $0.1\ V\,s^{-1}$. During this potential ramp, the current increased. When the potential maintained constant, the current decreased initially and started to increase again. After some time it reached a steady state value. Anodization was continued typically for 4 h after reaching a steady state value. Finally, it was calcinated at 500 °C for 1 h with a heating/cooling rate of $2\,^{\circ}C\,min^{-1}$ and annealed to room temperature.

2.2. Characterization of TiO_2 nanotube

The morphological of TiO_2 nanotube-arrays was characterized using environmental scanning electron microscopy (ESEM, FEI QUANTA 200 FEG, Holand FEI Company) operating an accelerating voltage of 30 kV. The crystalline structure of TiO_2 nanotube was determined by X-ray diffraction (XRD, RIGAKU, Dmax22000) using a diffractometer with Cu Kα radiation over the 2θ range of 20–80°. The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. The nitrogen adsorption–desorption isotherms were measured at 77 K on a SA3100 surface area and pore size analyzer. Samples were degassed in a vacuum at 200 °C for 3 h prior to each measurement. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas S_{BET}.

2.3. Photoelectrocatalytic reactor system

The PEC of 4-CP degradation experiment was performed in a columned quartz glass reactor. It was made up of a TiO_2 nanotube electrode as photoanode, a Pt foil electrode as cathode, a 200 W high-pressure mercury lamp with a maximum wavelength of 365 nm, and a potentiostat (DJS-292) to supply bias potential. The lamp was positioned vertically in a double-welled U-tube outside the reactor surrounded by circulating water to decrease the heating effect of the lamp. The anode and cathode were placed in parallel and a saturated calomel electrode (SCE) served as the reference electrode. Solution pH was varied by using sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH). The experiment was carried out at different bias potential, initial concentration of 4-CP, initial solution pH, UV light intensity and electrolyte concentration.

2.4. Analytical methods

Concentration of 4-CP was quantified with an Agilent 1100 HPLC (Shanghai Agilent Ltd.) equipped with a C^{18} column and an L-4000 UV–vis detector. The mobile phase for 4-CP consisted of 55% methanol and 45% water distilled three times. The flow rate was 1 mL/min and the detector wavelength was 280 nm for 4-CP. UV–vis recording spectrophotometer (UV 1100) was also used to measure the absorbance of 4-CP before and after reaction.

Total organic carbon analyzer (TOC-V_{CPH}, Shimadzu, Japan) was employed for mineralization degree of the 4-CP solutions. Prior to injection into the TOC analyzer, 10–15 mL were collected from the aqueous solutions and filtered with a 0.45 μm Millipore filter to remove any particles. The concentration of chloride ions was measured by ionic chromatography (Dx-120, Dionex) with an ASA4-SC column, the mobile phase of a mixture of 1.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ was used at a flow rate of 1.30 mL/min and volume of samples was 25 μL.

3. Results and discussion

3.1. Characterization of TiO_2 nanotube

The sizes of nanotube were measured by the SEM micrographs. The SEM image of the TiO_2 nanotube is illustrated in Fig. 1. It can be seen that the nanotube array is more uniform and well-oriented

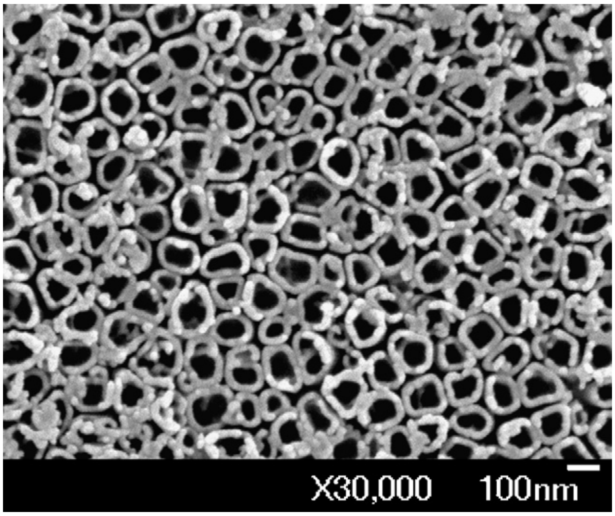

Fig. 1. SEM image of TiO_2 nanotube.

