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CONTENTS

Photoelectrocatalytic degradation of high COD dipterex pesticide by using TiO$_2$/Ni photo electrode

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Abstract

A TiO$_2$ thin film electrode deposited on porous nickel net (TiO$_2$/Ni) was prepared by the sol-gel method, and the surface morphology, crystal structure features and the grain size were characterized by Field emission scan electron microscopy (FESEM) and X-ray diffraction (XRD). The photoelectrocatalytic system was set up using a UV high-pressure mercury lamp as the light source, TiO$_2$ coated on foamed nickel as photo anode, Pt sheet as counter electrode and the pesticide dipterex in synthetic wastewater. Various factors that influence the photoelectrocatalytic decomposition of dipterex pesticide have been studied, such as degradation time, the type of electrolyte, current density, original pH value and different degradation methods. The prepared catalysts were employed to photoelectrocatalytically degrade the pesticide dipterex under UV irradiation, comparing the results with photocatalytic degradation and electrochemical oxidation. The results indicated that under the optimal conditions of 0.02 mol/L NaCl as the supporting electrolyte, current density = 2.5 mA/cm^2, pH 6.0 and dipterex pesticide 40 mg/L, and reaction time 2 hr, dipterex chemical oxygen demand (COD) removal rate and organophosphorous conversion of up to 82.6% and 83.5% were achieved, respectively. The method of photoelectrocatalytic degradation is more efficient than photocatalysis and electrochemical oxidation. The possible roles of the electrolytes on the reactions and probable mechanisms were also discussed.

Key words: photoelectrocatalysis; COD removal; TiO$_2$; dipterex; pesticide

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Introduction

Since pesticides were invented, almost every country in the world has used various pesticides to protect the agriculture from pest hazards (Singer et al., 2010). Nowadays, the output of agricultural chemicals has exceeded six million tons every year world-wide. In addition, the produced quantity of organophosphorous insecticides is 70% of total pesticides, and dipterex is one of the most widely used organophosphorous pesticides at present (Jin et al., 2010; Zapata et al., 2010). With the vast amount of pesticides used, people have begun to realize that application of pesticides has brought great agricultural production and more profits, but at the same time, they also inevitably have brought about many negative impacts, such as human and livestock poisoning, environmental pollution, agricultural chemical residues and so on (Li et al., 2009). More-over, with the enhanced consciousness of environmental protection in mind, people have come to attach more and more importance to the impact of agrochemicals on human health and the environment. Therefore, treatment of pesticide wastewater is becoming a hot topic in the field of

environment protection research. Many investigators have carried out a large amount of research on the experimental and theoretical aspects of wastewater treatment (Yu, 2002; Lafi and Qodah, 2006; Badawy et al., 2006; Basheer et al., 2007; Clarke et al., 2010).

The semiconductor TiO$_2$ has received particular attention in the environmental domain because of its high catalytic activity, good stability and excellent photo-electrochemical properties (Liu et al., 2009; Ballesteros Martín et al., 2009). The use of TiO$_2$ particle suspensions is widely employed to degrade organic wastes in water. Nevertheless, there are two obvious shortcomings in actual application: first is that the powdered catalyst is difficult to recover and reuse, leading to secondary pollution; second is that the photo-induced electrons and holes undergo easy recombination, resulting in low quantum yield (Marinas et al., 2001; Konstantinou and Albanis, 2003). To solve these problems, many researchers have investigated the photoelectrocatalytic degradation of organically polluted wastewater in UV light photoreactors employing photo-anodes consisting of the photocatalyst TiO$_2$ supported on electrically conducting carrier substrates (Ti, ITO), with considerable success (Xie and Li, 2006; Zhao et al., 2007; Muff et al., 2009; Zhang and Pagilla, 2010; Ahmed et

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al., 2011). Therefore, photoelectrocatalysis has become an attractive way to increase the photocatalytic efficiency. However, research on the treatment of dipterex pesticide wastewater using a TiO$_2$ film electrode coated on porous nickel net is rare in related domestic and international reports. The most likely reason for this is the toxicity of dipterex.

In this study, porous nickel net, which has large specific surface area, great electrical conductivity and a high capability/price ratio compared to the most commonly used Ti metal carriers (Zhou and Ma, 2009), was used as the photocatalyst carrier. TiO$_2$ supported on a nickel foam electrode prepared by the sol-gel method was used as the photo anode, Pt sheet was the counter electrode and the pesticide dipterex, which is a typical organophosphorous pesticide widely used in the world, was used as the simulated organic pollutant. The effects of various parameters, such as the degradation time, the amount of electrolytes, Cl$^-$ concentration, current density, initial pH value and different degradation methods on the photoelectrocatalytic degradation of high COD dipterex were researched. From the investigation, the optimum technological conditions for photoelectrocatalytic treatment of dipterex and the different effects of the parameters on the photoelectrocatalytic COD removal of dipterex were obtained.

