

# PHOTOELECTROCATALYTIC DEGRADATION OF HUMIC ACID IN AQUEOUS SOLUTION USING A Ti/TiO<sub>2</sub> MESH PHOTOELECTRODE

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## ABSTRACT

Humic acid (HA) is one of natural organics existing in water supply as a precursor of trihalomethanes formation in chlorination. The photo-degradation of HA in aqueous solution by photoelectrocatalytic (PEC) oxidation using a Ti/TiO<sub>2</sub> mesh electrode was investigated in terms of UV absorbance at 254 nm, colour and TOC concentration. The key factors affecting the PEC oxidation efficiency were studied, including the concentration of electrolyte, electrical bias applied, pH value of HA solution, the intensity of incident light and the area of Ti/TiO<sub>2</sub> mesh photoelectrodes. The first order kinetic model was applied to describe the PEC oxidation, in which the kinetic constant  $k$  was verified by the experimental data as a function of the concentration of electrolyte, light intensity, the area of Ti/TiO<sub>2</sub> mesh electrode and the voltage of electrical bias applied. It was found that there was an optimal bias voltage of 1.63V and low pH value was favourable for TOC removal in HA solution. Our investigation showed that PEC oxidation was a convenient way to mineralise the organic matters with high efficiency.

## KEYWORDS

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Humic acid; Photoelectrocatalytic degradation; Ti/TiO<sub>2</sub> mesh; First-order kinetic constant;

Sodium peroxodisulphate

## INTRODUCTION

In Hong Kong, more than 70% of water supply comes from the East River of China Mainland now. It has been confirmed that the quality of raw water from the East River was deteriorating during the last few years, due to the rapid industrialization in the region. The main pollutants concerned in the raw water include ammonia nitrogen, organics and pathogens. To ensure the drinking water quality in Hong Kong, the local water supply treatment works had to raise the chlorine dosage in the disinfection processes from 2.5 mg/l in 1994 to 7.7 mg/l in 1997, which was mainly used to neutralize a higher amount of ammonia nitrogen in raw water. However, this high dosage of chlorine resulted in both a higher chlorine residual concentration up to 2.6 mg/l and also a higher trihalomethanes (THMs) concentration up to 90 µg/l in product water. The presence of humic acids (HA) have been a problem in the water industry due to their water-soluble formation, a wide range of distribution in molecular weight and size, and their non-biodegradability. It has been confirmed that humic substances play a role as precursors of disinfected by-product (DBPs) in chlorination processes (Singer, 1999; Li *et al.*, 1996; NCI, 1978).

Titanium dioxide (TiO<sub>2</sub>)-based photo-catalysis has been the focus of numerous investigations in recent years, particularly owing to its application for the complete mineralisation of undesirable organic contaminants to CO<sub>2</sub>, H<sub>2</sub>O and inorganic constituent (Hoffmann *et al.*, 1995). Some papers reported that humic substances could be effectively degraded in TiO<sub>2</sub> suspension system UV irradiation (Bekbölet *et al.*, 1996a, 1996b, 1996c; Eggins *et al.*, 1997). However, it has been also known that this type of photo-oxidation has two typical drawbacks of the difficulty to separate TiO<sub>2</sub> particles from its aqueous suspension and a low quantum yield (less than 10%, generally) (Choi *et al.* 1994). To solve the problem of TiO<sub>2</sub> particle separation from wastewater,

many efforts and attempts done by researchers were trying to immobilize TiO<sub>2</sub> film on solid carriers such as sand, glass media or resins by coating, soaking, precipitating or spanning methods. However while these immobilized TiO<sub>2</sub> photo-oxidation processes made the TiO<sub>2</sub> separation from water phase much easier, they did not improve its low quantum efficiency very much in photo-oxidation reaction.

