

Phenol degradation by anodic oxidation on boron-doped diamond electrode combining TiO₂ Photocatalysis

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Abstract: Boron-doped diamond (BDD) electrocatalysis is combined with photocatalysis using titanium dioxide (TiO₂) as a catalyst to improve pollutant-oxidation efficiency. Phenol solution is chosen as model wastewater. Different methods involving BDD and/or TiO₂ during the degradation processes are compared. Parameters such as the current density and initial concentration are varied in order to determine their effects on the oxidation process. Moreover, the degradation kinetics of phenol is experimentally studied. The results reveal the superiority of series combination of BDD and TiO₂, especially the treatment process of electrocatalysis and succedent photocatalysis, and the optimum working current density for electrocatalysis is 25.48 mA/cm². The removal rate decreases with the increase in the initial phenol concentration and the degradation reaction follows quasi-first-order kinetics equation.

Key words: boron-doped diamond (BDD); anodic oxidation; titanium dioxide; phenol

Phenols are a group of typical pollutants which can be easily found in many industrial wastewaters such as petroleum, petrochemicals, coal conversion, pesticides manufacture and metallurgical operations^[1-2]. Most of these compounds are labeled as being at a high toxicity level and persistence^[3], and thus their recovery or elimination justifies the search for new and improved techniques.

Advanced oxidation processes (AOPs) are widely used techniques in wastewater treatment due to their strong oxidative ability, great efficiency and low selectivity. They are often used in the removal of persistent organic pollutants. AOPs generate hydroxyl radicals ($\cdot\text{OH}$), the second strongest oxidants known after fluorine^[4]. Hydroxyl radicals can react with organics producing dehydrogenated or hydroxylated derivatives, up to the complete mineralization of organics^[5]. One emerging technology, which belongs to AOPs, utilizes illuminated semiconductors and is commonly referred to as photocatalysis^[4,6]. Among the used semiconductors, TiO₂ is the most dominant photocatalyst and is considered very efficient due to the fact that, unlike other semiconductors, it is non-toxic, stable under photocorrosion,

low cost and suitable to work using sunlight energy sources^[7]. Another preferred AOP applied in organics degradation is electrochemical treatment, especially the anodic oxidation. To some extent, the efficiency of anodic oxidation depends on the material of the anode^[8]. The current use of a BDD thin-film electrode in anodic oxidation shows that it possesses technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability and an extremely wide potential window in aqueous media^[9]. All the strengths make BDD an ideal material for the anode in the oxidation of a broad range of organic compounds.

Many studies were carried out using BDD anodic oxidation or TiO₂ photocatalysis (In the following text, the two methods are referred to as BDD or TiO₂ for short) separately in literature to remove or treat phenol compounds^[10-11]. Many of the studies resulted in successful degradation. However, there are still problems concerning incomplete mineralization due to economical or technical reasons. In recent years, efforts have been made to develop systems combining two AOPs^[12-13], yet there are limited studies considering phenol degradation by combining BDD and TiO₂.

This paper compares different ways of treatment for phenol model wastewater based on BDD and TiO₂, and investigates the efficiency of the removal of phenol under corresponding conditions. The influence of applied current and initial concentration of phenol on the mineralization degree is examined and the reaction kinetics is also discussed.

1 Methods

1.1 Materials

Phenol and anhydrous sodium sulfate are obtained from the Guoyao Company, China, both of which are of analytical grade and used as received without further purification. HPLC-grade methanol is purchased from Merck (Germany). The water employed in this study is from AVP-2-35G-01 water-system (Millipore, USA). The TiO₂ sol is prepared as reported by Xu in Ref. [14]. The UV lamp with a maximal wavelength of 365 nm is supplied by Everbright Electronics (Foshan, China)

BDD electrode (boron-doped diamond thin film deposited on a single crystal p-type Si (100) wafer by CVD technology) is supplied by Kanagawa Academy of Science and Technology (Japan); the same size stainless steel plate with high dimensional precision and a fine-polished surface is supplied by Nanjing Jinlian Manufacturing Factory (Nanjing, China). Both electrodes are square type plates with an effective surface area of 3.74 cm².

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1.2 Reactor system

The system has two major parts in this experiment, namely the electrochemical reactor (a 50 mL open and undivided cylindrical glass cell) and the photocatalytic reactor. In the electrochemical reactor, the anode is a BDD electrode and the cathode is a stainless plate. The two electrodes are installed parallel to each other, keeping a 1.4 cm separation. The photocatalytic part is integrated with the electrochemical reactor, including a 9 W UV lamp placed in the center and TiO_2 coated on the interior wall of the container, which finally merges into a combining system, as shown in Fig. 1. The electrodes are not used in separate photocatalysis for sure. Actually the reactor is so designed for the convenience of the whole process. In other words, all the experiments are conducted in the same reactor, but the initiation of the electrocatalysis or the photocatalysis pattern is due to the experimental design.