1 Materials and methods

1.1 Main materials and apparatus

Porous nickel (purity 99.9%, thickness 1.0 mm) was obtained from Changsha Liyuan New Material Co., Ltd., China. Dipterex (O,O-dimethyl-1-hydroxy-2,2,2-trichloroethyl phosphonate, C$_4$H$_8$Cl$_3$O$_4$P, its molecular structure is given in Fig. 1) was purchased from the Hunan Nantian Industrial Co., Ltd., China. Tetrabutyl titanate, absolute ethyl alcohol, silver nitrate and potassium dichromate, 1,10-phenanthroline, ferrous ammonium sulfate, and silver sulfate were of analytical grade and were used as received without further purification. Deionized and doubly distilled water was used throughout the study.
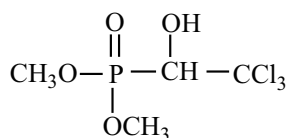

Fig. 1 Molecular structure of dipterex.

Apparatus included a self-made photoelectrocatalytic reactor, 125 W high pressure mercury lamp, ultraviolet spectrum radiometer (USR), UV-Visible spectrometer (UV-Vis), 78–1 magnetic agitator, 101-A-1 electric-blasting drying oven, F48020–33 muffle furnace, LW5J5 D.C.-stabilized power supply, COD detector (Hana Co., Ltd., Italy), Field Emission Scanning Electron Microscope (Dutch FEI Sirion 200) and Crystal X-ray Diffractometer (Shimadzu D/MAX-3B, Cu target).

1.2 Preparation of TiO$_2$/Ni photo electrode

The 40 mL absolute ethyl alcohol and 10 mL Ti(OC$_4$H$_9$)$_4$ were added to a beaker, and stirred to form solution A; 10 mL anhydrous ethyl alcohol and 3 mL distilled water were placed into another beaker, with nitric acid added to adjust the pH to 3–4 to form solution B, respectively. Solution A was mixed with solution B at 1–2 drops/sec and magnetic mixing for 15 min, and the resulting precipitate was continuously stirred until it was completely peptized to form a stable colloidal suspension. Thin-film photo electrodes were dip-coated onto both sides of pretreated porous nickel net. A sequence of dipping, drying and firing at 500°C for 2 hr was used after each coating (five repetitions), then the TiO$_2$/Ni electrode was obtained after natural cooling (Guaraldo et al., 2011).

1.3 Experimental setup and analytical method

A diagram of the experimental apparatus and the electrode assembly used for photoelectrocatalytic degradation of dipterex is shown schematically in Fig. 2. The photoreactor system consisted of a cylindrical quartz glass with a double electrode configuration and a 125 W high pressure mercury lamp with a main emission at 365 nm as an external UV light source. The lamp was positioned parallel with the anode, at a distance of about 15 cm; the irradiance was measured to be 4.23 mW/cm^2 by USR detection. In this reactor, the TiO$_2$/Ni electrode served the photo anode, Pt sheet was the cathode, and the electrode pair was dipped in the dipterex pesticide wastewater to a depth of 10 cm, with the electrodes approximately 4 cm apart. The effective area of the electrode pair was 10 cm^2. Electrical voltage was provided by a manually controllable D.C power supply operating in the constant current mode (range: 0–400 mA). The COD value of the dipterex solution before and after degradation was determined using the COD detector according to the GB11914–89 method. After sampling every 30 min and testing the COD value, the COD removal rate (η) can be described as Eq. (1) (Guida et al., 2007):

$$\eta = \frac{COD_0 - COD_t}{COD_0} \times 100\% \tag{1}$$

where, η is the COD removal rate of the dipterex, COD$_0$ is chemical oxygen demand of the initial solution, and COD$_t$ is chemical oxygen demand of the solution after reaction t
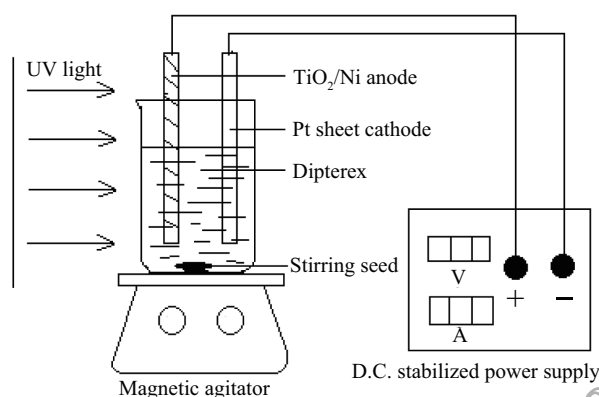

Fig. 2 Schematic diagram of the experimental setup.

time.