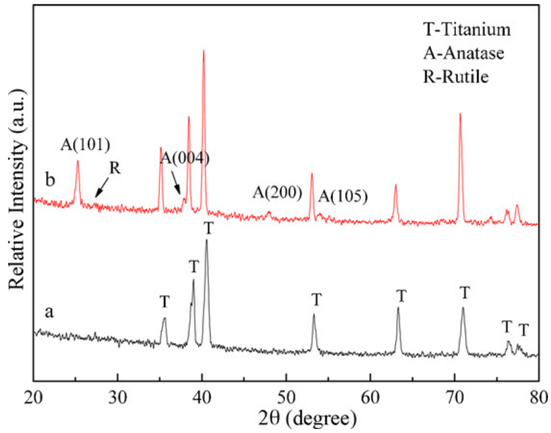

Fig. 2. X-ray diffraction patterns of TiO_2 nanotube: (a) without calcination; (b) after calcination at 773 K for 1 h.

over the substrate. The diameters of these nanotubes range from 60 to 100 nm. The BET specific surface area of the TiO_2 nanotube was 285 $m^2\,g^{-1}$. This value is much higher than TiO_2 particulate films of ~50 $m^2\,g^{-1}$. It shows that TiO_2 nanotubes have larger surface area than other structure of TiO_2 materials, which provide larger contact area and infer higher PEC degradation efficiency.

The crystal behavior of anodized TiO_2 nanotube is characterized by XRD measurement as shown in Fig. 2. Obviously there are only peaks of Ti substrate in existence before calcinations. So an amorphous phase is dominant. After calcined at 500 °C for 1 h, it show the anatase peaks at $2\theta = 25.2°$, 38°, 48°, 54° and a small fraction of rutile at $2\theta = 27°$. Many studies have demonstrated that the mixture of anatase and rutile TiO_2 have greater degradation efficiency than either anatase or rutile TiO_2 alone. So the TiO_2 nanotube fabricated in this paper can improve the PEC degradation efficiency.

3.2. Comparison of different electrode for 4-chlorophenol degradation

In order to compare the PEC capability of the TiO_2 nanotube and TiO_2 film, TiO_2 film was fabricated using sol–gel method [33], and then calcined at 500 °C for 1 h. It was easily seen from Fig. 3 that the TiO_2 nanotube and TiO_2 film exhibited different PEC activity. The degradation of 4-CP on TiO_2 nanotube is faster than that on TiO_2 film. The enhancement was attributed partly to the larger special surface area of the nanotube structure, and partly to unknown factors.

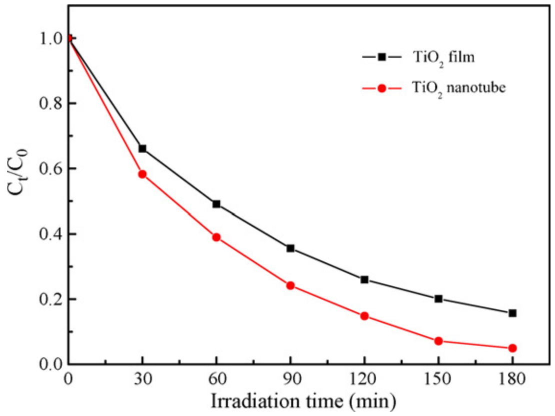

Fig. 3. Comparison of 4-CP degradation using two different electrodes (the initial concentration of 4-CP 20 ppm, bias potential 0.6 V, concentration of Na_2SO_4 0.1 M, and UV light intensity 2.5 mW/cm^2).

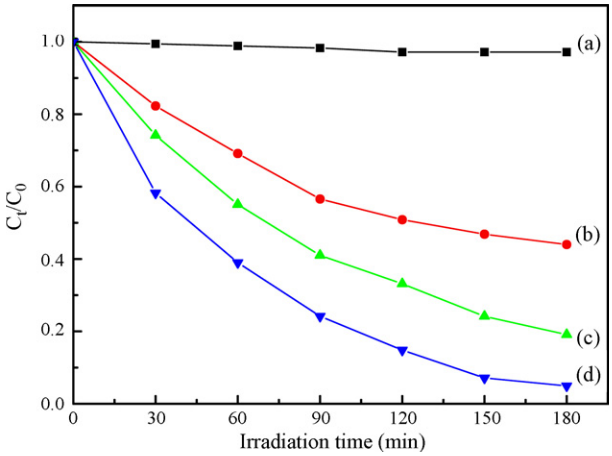

Fig. 4. Degradation of 4-CP using different process (initial concentration = 20 mg/L, applied bias potential = 0.6 V, light intensity = 2.5 mW/cm^2): (a) electrochemical (EC); (b) direct photolysis (DP); (c) photocatalysis (PC); (d) photoelectrocatalysis (PEC).