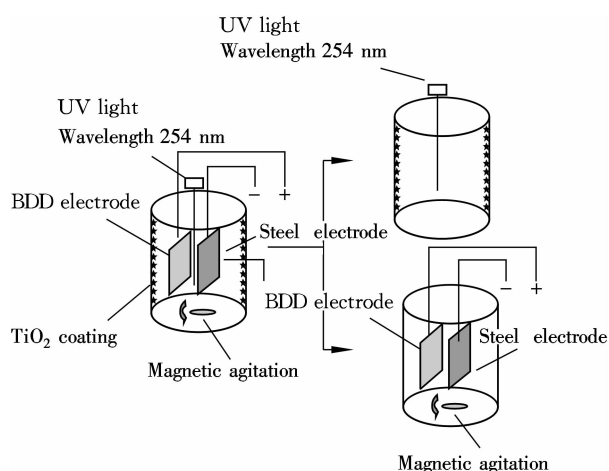


Fig. 1 Electrocatalysis/photocatalysis reactor used for phenol degradation

1.3 Analytical procedure

The substrate conversions during the anodic oxidation of phenol are monitored by HPLC on an Aligent 1100 series, using a reversed-phase Kromasil C18 column (4.6 mm × 250 mm, 5 μm). The UV detector wavelength is set at 256 nm. The mobile phase consists of methanol and double distilled water and the v/v ratio of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ is 68/32 with a flow rate of 0.60 mL/min.

The total organic carbon (TOC) values of the solutions are analyzed using a multi N/C 3000 in order to assess the efficiency of mineralization.

1.4 Experimental procedures

Four groups of experiments with different combinations on the basis of BDD and TiO_2 are conducted so as to acquire the best method for phenol degradation (see Fig. 2). For the experiments of separate photocatalysis, effluent is treated in a photocatalytic pattern for 60 min, while in those of electrocatalysis alone, the same amount of effluent is treated in the electrochemical pattern for 60 min. The series combinations are also applied, that is to treat the effluent in the photocatalytic pattern for 30 min and then the electrocatalysis is followed for another 30 min and vice versa. The reacting

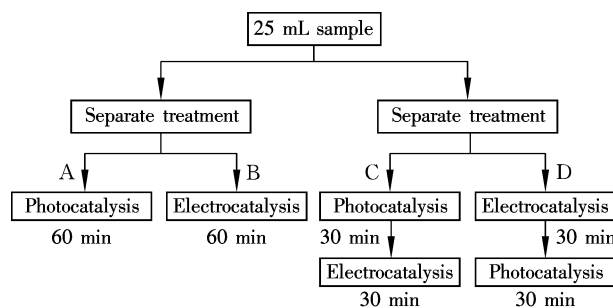


Fig. 2 Experimental flow for finding the most efficient way to remove phenol from model wastewater

time of each group is marked in Fig. 2. Most of the water samples have an initial phenol concentration of 100 mg/L and different phenol concentrations (from 50 to 400 mg/L) are adopted when investigating the effect of the initial concentration on the treatment. The reaction temperature is maintained at 25°C by a cooling jacket and the reaction solution is continuously stirred at a rate of 350 r/min in order to keep it homogeneous. Prior to each reaction, the surface of the electrode should be washed clean with ethanol and ultra-pure water, respectively. Take the BDD + TiO_2 process (see Fig. 2, part D) for example. Reactions are started by adding 25 mL electrolyte into the reactor in the presence of a low concentration supporting electrolyte of 0.1 mol/L Na_2SO_4 and ceased immediately with a power switch at predefined times. After a certain period of electrolyzing time, the system changes to a photocatalysis pattern. Air is sparged using an air distributor through the whole process so as to ensure the sufficiency of oxygen supply^[7]. The concentration of residual phenol in the reaction mixture is analyzed by the HPLC.