Photoelectrocatalytic degradation of dipterex and one of the products (PO_4^{3-}) in the solution were investigated using a molybdate-antimony-scandium spectrophotometry method at the wavelength 650 nm. The concentration of organophosphorus in the initial dipterex pesticide was 0.155 mmol/L. The organophosphorous conversion (R) of dipterex was calculated as shown in Eq. (2):

$$R = \frac{P_t}{P_0} \times 100\% \tag{2}$$

where, P_t is the content of inorganic phosphorus in the solution after reaction t time, and P_0 is the content of organic phosphorus in the initial solution.

2 Results and discussion

2.1 SEM and XRD analysis of TiO$_2$/Ni electrode

The microstructures of the TiO$_2$/Ni electrode and sintered bulk materials were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The SEM images are displayed in Figure 3a, b. From Fig. 3a, we can see that the surface of the nickel foam skeleton is covered with sintered TiO$_2$. The results indicated that the foamed nickel net is a good electrode material due to its huge specific surface area, which greatly improves its ability to adsorb the pollutants. This created favorable conditions for the degradation of dipterex. Figure 3b shows a 35,000-fold magnification of the TiO$_2$/Ni electrode, and the sintered TiO$_2$ layer with network surface morphology was observed. It has been shown that the TiO$_2$ disperses uniformly on the surface of the skeleton.

The crystal structure of the TiO$_2$ electrodes coated on the porous nickel net (TiO$_2$/Ni) was analyzed with the X-ray apparatus and the XRD patterns of TiO$_2$/Ni are shown in Fig. 4. The patterns show that the peaks of foamed nickel appear at 2θ of 44.635°, 52.147° and 77.621°. The other six peaks at 2θ of 25.556°, 37.318°, 48.279°, 54.362°, 56.636° and 62.845° correspond to the TiO$_2$ (101), (004), (200), (105), (211) and (204) reflections, respectively. The target product of anatase TiO$_2$ was verified by comparison with the JCPDS standard diffraction card. From the XRD patterns, no other diffraction peaks except for the peaks of the foam nickel and TiO$_2$ anatase structure were detected. The average crystallite size of TiO$_2$ (D) was calculated by the Debye-Scherrer Equation (Klug and Alexander, 1974):

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{3}$$

where, K is the Scherrer constant $K = 0.89$, and β is the peak width at half maximum. The calculated average particle size perpendicular to the TiO$_2$ (101) crystal plane was 23.7 nm. The result revealed that nanometer-size TiO$_2$ had been prepared on the nickel foam net surface.

To optimize the photoelectrocatalytic system with respect to maximum performance for dipterex degradation, several parameters including degradation time, different electrolytes, chloride concentration, current density, pH, and four kinds of degradation methods in the photoelectrocatalytic process were tested.

2.2 Effect of degradation time

Under the photoelectrocatalytic conditions of initial concentration of dipterex 40 mg/L, 0.02 mol/L NaCl as the supporting electrolyte, current density $j = 2.0$ mA/cm^2 and neutral pH, the relationship between the dipterex COD removal rate and degradation time is shown in Fig. 5.
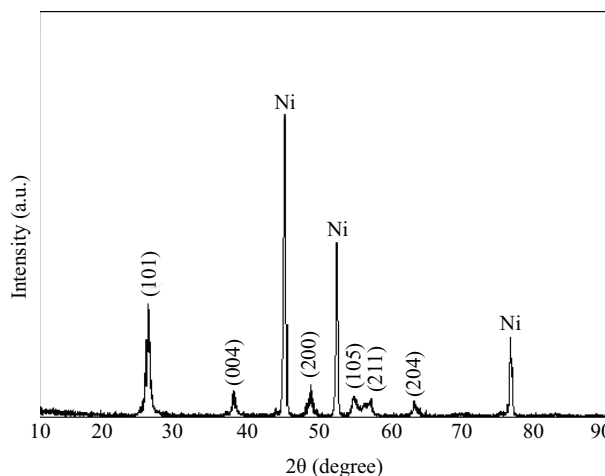