Since 1986, a number of studies demonstrated that a photoelectrocatalytic (PEC) oxidation process achieved higher efficiency by applying an electrical bias between a working electrode and a counter electrode for organic degradation, which can prevent carrier charge recombination and results in an extension of the active holes lifetime (Kesselman et al., 1997; Hidaka et al., 1997; Vindogopal et al. 1993). In their studies, the photo-anodes were prepared by coating TiO<sub>2</sub> on a conducting glass initially covered by an indium tin-oxide. It was found that electron mass transfer between TiO<sub>2</sub> films and supporting carriers was not very efficient due to a poor mass transmission between the two materials. Recently, our research group successfully prepared an innovative Ti/TiO<sub>2</sub> mesh photoelectrode by anodising a TiO<sub>2</sub> film on titanium (Ti) mesh for PEC degradation of rose Bengal (Li *et al.*, 2000). This electrode had a large surface area and its microporous surface structure achieved an excellent adsorption of substances. In this study, humic acid was used as a model chemical to conduct the PEC oxidation experiments using the Ti/TiO<sub>2</sub> mesh photoelectrode. The aim of the study was to determine the photooxidation efficiency of this innovative Ti/TiO<sub>2</sub> mesh photoelectrode for the degradation of HA at different reaction conditions, and also to set up a kinetic model to describe the effects of main factors in order to optimise its reaction conditions.

## **EXPERIMENTAL**

### *Materials*

Titanium (Ti) mesh (purity > 99.6%, nominal aperture 0.19 mm, wire diameter 0.23 mm, wires/inch 60 x 60, open area 20%, twill weave) was purchased from Goodfellow Cambridge Limited. Commercially available HA chemical was supplied by Fluka with an ash content of about 20% and used without any further purification. All other chemicals were used with GPR grade.

### *Preparation of Ti/TiO<sub>2</sub> mesh electrode*

A large piece of raw Ti mesh with a thickness of 0.5 mm was cut into small rectangle pieces of 25 mm × 10 mm, which were then cleaned with alcohol and acetone solution respectively. The treated Ti mesh and a copper (Cu) plate with same size were submerged in 0.5M H<sub>2</sub>SO<sub>4</sub> solution and an electrical current was applied between the Ti mesh and Cu plate using a laboratory-made DC power supply with a maximum potential of 200V. An anodisation process was conducted in two stages, in which the galvanostatic anodisation with a constant current density of 100 mA/cm<sup>2</sup> was first performed until a designated anode-to-cathode voltage (160V) reached. Then the constant voltage was maintained until the anodisation process completed. In the meantime, the current intensity was decreasing gradually. The freshly generated Ti/TiO<sub>2</sub>-mesh photoelectrode was then rinsed by distilled water and dried at 105°C in an oven for half an hour. Before the Ti/TiO<sub>2</sub>-mesh electrode was used for the photo-oxidation study, its structural and surface morphology were examined and studied using Raman Spectroscopy and Scanning Electron Microscopy (SEM) respectively. The characteristics of Ti/TiO<sub>2</sub>-mesh electrode were precisely described in our previous study (Li, *et al.* 2000b). The results showed a microporous surface structure and a mixture crystal phase of anatase and rutile.

### *Photo-reactor and light source*

The PEC oxidation experiment was performed in a batch photo-reactor system as shown in Fig.1, which consisted of a cylindrical borosilicon glass reactor, a 125W high-pressure mercury lamp (Institute of Electric Light Source, Beijing), a potentiostat (ISO-TECH 1PS 1810H) and electrodes. The 125W high-pressure mercury lamp was positioned inside the cylindrical reactor surrounded by a circulating water jacket (Pyrex) to control temperature. The photo-reactor has an effective volume of 165 ml, in which both a Ti/TiO<sub>2</sub>-mesh electrode as anode and a copper plate electrode (50 mm × 10 mm) as cathode were placed in parallel and connected with the potentiostat. During the photoreaction, the HA solution was aerated by bubbling air and irradiated by UV light. At different irradiation time intervals, the samples of HA solution were taken and analysed for determination of UV-absorption at 254nm, colour and total organic carbon (TOC) concentration.