2 Results and Discussion

2.1 Comparison of different combinations

The efficiency of phenol degradation with the help of the oxidation system in different combinations of TiO_2 and BDD is investigated, including the separate treatment and the series treatment. The rate of degradation is depicted in Fig. 3 as a function of treatment time. For each experiment, all the conditions are adjusted to the same level except for different patterns involved. As shown in Fig. 3, the removal rates of phenol by the process of combining BDD and TiO_2 are 85.88% and 96.78%, which are higher than those of

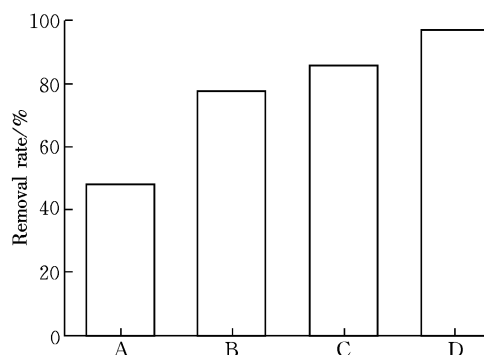
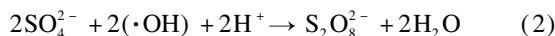
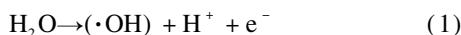


Fig. 3 Removal rate of phenol in different combinations (A, B, C and D are the four groups tested in Fig. 2)

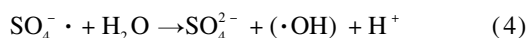
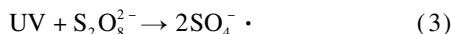
using BDD or TiO₂ separately. The latter groups only achieve a removal rate of 77.61% and 48.01%, respectively. Furthermore, it also shows that the process of electrocatalysis and succedent photocatalysis results in the maximum removal rate.

As is known to all, the photocatalysis that involves the generation of conduction band electrons and valence band holes by the illumination of TiO₂ with light energy is greater than the band gap energy. The holes can act with the donors of electrons such as water, anions OH⁻ and organic products, absorbed at the surface of the semiconductor forming the hydroxyl radicals ($\cdot\text{OH}$). However, there is an unsolved problem existing in photocatalysis, i. e., the recombination of holes and electrons, which greatly influences the efficiency of pollutant degradation. The electrons generated by the radiation of light can easily recombine with holes on TiO₂ and dissipate energy in the form of light/heat. Therefore, electron acceptors are designed to inhibit the process of recombination. O₂ is the most widely employed electron acceptor in many cases and the inorganic peroxides such as hydrogen peroxide and persulphate can also provide positive effects^[15].

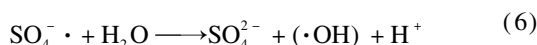
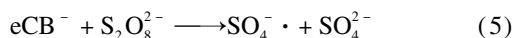
Interestingly, BDD can generate a certain amount of peroxodisulphate from the supporting electrolyte Na₂SO₄^[16-18],



However, peroxodisulphate (mediated electroreagents) is not a very good oxidant itself, and it is even less efficient than conventional oxidation carried out by hydrogen peroxide^[19]. It is probably because peroxodisulphate needs UV radiation or heating to be activated. Therefore, in most cases BDD is applied only in removing phenol, and SO₄²⁻ does not contribute much to the oxidation process. In photocatalysis, peroxodisulphate realizes its function in two ways. On the one hand, the UV lights activate peroxodisulphate to form hydroxyl radicals ($\cdot\text{OH}$),



On the other hand, there are several kinds of electron acceptors such as hydrogen peroxide, potassium bromate and potassium persulphate, etc. Among them, potassium persulphate is proved to be the most effective one^[7]. It can generate reactive species,



Therefore, it is reasonable to combine BDD with TiO₂, making full use of S₂O₈²⁻ produced in electrocatalysis, and finally leading to a higher removal rate of phenol. The BDD + TiO₂ process (shown in Fig. 2, part D) is a promising alternative for the treatment of phenol.

In the following experiments, the BDD + TiO₂ process is used since it exhibits the highest overall activity for degradation

of the model compound under investigation.

2.2 Effect of current density

The current density is an important factor in the electrochemical reaction and it has a great influence on degradation effects. The degradation of 25 mL solution with 100 mg/L of phenol and 0.1 mol/L Na₂SO₄ is done by BDD first at the constant current densities of 10.70, 25.48, 101.91, 133.69 mA/cm². Fig. 4 shows the effects of the current densities. It can be seen from Fig. 4 that higher current densities increase the initial reaction rate and obviously have higher removal efficiency. The results may be attributed to the increase of active intermediates such as hydroxyl and peroxodisulphate. Hydroxyl radical ($\cdot\text{OH}$) is increased dramatically on the surface of BDD under a relatively high current density. It enhances indirect oxidation of phenol on BDD as well as electron transfer speed, namely the direct oxidation speed of phenol. On the other hand, the growing production of S₂O₈²⁻ does not only contribute to electrolysis itself but more importantly, serves as a powerful electron acceptor in the process of photocatalysis. After 30 min, the removal rates of phenol are more than 90%.