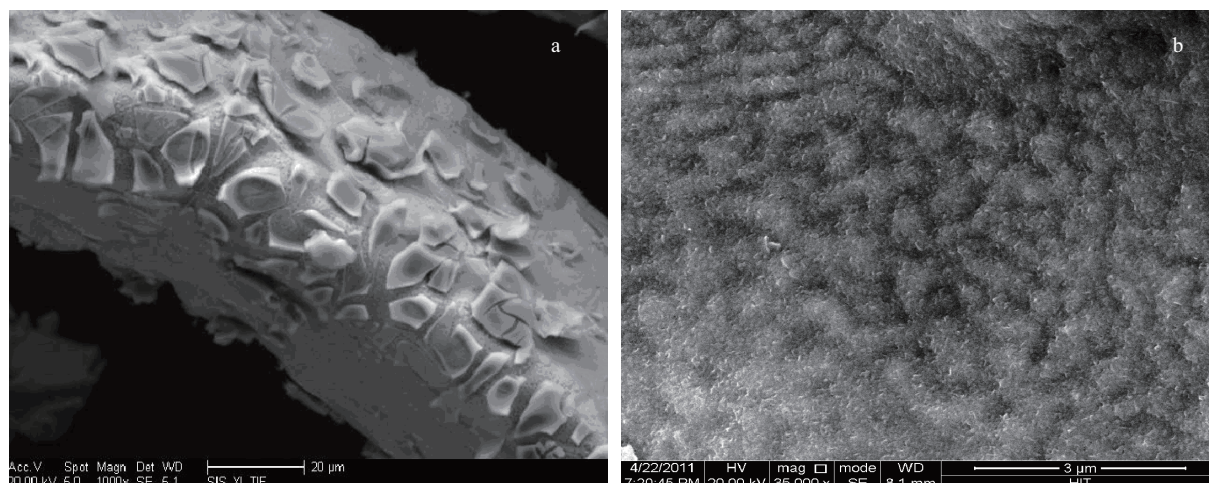**Fig. 4** XRD patterns of TiO$_2$/Ni electrode.

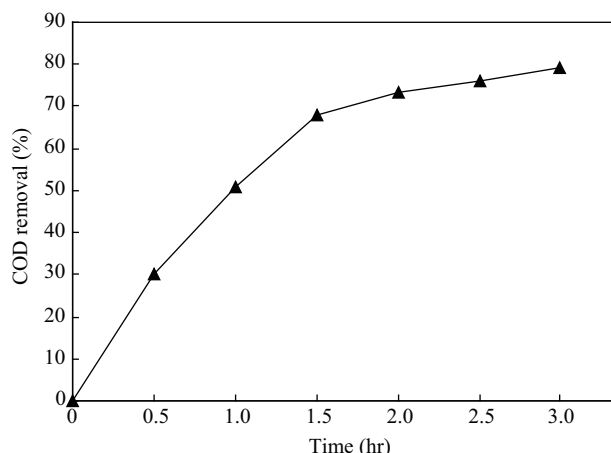
Fig. 3 SEM images of TiO$_2$/Ni electrode.

Fig. 5 Effect of time on dipterex COD removal. Conditions: dipterex 40 mg/L; NaCl 0.02 mol/L; j 2.0 mA/cm^2; natural pH.

The results show that during the initial 2 hr of the photoelectrocatalytic reaction, the COD degradation rate of dipterex continuously increased with increasing time. The dipterex COD removal rate was 76.2% at 2 hr, whereas the COD degradation rate change was very slow in the next hour, and the COD degradation rate only reached 79.4% after 3 hr. Consequently, we considered that the reaction had been essentially completed, and 2 hr was selected as the chemical reaction time in subsequent experiments.
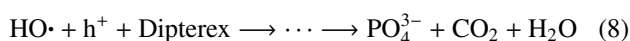
The photocatalytic degradation of dipterex is believed to take place according to the following mechanism. When TiO$_2$ is exposed to UV radiation, electrons are promoted from the valence band to the conduction band. As a result the electron-hole pairs are produced (Bukallah et al., 2007; Phanikrishna et al., 2008):

$$TiO_2 + h\nu \longrightarrow e_{cb}^- + h_{vb}^+ \tag{4}$$

where, e_{cb}^- and h_{vb}^+ are electrons in the conduction band and electron vacancies in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they can enter a redox reaction with other species present on the surface. In most cases, h_{vb}^+ can react easily with surface-bound H$_2$O to produce hydroxyl radicals (HO·), whereas, e_{cb}^- can react with O$_2$ to produce the superoxide radical anion of oxygen.