3.3. Comparison of different process for 4-chlorophenol degradation

Experiments on electrochemical (EC), direct photolysis (DP), photocatalysis (PC) and photoelectrocatalysis (PEC) degradation of 4-CP were carried out in order to compare 4-CP degradation efficiencies among four individual processes. The variation of relative concentration of 4-CP (C_t/C_0) as a function of reaction time was shown in Fig. 4. Almost no 4-CP removal was observed in the EC process under 0.6 V (vs. SCE) bias potential. Direct UV irradiation degraded 56% of the 4-CP in 3 h. Compared to direct photolysis, the TiO_2 nanotube electrode (without bias potential) degraded 80.7% of 4-CP during the same time. Clearly, the degradation rate of 4-CP was the largest under PEC process with the same bias potential and UV light intensity. It is well recognized that the PEC degradation of organic pollutants follows pseudo-first-order kinetics [34]. Herein, pseudo-first-order kinetics was also confirmed in the four processes by the linear transform of $\ln(4 - CP_0/4 - CP_t) = K_t$ (K is the kinetic constant). As shown in Table 1, the pseudo-first kinetic constant of 4-CP for PEC process is larger than the sum of the EC and PC processes individually. Thus, it is reasonable to conclude that a sort of synergetic effect occurs during the PEC degradation of 4-CP.

The UV–vis spectral changes of 20 mg/L 4-CP as a function of irradiation time during the course of PEC degradation were shown in Fig. 5. With the increase in irradiation time, the specific adsorption peaks of 4-CP at 225 and 280 nm disappeared within 3 h. The disappearance of the specific features agrees with the change of the solution color. The color of the solution changed from colorless to yellowish within 3 min during the PEC process, and then changed to colorless after 3 h. This result indicated that the 4-CP was completely dechlorinated.

Table 1
Pseudo-first-order rates of 4-CP degradation under different process

Method	k (min^{-1})	R^2
Electrochemical	0.0002	0.9286
Direct photolysis	0.0052	0.9614
Photocatalysis	0.0094	0.9981
Photoelectrocatalysis	0.0167	0.9948

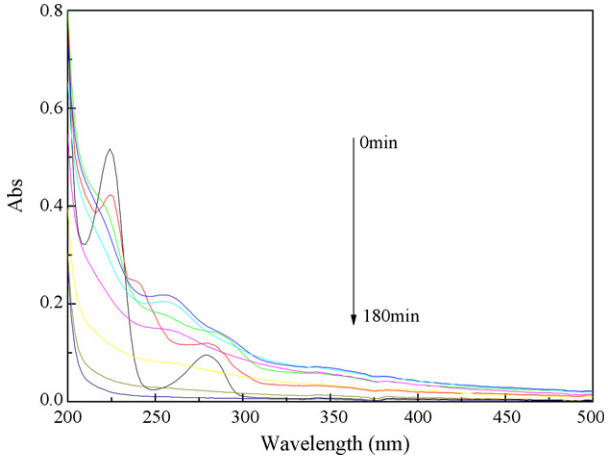

Fig. 5. UV–vis spectra of 4-CP using PEC degradation.

