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Research Article

Photoelectrocatalytic Degradation of Sodium Oxalate by TiO_2/Ti Thin Film Electrode

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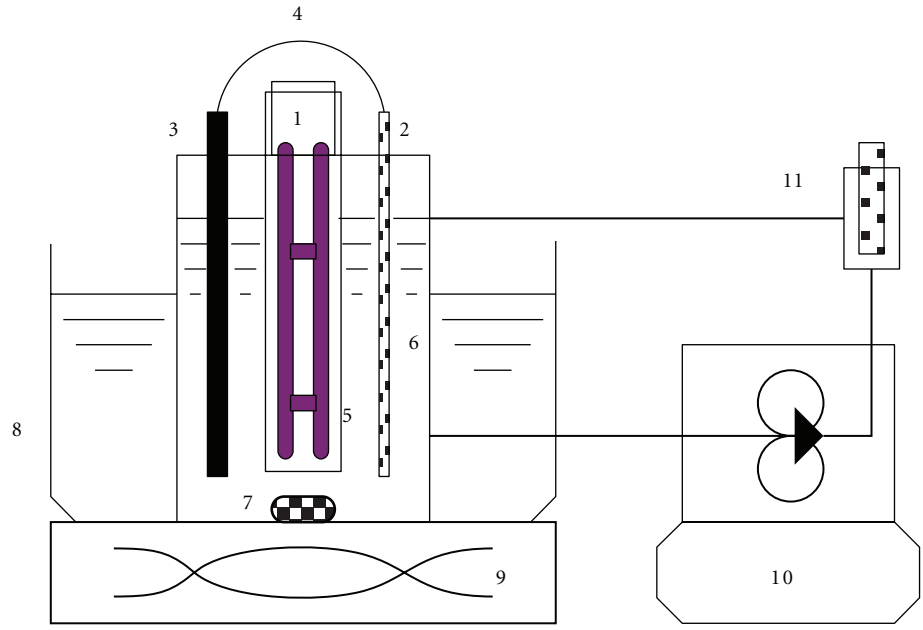
The photocatalytically active TiO_2 thin film was deposited on the titanium substrate plate by chemical vapor deposition (CVD) method, and the photoelectrocatalytic degradation of sodium oxalate was investigated by TiO_2 thin film reactor prepared in this study with additional electric potential at 365 nm irradiation. The batch system was chosen in this experiment, and the controlled parameters were pH, different supporting electrolytes, applied additional potential, and different electrolyte solutions that were examined and discussed. The experimental results revealed that the additional applied potential in photocatalytic reaction could prohibit recombination of electron/hole pairs, but the photoelectrocatalytic effect was decreased when the applied electric potential was over 0.25 V. Among the electrolyte solutions added, sodium sulfate improved the photoelectrocatalytic effect most significantly. At last, the better photoelectrocatalytic degradation of sodium oxalate occurred at pH 3 when comparing the pH influence.

1. Introduction

Oxalic acid is frequently used in leather bleaching, chemical synthesis, printing and dye industries, rust removal, metal decontamination, and household bathroom cleaning. Therefore, cases of accidental oxalic acid poisoning are common. In addition, oxalic acid and its soluble salts can cause poisoning through the stomach and intestines, respiratory tract, skin, and eye contact with LD_{50} between 375 and 475 mg Kg^{-1}. Oxalate itself is also toxic to the kidney. In recent years, advanced oxidation processes have been extensively used in decomposing harmful or decomposition-resistant pollutants in the environment. Among them, the photocatalysis reaction using UV together with semiconductor is thought to be a treatment technology with high potential. Compared to other semiconductor metal oxides, titanium dioxide (TiO_2) is the most frequently used photocatalyst for photochemical reaction due to the cheap cost, stable properties, and high photocatalytic effect. However, the recombination of electron-hole pairs occurs during the photocatalytic reaction process, resulting in the reduction of decomposition efficiency. In order to resolve such a problem for the increase of quantum efficiency, the following approaches are frequently adopted: (1) application of a positive electric potential on the TiO_2 electrode to use the electric field force to drive away electrons in order to prevent further recombination; (2) combination of 2 semiconductors (such as TiO_2/SnO_2) at comparable energy levels to allow one (like SnO_2) to absorb electrons during photoexcitation in order to improve decomposition efficiency; (3) addition of precious metal ions such as Ag or Pt in the reaction solution for the absorption for electrons [1–5]. This study used UV light of high energy to excite the photocatalyst to form hydroxyl radicals with high oxidizing ability to efficiently decompose organic pollutants in water in order to attain the goals of removal and mineralization [6–19].