$$H_2O + h_{vb}^+ \longrightarrow HO\cdot + H^+ \tag{5}$$

$$O_2 + e_{cb}^- \longrightarrow O_2^-\cdot \tag{6}$$

This reaction prevents the recombination of the electron and the hole which are produced in the first step. The HO·, H$^+$ and O$_2^{\bullet-}$ produced in the above manner can then react with the dipterex molecule to form other species and are thus responsible for the COD removal of the dipterex.

$$O_2^-\cdot + H_2O \longrightarrow H_2O_2 \longrightarrow 2HO\cdot \tag{7}$$

$$HO\cdot + h^+ + Dipterex \longrightarrow \cdots \longrightarrow PO_4^{3-} + CO_2 + H_2O \tag{8}$$

2.3 Effect of different electrolytes

To further study the effects of different electrolytes on the degradation of dipterex, 0.02 mol/L of NaNO$_3$, Na$_2$SO$_4$ and NaCl electrolyte were used in the reaction system, respectively. For initial concentration of dipterex of 40 mg/L, current density $j = 2.0$ mA/cm^2, and photoelectrocatalytic degradation time of 2 hr, the result is shown in Fig. 6.

It can be seen that at different reaction phases, the COD removal rate of dipterex with NaCl as the electrolyte is significantly higher than with the NaNO$_3$ and Na$_2$SO$_4$ electrolytes. After 2 hr reaction the COD removal rates of the Na$_2$SO$_4$ and NaNO$_3$ electrolyte systems were 59.7% and 53.8%, respectively. However, the removal rate reached 78.8% in the NaCl electrolyte system. The results indicated that adding NaCl to the wastewater increases the solution conductivity, decreases the energy consumption, and promotes indirect anodic oxidation by producing hypochlorite at the anode. The participation of Cl$^-$ can significantly reduce the COD value of dipterex. Furthermore, the effect of different concentrations of NaCl on the degradation of dipterex was also investigated, and the results are shown in Fig. 7. NaCl electrolytes (0.01, 0.02, 0.05 and 0.10 mol/L) were added to the photoelectrocatalytic system, respectively. It can be seen from Fig. 7 that the greater the NaCl concentration, the higher the COD removal rate of dipterex. The results may be attributed to two aspects: First, the TiO$_2$/Ni electrode
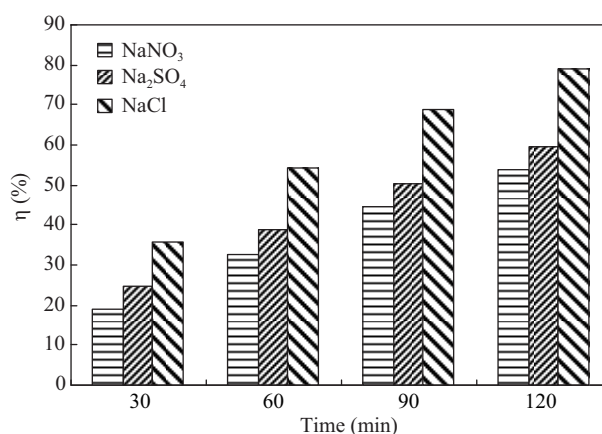

Fig. 6 Effect of various electrolytes on dipterex COD removal. Conditions: dipterex 40 mg/L; NaNO$_3$, Na$_2$SO$_4$, and NaCl 0.02 mol/L; j 2.0 mA/cm^2, time 2 hr.
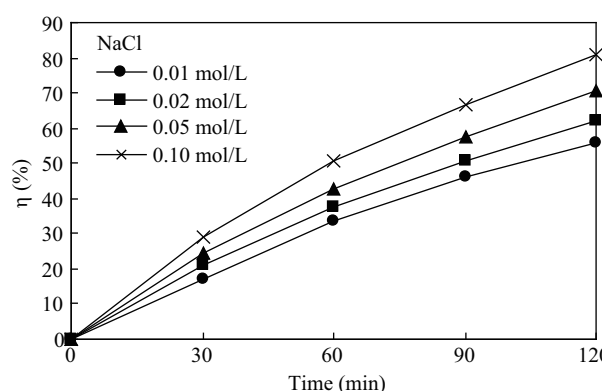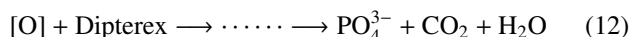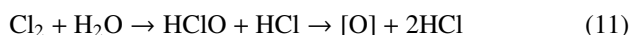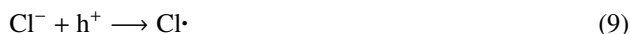