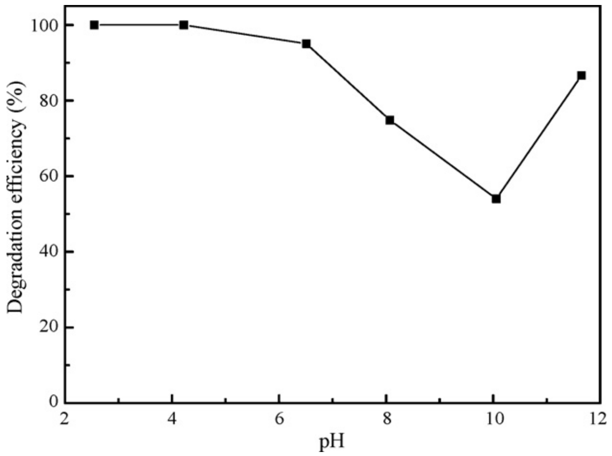

Fig. 7. The PEC degradation efficiency of different pH about 3 h in 225 nm.

3.4. Effect of influencing parameters on the PEC degradation

Bias potential is a key factor that influences PEC efficiency, which draws the photo-generated electrons to the counter electrode. The effect of the bias potential on the PEC degradation rate of 4-CP was further investigated. As seen in Fig. 6, it is clearly shown that the degradation rate of 4-CP was increased from the bias potential of 0.0 to 0.6 V and reached the largest value at the bias potential of 0.6 V. 95.05% of 4-CP was degraded at a bias potential of 0.6 V in 3 h, whereas it was only 80.7% without bias potential supply. In this case, the degradation of 4-CP was carried out by the combined electro-oxidation and photocatalysis simultaneously. The given bias potential supplied to the TiO_2 nanotube contributes to the separation of the photo-generated electrons and the holes. The charge separation prevents the recombination of photo-generated hole-electron pairs. Thus the electrons and holes have more opportunities to participate in degradation reaction, which causes to increase the quantity of active species. Consequently, the degradation efficiency increases. However, with the higher bias potential, the effect of degradation decreases. It is because that due to a certain thickness of TiO_2 nanotube, number of photo-generated electron is finite under a fixed light intensity. So saturation current is formed when bias potential reached a certain value, PEC degradation efficiency has no longer to increase. This phenomenon was similar to that reported by Zhao et al. [35]. Therefore the supplied bias potential has an optimal value (Fig. 7).

Solution pH is a common factor that influences the removal of pollutants in many processes. It influences adsorption and dissociation of the substrate, catalyst surface charge, oxidation potential of the valence band and other physiochemical properties. The dependence of 4-CP PEC degradation on the pH value of the solution was examined with the constant bias potential of 0.6 V and light intensity of 2.5 mW/cm^2. The degradation was enhanced in both an alkaline medium and an acid medium. Ai et al. [36] observed similar phenomenon from the microwave assisted PC degradation of 4-CP. However, Hepel and Luo [37] reported reversed pH dependence for a diazo degradation. This phenomenon may be attributed to the follow reasons: (1) it is easier for 4-CP to absorb UV light as it is present in its anionic state; (2) more hydroxide ions (OH^-) in the solution produced more hydroxyl radicals ($^\bullet OH$). Since hydroxyl radical is the dominant oxidizing species in the PEC process, the degradation of 4-CP is therefore accelerated in an alkaline medium. The reason for increase of degradation at low initial pH is because that the more H^+ ions in the solution, the more conduction bend electrons (e^-) can transfer to the surface of TiO_2 in order to react with O_2 and produce more hydroxyl radicals.

The PEC degradation of 4-CP at different initial concentrations were compared in Fig. 8. When 4-CP concentration below 15 mg/L,

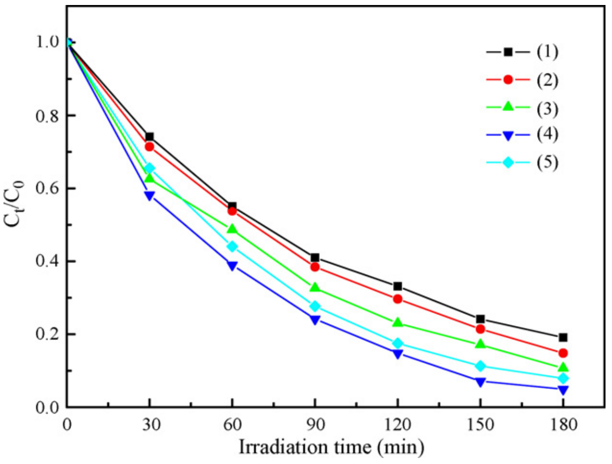

Fig. 6. The PEC degradation of 4-CP affected by bias potential: (1) 0 V; (2) 0.2 V; (3) 0.4 V; (4) 0.6 V; (5) 0.8 V.