2. Experimental Details

2.1. Preparation of TiO_2 Photoreactor. The modified chemical vapor deposition (CVD) [20] was used for the catalyst preparation used in the present study. The procedure is described as follows: The tetraisopropyl orthotitanate ($Ti(OC_3H_7)_4$) (TTIP >98%, Merck Co.) solution and deionized water were placed in two aeration bottles separately. In the 60°C water bath, the aeration bottles were flushed with



(1) UV lamp, (2) anode (TiO_2/Ti plates), (3) cathode (graphite), (4) external loop, (5) annular quartz tube, (6) reactor (pyrex), (7) magnetic stone, (8) water bath, (9) magnetic stirrer/hot plate, (10) circulating pump, and (11) pH meter.

Figure 1: Photoelectrocatalytic apparatus.

high-purity nitrogen gas to take out the airflow containing TiO_2 and water vapor. Teflon tubing was used on the other end into the reactor. The tubing was wrapped with heating tapes to approximately 95 ± 5°C to avoid condensation. The substrate to be coated with the catalyst was placed in the tubular high-temperature oven to maintain the reaction temperature at 400°C. During the preparation, the formation of white smoke inside the reactor was observed with the naked eye, indicating that the TiO_2 crystal nucleus has started to grow on the wall of the tubing. The reactor was rotated to alter the position of the TiO_2 coating to allow it to coat evenly on the entire titanium substrate. Finally, the reactor was calcined at 500°C for 24 hours to eliminate impurities and purify TiO_2 to achieve the anatase as the major crystal form.

2.2. Photoelectrocatalytic Procedure. The liquid-phase photoelectrocatalytic system consisted of a UV lamp of 13 W and 365 nm, an annular reactor, a completely mixing chamber, a magnetic stirrer, a voltage supplier, and a circulating water bath. The apparatus is illustrated in Figure 1. In this study, the experiments were conducted in batches at constant temperature and sample volume. Other parameters including pH values, additional applied electric potentials, and the type of electrolytes were under control in the experiments (Table 1). 1 N $HClO_4$ and 4 N NaOH were used to adjust the pH value of aqueous samples. Besides, a peristaltic pump was used to draw sample into the reactor for the continuous refluxing batch experiments for 4 hours.

Table 1: Reaction conditions.

Conditions	Range
Water bath temperature	20 ± 1°C
The initial concentration of sodium oxalate	2 mM
Sample volume	350 mL
Flow rate	300 mL min^{-1}
Refluxing time	4 hours
UV wavelength	365 nm
Irradiation intensity	3 mW cm^{-2}
pH	3~7
Additional applied electric potentials	0, 0.25, 0.5, 1 V
Electrolyte solution (2 mM)	NaCl, $NaNO_3$, Na_2SO_4, Na_2CO_3

2.3. Quantitation of Species. The relationships between the residual rates of sodium oxalate and the various controlled parameters were investigated in order to obtain the effect of TiO_2/Ti thin film electrode. Ion chromatograph (IC; JASCO, Japan, Model PU-1580i) equipped with the Shodex IC SI-90-4E column and total organic carbon instruments (TOC; Shimadzu, Japan, Model TOC-VCSN) were employed for the analysis of the experiment to investigate the variations of the residual rates and the mineralization rates under parameters described above.