Fig. 7 Effect of NaCl concentrations on dipterex COD removal. Conditions: dipterex 40 mg/L; j 2.0 mA/cm^2, time 2 hr.

under UV radiation can generate electron-hole pairs by the application of current, and the COD removal of dipterex can take place in accordance with the above photocatalytic reaction (Reactions (4)–(8)). Second, Cl⁻ can adsorb on the surface of titanium dioxide and be converted to high oxidative activity groups (Cl·, Cl₂ and HClO) by electron-hole pairs. The groups can then oxidize the pollutants effectively, therefore the removal efficiency of dipterex COD will increase. The reaction process is as follows (Ghaly et al., 2007):

$$Cl^- + h^+ \longrightarrow Cl\cdot \qquad (9)$$

$$Cl\cdot + Cl\cdot \longrightarrow Cl_2 \qquad (10)$$

$$Cl_2 + H_2O \rightarrow HClO + HCl \rightarrow [O] + 2HCl \qquad (11)$$

$$[O] + Dipterex \longrightarrow \cdots\cdots \longrightarrow PO_4^{3-} + CO_2 + H_2O \qquad (12)$$

With the increase of NaCl, the degradation of dipterex may be aided in this way. Nonetheless, excessive NaCl has been found to have an inhibitory effect on COD removal, and h⁺ react faster with Cl⁻ than with undissociated dipterex molecules. Therefore, 0.02 mol/L NaCl was chosen for further study.

2.4 Effect of current density

Current density is a very important variable in photoelectrocatalytic engineering. The effects of current density on COD removal are displayed in Fig. 8. As can be seen, the COD removal rate of dipterex increased with increasing current density. When current density was 0.5, 1.0, 1.5, 2.0 and 2.5 mA/cm², the dipterex COD removal rate was 55.8%, 62.3%, 69.9%, 77.8% and 80.9%, respectively. The amount of hypochlorite produced increased with increasing applied current density: the higher the current density and the more hypochlorite produced, the more COD was removed by the reaction of dipterex and hypochlorite. Thus, the electron and hole recombination process was inhibited, and the photoelectrocatalytic reaction system had more holes h⁺ present (Wang et al., 2009). The results demonstrated that the more active groups (HClO, Cl₂, Cl·, OCl⁻) greatly increased the removal efficiency of dipterex COD. In addition, the electrical conductivity of the Ni carrier is six times that of a Ti substrate, so the nickel electrode current density will be greater than that of a Ti electrode for the the same bias voltage in a photoelectrocatalytic system,
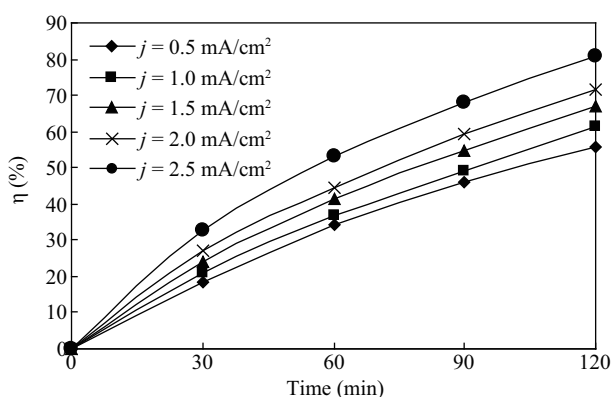
which results in better separation of electron-hole pairs and further increase in the COD removal rate of dipterex. Therefore, we chose the current density $j = 2.5$ mA/cm² for subsequent research.

2.5 Effect of initial pH

Under the conditions of 0.02 mol/L NaCl and $j = 2.5$ mA/cm², the effect of the original pH value (pH 1.0, 3.0, 5.0, 6.0 and 7.0) on the photoelectrocatalytic degradation of dipterex was investigated. The results are shown in Fig. 9.