[Figure 1]

### *Procedures of PEC degradation experiment*

In this study, a total of six sets of tests were carried out with different purposes. The first set of tests was conducted under different experimental conditions including UV irradiation, addition of electrolyte and electrical connection of electrodes to identify the critical conditions. The second set of tests was performed with different pH values to seek for an optimal pH condition. To study the PEC oxidation affected by electrolyte existence, the third set of tests was carried out by adding sodium peroxodisulphate with different dosage. The fourth set of tests was executed by applying different electrical potentials between the two electrodes to determine an optimal electrical potential required. The fifth set of tests was performed with different light intensities to investigate the relationship between light intensity and PEC reaction rate. To study the PEC oxidation affected by the surface area of TiO<sub>2</sub> film, the sixth set of tests was carried out using Ti/TiO<sub>2</sub> mesh with different size. The experimental conditions are summarized in Table 1.

### *Analytical methods*

The UV absorption of HA in aqueous solution was measured by a spectrophotometer (GENESYS 5 UV-VIS) at 254 nm. The colour of the solution was measured by a Tintometer (Model PFX190) and expressed in Hazen units. TOC concentration was measured by a TOC analyser (Shimadzu TOC-5000A) to determine the degree of HA degradation in the PEC oxidation. The light intensity was measured by a Black-Ray UV meter (UVP Inc, Model No. J 221).

## **RESULTS AND DISCUSSION**

### *Photodegradation of HA under different experimental conditions*

To determine the key factors affecting the photodegradation of HA in aqueous solution, the first set of tests was carried out under different experimental conditions as shown in Table 1, in which the deduction of colour,  $UV_{254}$  and TOC were monitored. The experimental results are shown in Figure 2-1, Figure 2-2 and Figure 2-3 respectively. Test 1 (Dark) was conducted in a dark condition with the Ti/TiO<sub>2</sub>-mesh electrodes but not connected with the counter electrode. The experiment demonstrated a slight decrease of UV absorption and TOC concentration only at the early stage of experiment due to adsorption of HA by the Ti/TiO<sub>2</sub> electrode. Test 2 (UV) was performed under UV irradiation with a light intensity of 4.38 mW.cm<sup>-2</sup> only without using the electrodes. The UV absorbance and TOC concentration decreased also insignificantly. Test 3 (UV/SP) was executed under UV irradiation with the intensity of 4.38 mW.cm<sup>-2</sup> without existence of electrodes, but with addition of sodium peroxodisulphate (SP) up to 80mg.l<sup>-1</sup> in the HA solution, in which a significant reduction of colour, UV absorbance and TOC concentration occurred. Test 4 (PC) was carried out under UV irradiation using Ti/TiO<sub>2</sub> electrode but not

connected with the counter electrode. It was found the significant reduction of colour, UV absorbance and TOC concentration. Test 5 (PEC) was carried out under UV irradiation using the Ti/TiO<sub>2</sub> electrode as a working electrode and also a copper electrode as a counter electrode, in which the two electrodes were connected by the potentiostat but without applying any electrical bias. It was found that colour, UV absorbance and TOC concentration in Test 5 were reduced faster than that in Test 4, but not as fast as that in Test 3. The results of test 3 - 5 demonstrated that the addition of SP, UV irradiation and connection between the Ti/TiO<sub>2</sub> electrode and copper electrode were three essential conditions to promote the photooxidation efficiency. The addition of SP to HA solution was especially effective for reduction of colour and UV<sub>254</sub>, but not for TOC reduction.