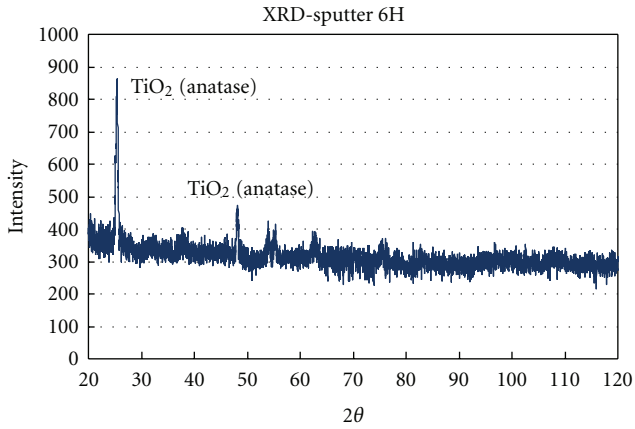


Figure 2: XRD spectrum of TiO_2 prepared by CVD method.

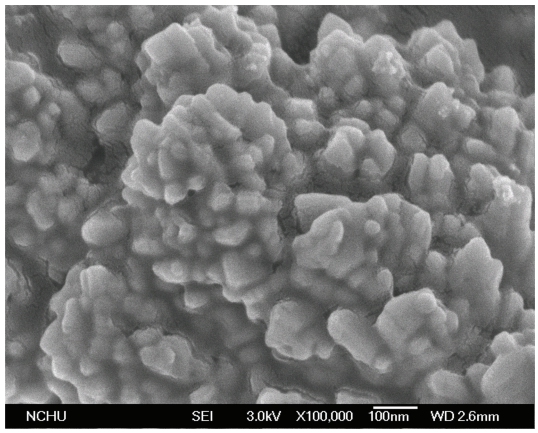


Figure 3: SEM image of TiO_2 prepared by CVD method.

3. Results and Discussion

3.1. Photocatalyst Properties. The photocatalyst prepared by the modified CVD method under the optimal conditions described above was analyzed by the X-ray diffractometer (XRD) to examine the crystals form. As illustrated in Figure 2, the three major diffraction peaks of the anatase crystal structure appear at the 2θ values of 25.4 and 48.2; Compared with the JCPDS database (nos. 21-1276 and 21-1272), the crystal structure of the photocatalyst prepared in the experiment was mostly in the anatase form. The SEM image of the catalyst at magnification of 100,000 times illustrated in Figure 3, the structures of TiO_2 particles were not rather uniform, with the appearance of clustered ball shape and the crystal surface of porous structure.

3.2. Photoelectrocatalytic Tests. Figure 4 shows the residuals of sodium oxalate in the TiO_2 photocatalytic reaction alone, direct electrolysis alone, and photoelectrocatalytic process. It was clearly observed in the experimental data that at 20°C, pH 4, a volume flow rate of 300 mL min^{-1}, and sodium oxalate of 2 mM in the batch completely mixing reactor with the additional applied electric potential of 1 V and the UV

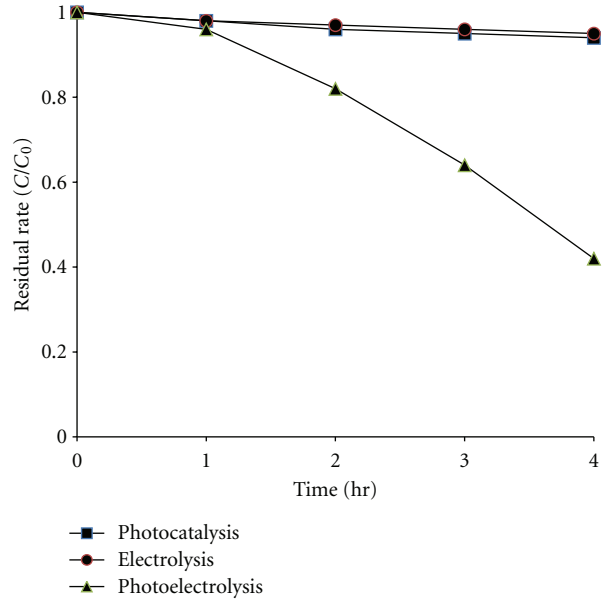


Figure 4: Residual rates of sodium oxalate under the different reactions at pH 4.