Dipterex, which is a weak acid pesticide with a p$K\alpha$ value of 6.18, can quickly yield more poisonous DDVP on basic hydrolysis. Therefore, effects of pH on the dipterex COD removal rate were studied under acidic and neutral conditions. As can been seen from Fig. 9, with the pH from 1.0 to 7.0, the dipterex degradation rate was optimal at pH 6.0. This result was consistent with observations by researchers studying PEC degradation of imidacloprid (Philippidis et al., 2009). The pH influences the PEC process in many ways, such as TiO₂ flat-band potential variation and changes in adsorption ability of the dipterex on the TiO₂ film (Kesselman et al., 1997). The most likely reason for this is that the TiO₂ isoelectric point pH is 6.28; when the initial solution pH lower than 6.28, the TiO₂ surface carries a positive charge, increasing the tendency of dipterex negative ions to migrate and adsorb on the surface of TiO₂, which is beneficial to the beginning of the photoelectrocatalytic reaction. However, increased acidity protonates the molecules of dipterex so that they are no longer negatively charged, and reduces their adsorption and the photoelectrocatalytic activity of TiO₂. Moreover, the acid solution could increase the corrosion of the foamed nickel carrier, and disrupt the normal conduction of the TiO₂ catalyst. This may be one of the causes of its lower catalytic activity. The experimental result showed that the optimum pH value was 6.0.

2.6 Effect of different degradation methods

By a series of experiments, the optimal processing conditions were obtained as follows: the concentration of dipterex and the supporting electrolyte NaCl solution concentration were 40 mg/L and 0.02 mol/L, respectively, reaction time 2 hr, the current density $j = 2.5$ mA/cm² and initial pH of 6.0.

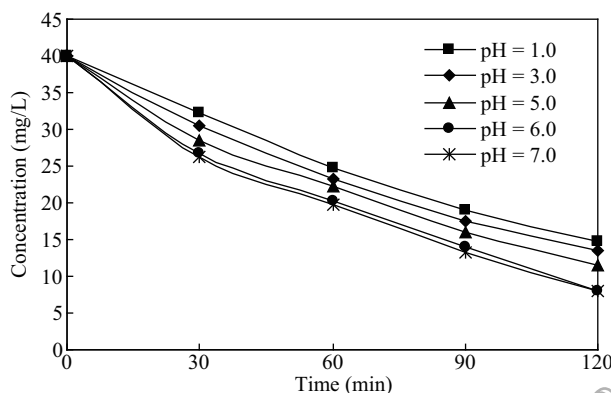**Fig. 8**   Effect of current density on dipterex COD removal.

Fig. 9   Effect of pH on dipterex concentration.

The effect of photodegradation (PD), photocatalytic degradation (PC), electrocatalytic degradation (EC) and photoelectrocatalytic degradation (PEC) on the degradation of dipterex were analyzed by four separate degradation experiments. From Fig. 10, the results revealed that the dipterex COD removal rate showed almost no change when induced by UV light after 2 hr. However, during the photocatalytic (PC), electrocatalytic (EC) and photoelectrocatalytic (PEC) reactive processes, the COD degradation rate reached 42.9%, 30.3% and 82.6%, respectively. The reason is that TiO_2 produced electron-hole pairs under the excitation of UV light, and the external potential applied to the anode prevented the electrons and holes' recombination. Moreover, the chloride ions were converted into more active groups by the electron-hole pairs' oxidation. The results also demonstrate that the photoelectrocatalytic efficiency was better than the photocatalytic efficiency and electrocatalytic efficiency, respectively. The results further confirm that the light and electrical power do play synergistic roles.

2.7　Organophosphorous conversion of dipterex and its oxidation products

The optimal conditions for photoelectrocatalytic degradation of high-COD dipterex wastewater were obtained by the above experiments. Tests show that the toxicity of the main intermediate product during the degradation is stronger than dipterex itself, so, only degrading dipterex completely can eliminate its toxicity. In order to get a clear understanding of whether the photoelectrocatalytic process degraded dipterex completely or not, therefore, the dipterex degradation rate was obtained by determination of the final product PO_4^{3-}. The concentration of inorganic PO_4^{3-} was measured using the molybdate-antimony-scandium spectrophotometry method. The organophosphorous conversion of dipterex was calculated according to the Eq. (2).