[Figure 2-1, Figure 2-3, Figure 2-3]

*The Kinetic model for the PEC oxidation of HA in aqueous solution*

To describe the kinetics of the PEC oxidation reaction, it was assumed that TOC deduction rate follows the first-order kinetic model as Equation 1, since TOC concentration during the reaction is low.

$$\frac{[TOC]_t}{[TOC]_0} = e^{-kt} \quad (1)$$

The TOC concentration [TOC]<sub>t</sub> has an exponential relationship to reaction time (*t*). The first-order kinetic constant *k* was used to characterize the observed PEC oxidation rate in this paper, which was assumed to be affected by several key factors of SP concentration (*C*), light intensity (*I*), total area of Ti/TiO<sub>2</sub> mesh electrodes (*A*) and voltage of electrical bias applied (*V*) at a certain pH condition in the following empirical form of Equation 2.

$$(2)$$

$$k = f(C, I, V, A) = m(C)^a (I)^b (V)^c (A)^d$$

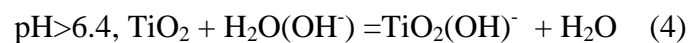
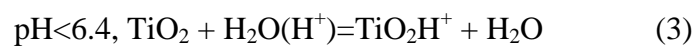
where  $m, a, b, c, d$  are constants.

#### *The PEC oxidation rate affected by pH*

To study the effect of pH value on the PEC degradation of HA solution, the second set of tests was carried out with the same light intensity of  $4.38 \text{ mW.cm}^{-2}$  but at different pH values of 3.01, 5.28, 8.25, and 10.11 respectively without applying electrical bias. The experimental results are shown in Figure 3. The experiment demonstrated that the TOC concentration of HA solution decreased much faster in acidic solution than that in alkaline solution.

[Figure 3]

Since the photocatalytic process mainly occurs on the photocatalyst surface, but not in bulk solution, the adsorption behaviour of Ti/TiO<sub>2</sub> mesh electrode surface plays an important role in this type of PEC oxidation reaction. In our previous study (Li and Li 2001), it was confirmed that the iso-electrical point of TiO<sub>2</sub> is pH 6.4. When pH < 6.4, the surface of Ti/TiO<sub>2</sub> mesh is positively charged and offers a favourable condition to adsorb negatively charged particles such as HA molecules. When pH > 6.4, the surface of Ti/TiO<sub>2</sub> is negatively charged and the adsorption of HA becomes difficult due to an electrostatic repulsive force. At different pH conditions, the adsorption capacity of Ti/TiO<sub>2</sub> mesh electrode instantly affects the activity of PEC oxidation. The polarity of Ti/TiO<sub>2</sub> mesh electrode surface can be expressed by Equations 3 and 4:





The relationship between the surface adsorption rate and photoreaction rate is further discussed in the later part of this paper.

*The PEC oxidation rate affected by addition of sodium peroxodisulphate (SP)*

Sodium peroxodisulphate (SP) is a kind of electrolyte and oxidative. The third set of test was carried out with addition of different amount of SP to investigate the effect of SP on the PEC oxidation of HA solution at pH=3.01. The experiment demonstrated that the TOC concentration of HA greatly decreased owing to the addition of SP as shown in Figure 4. The results showed the addition of SP was an effective way to improve the PEC degradation of HA. However, when the concentration of SP was low, the increase of SP concentration made the first-order kinetic constant increased rapidly; when the concentration of SP reached up to 80 mg.l<sup>-1</sup>, the first-order kinetic constant  $k$  only increased slightly. In this paper, we think a higher concentration of SP may not be economical and propose that the exponential dependence of the first-order kinetic constant ( $k$ ) on the concentration of SP ( $C$ ) be expressed as Equation 5:

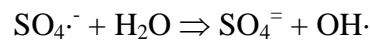
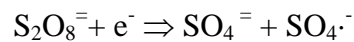
$$k = k_1 C^a \quad (5)$$

where  $a$  is a constants and  $k_1$  is the observed oxidation rate affected by the light intensity, bias voltage and the total area of Ti/TiO<sub>2</sub> mesh. According our experimental results,  $k_1$  equals to 0.00236 min<sup>-1</sup>, and  $a$  equals to 0.4199 ( $R^2=0.8909$ ). Equation 5 might be expressed as Equation 6:

$$k = 0.00236C^{0.4199} \quad (6)$$

[Figure 4]