irradiation of 365 nm for 4 hours for the photoelectrocatalytic degradation reaction experiment was able to increase the removal and mineralization rates of sodium oxalate from 6% to approximately 57%. According to Waldner's study, it was proposed that when TiO_2 generated electron-hole pairs under UV irradiation, the additional applied electric potential inhibited the recombination of electron-hole pairs. The holes interacted with the water molecules or hydroxide ion (OH^-) absorbed on the surface of TiO_2 to form hydroxyl radical ($^{\bullet}OH$), thus enhancing the oxidation reaction effect of holes [18, 19]. Moreover, according to the experimental results in Figure 5, it was observed that the mineralization rates of sodium oxalate had mostly comparable trends as the removal rate. It was suggested that the structure of sodium oxalate was rather simple, thus it was less likely to form intermediates. As a result, the degraded ones could be almost mineralized.

3.3. pH Effect. In general, as the pH of aqueous solution increases, the yield of hydroxyl radical in the photocatalytic reaction also increases. However, different pH values will directly affect the species distribution ratio of reactants in the solution. Moreover, pH values could also alter the surface electricity of photocatalyst, thus affecting the adsorption and desorption properties and abilities of reactants by the photocatalyst. Therefore, for different pollutants, the pH value controlled in the reaction could show a dramatic effect on the overall removal rate.

Figure 6 illustrated the residual rates of sodium oxalate at pH 3~7. The result indicated that sodium oxalate at 2 mM, applied voltage of 1 V, light intensity of 3 mW cm^{-2}, volume flow rate of 300 mL min^{-1}, temperature at 20 ± 1°C, and UV light irradiation at 365 nm on the titanium substrate plate coated with TiO_2 in the reactor for 4 hours to undergo

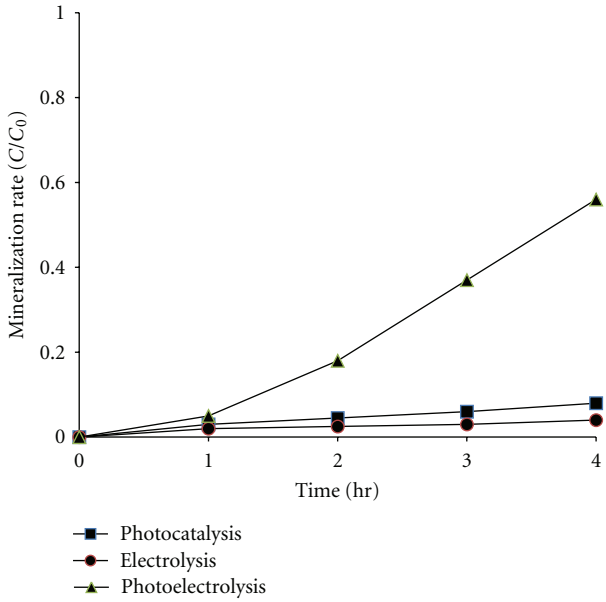


Figure 5: Mineralization rates of sodium oxalate under the different reactions at pH 4.

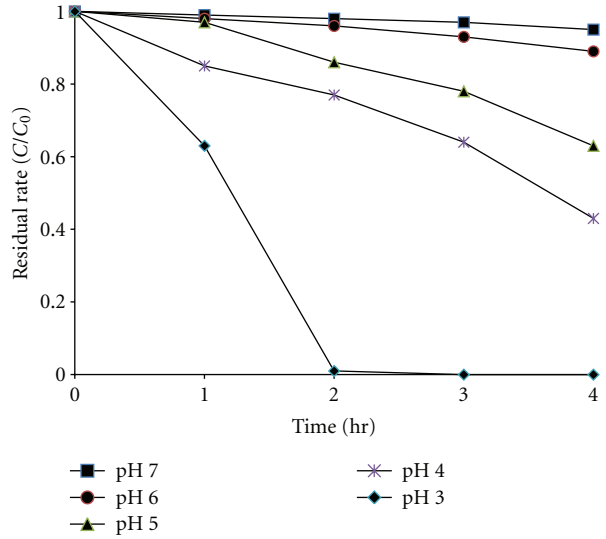


Figure 6: Residual rates of sodium oxalate under the photoelectrocatalytic reaction at different pH.