Figure 11 shows the change in the absorption spectrum of 40 mg/L dipterex during its photoelectrocatalytic degradation at the optimized conditions. The absorption is seen to decrease in intensity with increasing reaction time, vanishing almost completely within about 120 min.
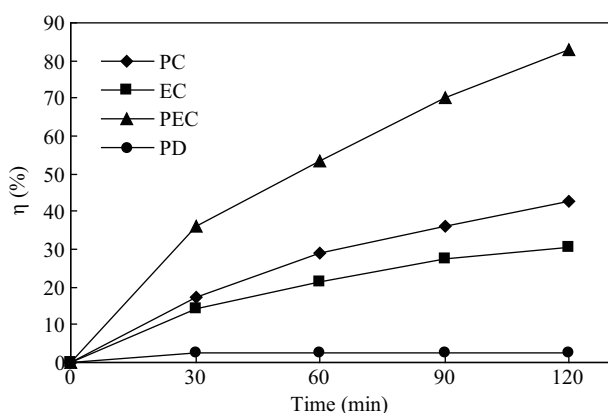

Fig. 10　Effect of different degradation methods on dipterex COD removal. PC: photocatalytic; EC: electrocatalytic; PEC: photoelectrocatalytic; PD: only photo. Conditions: dipterex 40 mg/L; NaCl 0.02 mol/L; j 2.5 mA/cm^2; time 2 hr; pH 6.0.
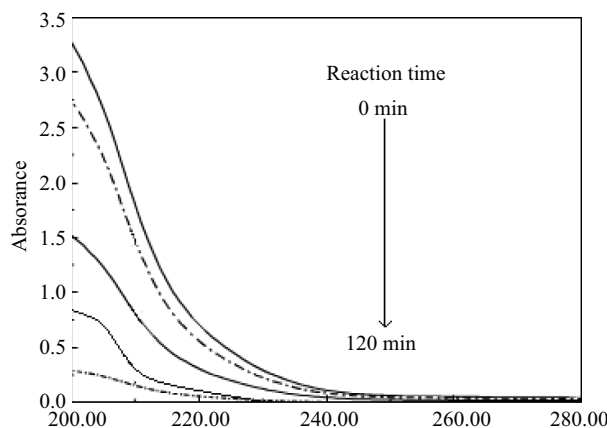

Fig. 11　UV-Vis absorption spectra of dipterex during the photoelectrocatalytic degradation at different reaction time.

The disappearance of the absorption peak with the reaction time indicates the effective decomposition of the dipterex molecule.

It can be seen from Fig. 12 that the removal rate of COD and organophosphorus conversion of dipterex would rise with the prolonging of reaction time, but the former is a bit lower than the latter; under the optimal conditions of photoelectrocatalysis, the degradation rates were up to 82.6% and 83.5%, respectively. Degradation of dipterex mainly depends on the OH·, activated Cl· and atomic state oxygen [O] and so on in the photoelectrocatalyitic system (Reactions (4)–(12)). These activated groups can break down the P=O bond, and finally it oxidizes into PO_4^{3-}, CO_2 and other end-products.
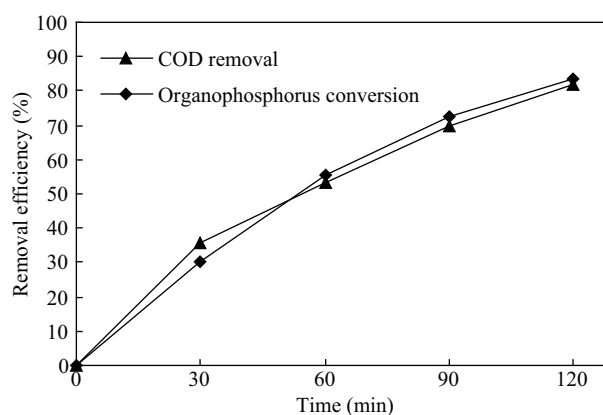

Fig. 12　COD removal contrast to organophosphorus conversion of dipterex under optimal conditions.

3　Conclusions

In this study, a nano TiO_2 thin film electrode deposited on porous nickel net was prepared by a sol-gel method, and was utilized in a self-made photoelectrocatalytic device for the degradation of dipterex. The most optimum conditions for dipterex COD removal and organophosphorous were analyzed. The results show that under the optimal conditions of 0.02 mol/L for the NaCl supporting electrolyte, current density j = 2.5 mA/cm^2, pH 6.0, and photoelectrocatalytic treatment of 40 mg/L dipterex for 2 hr,

the COD removal rate and organophosphorous conversion could reach 82.6% and 83.5%, respectively. This study offered a new porous nickel net photocatalyst carrier, which could inhibit the recombination of electrons and holes and enhance the efficiency of photoelectrocatalytic degradation of dipterex pesticide wastewater, compared with the commonly used Ti metal carrier. The research work also establishes a good foundation for subsequent research and practical application in the degradation of organphosphorous pesticide wastewater.

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