The mechanism of peroxydisulphate-UV-TiO<sub>2</sub> is that the oxidation proceeds mainly through formation of the strong oxidizing SO<sub>4</sub><sup>·-</sup> (E<sub>0</sub>=2.6V) and OH<sup>·</sup> species as Equation 1 and 2, which can directly participate in the degradation process (Minero et al., 1993). And the oxidant peroxydisulphate can trap the photo-generated electrons more efficiently than O<sub>2</sub> (Pelizzetti et al., 1991). Moreover, the direct photolytic oxidation may occur in the presence of peroxydisulphate-UV. From Fig. 4, when the concentration of SP was less than 40 mg/l, the first-order kinetic constant increased rapidly with the increase of the concentration of SP; when the concentration of SP was more than 40 mg/l, the first-order kinetic constant increased slowly. In this paper, we propose that peroxydisulphate acts mainly as electron trap at the lower concentration of peroxydisulphate and hinders the recombination of electron/hole pairs and enhances greatly the PEC oxidation reaction. And a part of peroxydisulphate participate the photolytic oxidation of humic acids at the higher concentration of peroxydisulphate.



#### *The PEC oxidation rate affected by light intensity*

To study the relationship between light intensity and PEC oxidation rate of HA, the fifth set of tests was conducted with the same bias voltage of 0.0V, but different light intensity of 0 (dark), 0.875 (LI1#), 1.58 (LI2#), 2.37 (LI3#), 3.01 (LI4#) and 4.38 mW.cm<sup>-2</sup> (LI5#) at pH=3.01 respectively. The results indicated the higher intensity of UV irradiation achieved the faster PEC degradation of HA as shown in Figure 5. In this study, we propose that the first-order kinetic constant *k* affected by the intensity of light (*I*) can be expressed as Equation 7:

$$k = k_2 I^b \quad (7)$$

where  $k_2$  and  $b$  are constants. According our experimental data, the value of  $k_2$  related to other factors equals to  $0.00512 \text{ min}^{-1}$ , and  $b$  equals to  $0.7796$  ( $R^2=0.9852$ ). In the study, it was proven that there was a power relationship between  $I$  and  $k$ . And the above relationship might be verified as Equation 8:

$$k = 0.00512I^{0.7796}$$

[Figure 5]

UV radiation intensity plays an important role in influencing the kinetic constant. Two kinds of dependence had been suggested: the kinetic constant can be a function of the square root of the radiation entering at high light intensities (Bahnmann et al., 1991) or a linear function of the radiation entering at low light intensities (Peterson et al., 1991). In fact, it is better to use the exponential dependence to express the relationship between the first-order kinetic constant and the light intensity. The experimental result of  $b=0.7796$  in this study indicates that the photoreaction behaved more close to a linear relationship in the range of light intensity applied, which would be valuable to design and operation consideration at any larger scale performance.

#### *The PEC oxidation affected by the electrical potentials voltage applied*

To study the effect of electrical bias voltage on the PEC degradation of HA, the fourth set of tests was conducted with the same light intensity of  $4.38 \text{ mW.cm}^{-2}$  and SP concentration of  $80 \text{ mg.l}^{-1}$ , but different bias voltage (V) of 0.0V, 0.3V, 0.6V, 1.0V, 1.5V and 2.5V respectively at pH 3.01 and the experimental results are shown in Figure 6-1. The results showed that 1.5V might be an optimal voltage for the PEC degradation of HA. When bias voltage was lower than 1.5V, the first-order kinetic constant  $k$  increased with the increase of bias voltage. And when bias voltage was higher than 1.5V, the first-order kinetic constant  $k$  decreased with the increase of

bias voltage. As shown in Figure 6-2, there was a parabolic relationship ( $R^2=0.9815$ ) between bias voltage ( $V$ ) and first-order kinetic constants  $k$ , described as Equation 9, where 0.0161 represented the statistic result of  $k$  with the light intensity of  $4.38 \text{ mW.cm}^{-2}$  and SP addition of ( $80\text{mg.l}^{-1}$ ) at pH 3.01. According to Equation 9, an optimal bias voltage to achieve the maximum  $k$  value was found to be  $+1.63\text{V}$ .