the photoelectrocatalytic reaction gave the most favorable treatment effect at pH 3. After a reaction for 150 minutes, the removal rate reached almost 100%. However, as pH values increased, the removal rate of sodium oxalate in the aqueous solution decreased. The cause of this phenomenon was probably that oxalate at the first ionization state (pK_{a1} = 1.2, pK_{a2} = 4.2) showed a more favorable reaction rate with $^{\bullet}OH$. Furthermore, in the solid-liquid interface reaction, a low pH value was favorable for the adsorption of oxalate on the TiO_2 surface, allowing the holes excited by UV/TiO_2 to undergo the direct or indirect oxidation reaction in order to achieve of goal of sodium oxalate degradation [19]. The

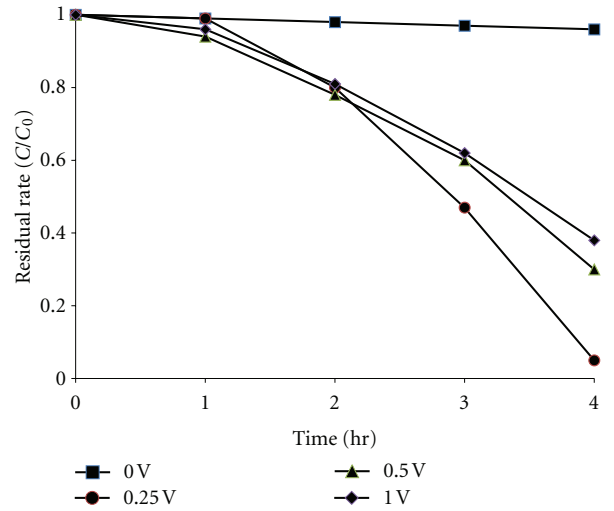


Figure 7: Residual rates of sodium oxalate under photoelectrocatalytic reactions with different additional applied electric potentials.

reason for the higher adsorption at lower pH was that the pHzpc of TiO_2 between 6.3~7.6 and the pKa values of oxalic acid were approximately 1.2 and 4.2. As a result, when the pH value of the solution was higher than the pKa of sodium oxalate but lower than the pHzpc of TiO_2, sodium oxalate ionized a Na^+ cation and formed $NaC_2O_4^-$ with a negative charge. Meanwhile, the TiO_2 surface carried a positive charge and a more favorable adsorption quantity was afforded due to the electrostatic attraction interaction between TiO_2 and oxalic acid.

3.4. Additional Applied Electric Potential Effect. Figure 7 illustrates the results of the different additional applied electric potentials of 0.25 V, 0.5 V, and 1 V to the photoelectrocatalytic experiment of sodium oxalate. From the result shown, it was evident that the sodium oxalate removal effect was quite limited in the absence of the additional applied electric potential for the photocatalytic reactions. It was proposed that the electron-hole pairs excited by UV/TiO_2 underwent the recombination reaction easily, leading to the consequence that the holes could not directly or indirectly oxidize organic substances. Consequently, the overall photocatalytic effect was reduced. However, the results of this experiment demonstrate that the additional applied electric potentials (0.25 V, 0.5 V, and 1 V) on the working electrode significantly improved the overall photoelectrocatalytic reactions. As the additional applied electric potentials varied, the degradation of sodium oxalate also varied to different degrees. Among them, the voltage of 0.25 V afforded a more favorable photoelectrocatalytic reaction. After 4 hours of the photoelectrocatalytic reaction, approximately 95% of sodium oxalate in the aqueous solution was removed. Nevertheless, when the additional applied electric potential was increased to 0.5 V, the sodium oxalate removal effect was lowered. Moreover, when it was increased to 1 V, the sodium oxalate removal rate was merely 57%. Therefore, the experimental results revealed that the applied voltage