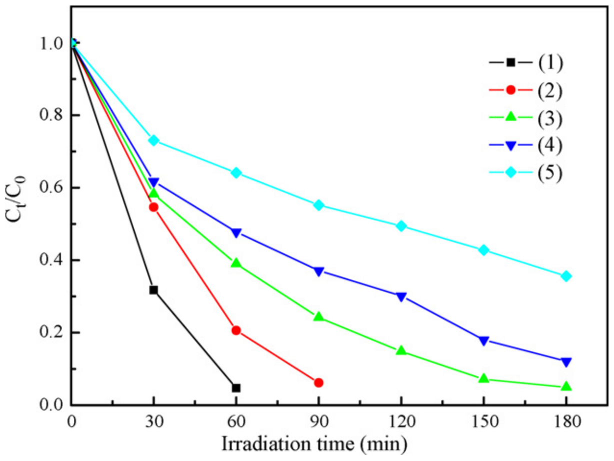

Fig. 8. The PEC degradation of 4-CP affected by different initial concentration: (1) 10 mg/L; (2) 15 mg/L; (3) 20 mg/L; (4) 30 mg/L; (5) 40 mg/L.

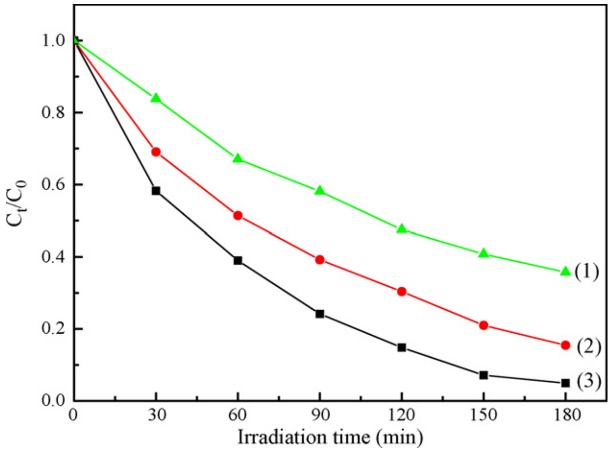

Fig. 9. The PEC degradation of 4-CP affected by different photointensity: (1) 700 μW/cm^2; (2) 1.2 mW/cm^2; (3) 2.5 mW/cm^2.

more than 95% of 4-CP was removed within 90 min. The present results indicated that the PEC process was rather promising at low organic pollutant concentrations which was attribute to the adequate of the electron-hole pairs and reactive species formed. When the concentration of 4-CP increased to 30 mg/L, the degradation rate exhibited a decrease, indicating that it was limited by the amount of reactive species produced by the UV illumination. The main reason is that, the formation of •OH is constant for a given amount of the catalyst and hence the available •OH radicals are insufficient for 4-CP degradation at higher concentration. Moreover the higher the 4-CP concentration, the higher concentrations of intermediate products are produced which compete for reacting with hydroxyl radical. So it can be concluded that the initial 4-CP concentration is also a significant factor affecting the degradation of 4-CP (Fig. 9).

The effect of light intensity was investigated from 700 μW/cm^2 to 2.5 mW/cm^2. The results revealed that the degradation rate increased with increasing in the light intensity up to 2.5 mW/cm^2. Venkatachalam et al. [38] have pointed out that electron-hole recombination is a commonly encountered problem in PC process which is similar to PEC process. Excitation of every catalyst by light irradiation at any instant cannot be possible. But the probability of excitation can be increased by increasing the intensity of incident light. It also increases the re-excitation of recombined electrons. This increasing light intensity enhances the formation of hydroxyl radical. Hence, the improved degradation rate was observed with increasing in the light intensity.