$$k' = -0.008V^2 + 0.026V + 0.0161$$

In this study, we propose that the first-order kinetic coefficient ( $k'$ ) is the function of bias voltage ( $V$ ). When the bias voltage is below its optimal value of  $+1.63\text{V}$ , a power formula may be applied to match the formula pattern of other factors as well as Equation 10.

$$k = 0.03325V^{0.2451} \quad (10)$$

[Figure 6-1, Figure 6-2]

*The PEC oxidation rate affected by the area of Ti/TiO<sub>2</sub>-mesh electrode*

To investigate the PEC degradation of HA by the total area of photo-anode, the sixth set of tests was conducted with the same light intensity of  $4.38 \text{ mW.cm}^{-2}$  and SP addition of  $80\text{mg.l}^{-1}$  without applying bias voltage, but using different number of Ti/TiO<sub>2</sub> meshes; no mesh, 1 mesh, 2 meshes, and 4 meshes, corresponding to the area ( $A$ ) of 0, 4, 8, and  $16 \text{ cm}^2$  respectively at pH 3.01. The results showed that the increasing the total area of Ti/TiO<sub>2</sub> meshes could improve the TOC removal of HA as shown in Figure 7. In the study, we propose that there be a power relationship between  $A$  and  $k$  as expressed in Equation 11:

$$k = k_3 A^d \quad (11)$$

where  $k_3$  and  $d$  are constants. According our experimental results,  $k_3$  equals to  $0.001 \text{ min}^{-1}$ , and  $d$  equals to  $0.6589$  ( $R^2=0.9577$ ). And the above equation might be expressed as Equation 12:

$$k = 0.0066A^{0.6293} \quad (12)$$

[Figure 7]

*An overall observed PEC oxidation rate*

According to the above results, the first-order kinetic constant  $k$  depends on the concentration of SP ( $C$ ), light intensity ( $I$ ), the total area of Ti/TiO<sub>2</sub> meshes ( $A$ ), and the bias voltage ( $V$ ) (when  $V$  is below 1.63V). In this paper, we propose an overall observed PEC oxidation rate as Equation 13 to describe the dependence of  $k$  on the factors of  $C$ ,  $I$ ,  $A$  and  $V$ . And on the basis of our experimental results, the value of  $a$ ,  $b$ ,  $c$ ,  $d$  are 0.4199, 0.7796, 0.6293, 0.2451 respectively, Equation 2 can be expressed as Equation 13:

$$k = m(C)^{0.4199} (I)^{0.7796} (A)^{0.6293} (V)^{0.2451} \quad (13)$$

Based on Equation 13, when PEC oxidation was carried out under the conditions of the light intensity =  $4.38 \text{mW.cm}^{-2}$ , the SP concentration =  $80 \text{mg.l}^{-1}$  and the area of mesh electrode =  $4 \text{cm}^2$ ,  $m$  equals to  $6.98 \times 10^{-4}$  and the overall PEC oxidation process of HA solution can be expressed as Equation 14 and 15.

$$k = 6.98 \times 10^{-4} (C)^{0.4199} (I)^{0.7796} (A)^{0.6293} (V)^{0.2451} \quad (14)$$

$$TOC_{(t)} = TOC_{(0)} e^{-6.98 \times 10^{-4} (C)^{0.4199} (I)^{0.7796} (A)^{0.6293} (V)^{0.2451} t} \quad (15)$$

Moreover, from Equation 14, it may be concluded that factors affecting PEC efficiency from strong to weak can be ranked as light intensity  $\rightarrow$  total area of Ti/TiO<sub>2</sub> meshes  $\rightarrow$  SP concentration  $\rightarrow$  electrical bias voltage. It might be a more effective way to enhance the PEC efficiency of HA by increasing light intensity and the total area of Ti/TiO<sub>2</sub> mesh.