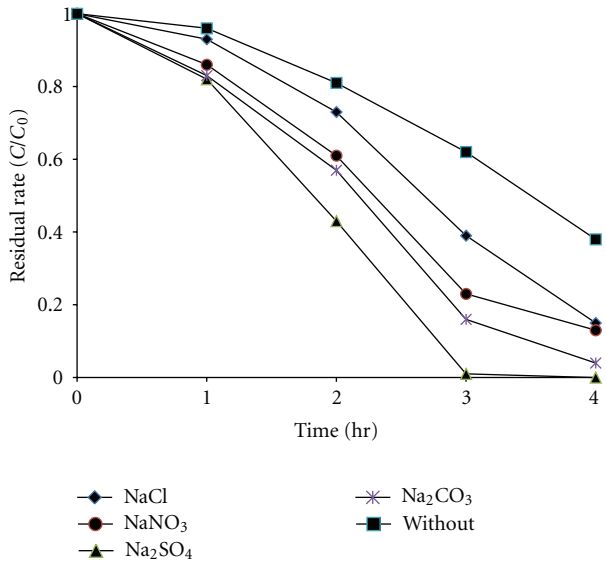


Figure 8: Residual rates of sodium oxalate under photoelectrocatalytic reactions with different electrolytes.

could reduce the recombination of electron-hole pairs, thus improving the overall removal effect. But, when an excess voltage was applied, the photoelectrocatalytic effect was worsened owing to the recombination reaction of the electrons of the additional applied electric potential itself and the holes carried on TiO_2.

3.5. Electrolyte Solution Effect. This experiment used sodium oxalate solution at an initial concentration of 2 mM followed by adding 0.2 mM of NaCl, $NaNO_3$, Na_2SO_4, and Na_2CO_3 electrolyte solution individually. The UV light at 365 nm was used to irradiate on the titanium substrate coated with TiO_2 and the extra applied potential of 1 V was applied. The pH of the aqueous solution was controlled at 4 ± 0.1 and the temperature at $20 \pm 1^{\circ}C$ for the photoelectrocatalytic reaction in the complete mixing chamber for 4 hours to examine the effect of each electrolyte solution on the degradation of sodium oxalate. The results of this experiment are shown in Figure 8. The sodium oxalate degradation reaction the added electrolyte solution (NaCl, $NaNO_3$, Na_2SO_4, and Na_2CO_3) was better than the one without the added electrolyte solution, indicating each electrolyte solution added was able to improve the photoelectrocatalytic reaction. Among them, adding Na_2SO_4 showed the most favorable effect, with the sodium oxalate degradation rate reaching over 99% after 3 hours of operation time. The effects in the improvement of photoelectrocatalysis by different electrolyte solutions were found to vary in the order of $Na_2SO_4 > Na_2CO_3 > NaNO_3 >$ NaCl. According to the study by Jorge, it was pointed out after adding different electrolyte solutions (Na_2SO_4, KNO_3, and NaCl) that Na_2SO_4 was able to enhance the photoelectrocatalytic reaction to a greater extent, followed by KNO_3 > NaCl. This was because more photoelectric current was generated after adding Na_2SO_4 to the system. The difference in the enhanced photoelectrocatalytic effects from adding Na_2SO_4 versus NaCl was found to be about over 10% [17]. This result was consistent with the conclusion of the present study.

4. Conclusions

The CVD method was used to prepare the TiO_2/Ti photocatalysis thin film reactor with the oxidation temperature controlled at 400°C and the calcination temperature at 550°C in this study. Not only the TiO_2 purity was improved, but also the crystal structure was maintained at the anatase crystal form. Under the controlled parameters, the optimal experimental conditions were pH 3, 0.25 additional applied electric potential, and adding Na_2SO_4 electrolyte in this study. The experimental results also showed that the effect of the photoelectrocatalytic process on the sodium oxalate removal efficiency was superior to that of the photocatalytic reaction alone. Moreover, it should be mentioned that the additional applied electric potential, in most cases, could enhance the overall degradation efficiency. However, the excessively high bias voltage could reduce the photocatalytic effect owing to the recombination of the electrons of the voltage itself and the holes carried on TiO_2. The search for the so-called "threshould dose" in the future study should be an attractive research subject.

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