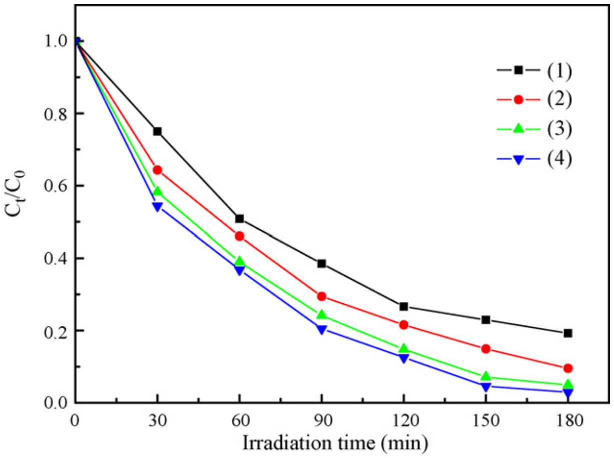

Fig. 10. The PEC degradation of 4-CP affected by concentration of Na_2SO_4: (1) 0 mol/L; (2) 0.05 mol/L; (3) 0.1 mol/L; (4) 0.2 mol/L.

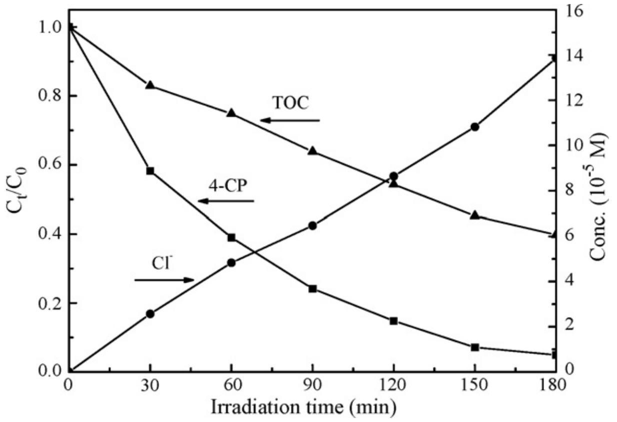

Fig. 11. Change in 4-CP concentration and TOC and the formation of Cl^- during the course of the PEC degradation of 4-CP (20 mg/L).

Selection and concentration of electrolytes can also affect the PEC degradation. As shown in Fig. 10, sodium sulfate was selected as the electrolytes and four levels of concentration were investigated. The results showed that degradation of 4-CP was enhanced when there was in presence of sodium sulfate, and the degradation efficiency was increased with the concentration of electrolytes rose from 0.05 to 0.2 mol/L. This observation may have been anticipated as the presence of electrolyte increases the conductivity of solutions. As a result, the PEC process was enhanced.

3.5. *Mineralization and Cl^- studies*

The decrease of TOC and the formation of Cl^- in the PEC of 4-CP by TiO_2 nanotube were also performed. The results were shown in Fig. 11. The rate of TOC reduction was remarkably slower than that of 4-CP. About 40% of TOC still remained after 3 h irradiation while 4-CP was almost completely dechlorinated, and the concentration of Cl^- rose to reach 89.1% (13.86×10^{-5} M) of the theoretical quantity (15.56×10^{-5} M). It can be concluded from this result that dechlorination of 4-CP was completely finished but about half of the 4-CP is not mineralized into CO_2 and H_2O.

4. Conclusions

TiO_2 nanotube fabricated using anodization method with large surface area showed relatively higher photoelectrocatalytic activity than TiO_2 film in 4-chlorophenol removal in aqueous solution. The combined use of TiO_2 nanotube, UV light and bias potential could greatly enhance the efficiency of 4-chlorophenol degradation. Photoelectrocatalytic process was much more effective than that with either photocatalytic or electrochemical process alone. Bias potential, pH, initial concentration of 4-chlorophenol, UV light intensity and electrolyte concentration were shown to be important factors influencing the efficiency of the photoelectrocatalytic process. 4-Chlorophenol removal increased with increasing UV light intensity and electrolyte concentration, but it decreased with increasing initial concentration of 4-chlorophenol. Since less than 0.6 V bias potential was supplied, the enhancement of 4-chlorophenol removal in the photoelectrocatalytic process was attributed to photo-generated electrons and holes separation by the bias potential. And the effect of pH was more complicated, the degradation was enhanced in both an alkaline medium and an acid medium. Moreover, results of mineralization and Cl^- studies indicated that dechlorination was completely accomplished but more time was required to completely mineralize 4-chlorophenol into water and carbon dioxide by photoelectrocatalytic.

Acknowledgments

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