In order to check the accuracy of Equation 15, we compare the theoretical data using Equation 15 with the experimental data under the conditions of light intensity = 4.38 mW.cm<sup>-2</sup>, SP concentration = 80mg.l<sup>-1</sup>, the total area of mesh = 4cm<sup>2</sup> and the electrical bias voltage = +1.5V, when the initial concentration of TOC equals to 7.854 mg.l<sup>-1</sup>. The experimental results shown in Figure 8 demonstrated that the estimated value of TOC<sub>(t)</sub> is slightly higher than the experimental data when the irradiation time is less than 40 min and slightly lower than the experimental data. In fact, the PEC oxidation of HA solution may include photochemical oxidation due to the presence of SP as well.

[Figure 8]

#### *The surface adsorption rate and photoreaction rate of Ti/TiO<sub>2</sub> mesh electrode*

The first-order kinetic constant  $k$  used in this study can only express the observed photooxidation rate, which is mainly controlled by two components of surface adsorption rate and photoreaction rate on the surface of Ti/TiO<sub>2</sub> mesh electrode. Since this photoelectrocatalytic oxidation mainly occurs on the surface of electrode, not in bulk solution, the ratio between surface adsorption rate and photoreaction rate plays a very important role. When the surface adsorption rate is faster than the photoreaction rate on the surface, the photoreaction rate would be a control factor for the observed photooxidation rate. Vice versa, when the photoreaction rate is faster than the surface adsorption rate, the surface adsorption rate would be a control factor for the observed

photooxidation rate. Theoretically, the photoreaction rate should be proportional to the light intensity and also to the total area of Ti/TiO<sub>2</sub> meshes used. However, the experimental results as shown in Figures 6 and 7 demonstrated that the observed photooxidation rate increased proportionally when light intensity was lower than 3 mW.cm<sup>-2</sup> and the total area of Ti/TiO<sub>2</sub> meshes was smaller than 8 cm<sup>-2</sup>. Beyond that, the observed photooxidation rate increased more slowly and the first-order kinetic constant *k* curves become more flat. This phenomenon may indicate that when the light intensity and the total area of Ti/TiO<sub>2</sub> meshes are in a low range, the surface adsorption rate is faster than the photoreaction rate and the photoreaction rate is the control factor for the observed photooxidation rate. But when light intensity and the total area of Ti/TiO<sub>2</sub> meshes beyond the critical points, the surface adsorption rate was behind the photoreaction rate and the further increase of the observed photooxidation rate would be restricted by the control factor of the surface adsorption rate.

## CONCLUSIONS

The experiment demonstrated that the photoelectrocatalysis using Ti/TiO<sub>2</sub> mesh electrode can degrade HA in aqueous solution efficiently in terms of UV-absorbance at 254 nm, colour in Hazen and TOC concentration after an irradiation time of 120 min. The key factors affecting the PEC oxidation rate include SP concentration, electrical bias voltage applied between the working electrode and counter electrode, pH value of HA solution, the intensity of incident light and the total area of Ti/TiO<sub>2</sub> meshes. The increase of the SP concentration, light intensity and the total area of Ti/TiO<sub>2</sub> meshes can enhance the TOC removal and raise the first-order kinetic constant *k*. In acidic solution, HA molecule is easily adsorbed on the surface of Ti/TiO<sub>2</sub> mesh, and is more quickly mineralised. The PEC oxidation by applying bias voltage between the anode and cathode enhanced the PEC oxidation efficiency. An optimal bias voltage was found to be 1.63V. A kinetic model was established to describe the relationship between first-order kinetic constant

and these factors. It has been found that factors affecting PEC efficiency from strong to weak queue the order of the light intensity, the total area of Ti/TiO<sub>2</sub> meshes, the SP concentration and bias voltage.

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