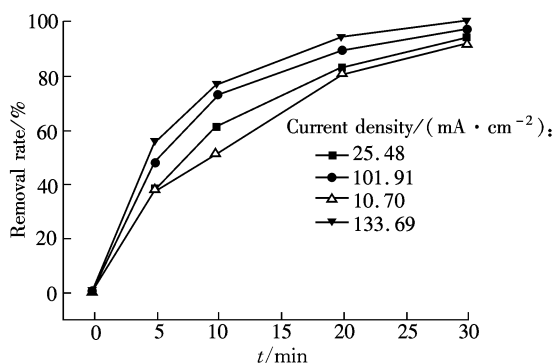


Fig. 4 Effect of current density on the removal rate of 100 mg/L phenol solution in 50 mmol/L Na₂SO₄ at 25°C

However, when the current density is over 101.91 mA/cm², the degradation efficiency increases slowly with the increase in the current density. It is because an overly high current density will severely accelerate anodic polarization and increase side effects such as oxygen generation. At the same time, a large amount of heat is produced, which can greatly reduce the efficiency of electrolysis.

With regard to both degradation efficiency and energy conservation, 25.48 mA/cm² is selected to be the most ideal working current density.

2.3 Effect of initial concentration

In order to find out the effect of initial concentration, experiments are carried out with different initial phenol concentrations (from 50 to 400 mg/L) and a constant current density. Fig. 5 illustrates that the removal rate decreases with the increase in the initial phenol concentration though the actual removed amount of phenol of high concentration outweighs that of low concentration. The inset panel presents corresponding kinetic analysis assuming a pseudo-first-order reaction for phenol.

As is known to all, the Langmuir-Hinshelwood kinetics rate model is widely applied to many works related to photo-

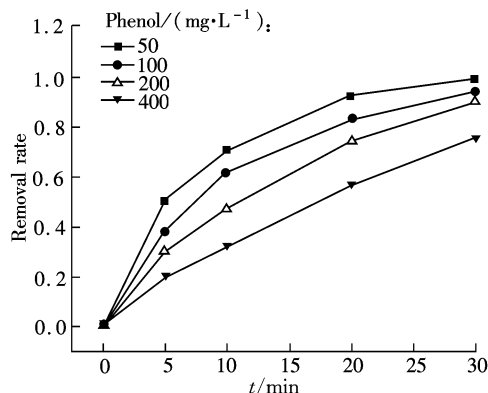


Fig. 5 Effect of initial concentration on the removal rate of different phenol solutions in 50 mmol/L Na_2SO_4 at 101.91 mA/cm^2 , 25 °C

catalysis^[20]. At the same time, an apparent first-order model is also proposed for phenol degradation in electrocatalysis^[21–22]. With regard to the combined effect of the two methods, the reaction kinetics of this experiment can be simplified to the model^[23]:

$$\ln \frac{C_0}{C} = kt$$

where C_0 is the initial phenol concentration, and C is the phenol concentration at any time t ; k is the rate constant for the reaction. Actually, as shown in Fig. 6, the decreasing k values of $2.20 \times 10^{-3} \text{ s}^{-1}$ (square regression coefficient $R^2 = 0.9977$), $1.80 \times 10^{-3} \text{ s}^{-1}$ ($R^2 = 0.9974$), $1.43 \times 10^{-3} \text{ s}^{-1}$ ($R^2 = 0.9869$) and $1.20 \times 10^{-3} \text{ s}^{-1}$ ($R^2 = 0.9678$) are found for the initial phenol concentrations of 50, 100, 200, 400 mg/L, respectively. This suggests a steady and limited production of hydroxyl radicals ($\cdot\text{OH}$) along the degradation process. Therefore, in practical applications, wastewater containing phenol should be treated in the first place so as to achieve the maximal efficiency.

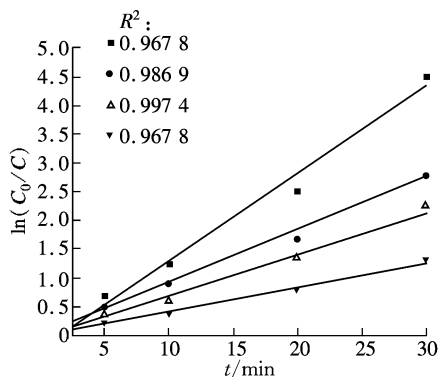


Fig. 6 Pseudo-first order kinetics fitting of phenol degradation

2.4 Mineralization

It is far less than needed that we only study the variation of phenol concentration because phenol can produce a series of intermediates^[24]. Therefore, the rate of TOC removal should also be given attention to ensure a final mineralization of phenol. A phenol solution of 100 mg/L is chosen to study the mineralization of phenol in the treatment process.

The composition in the reaction mixture is monitored both by HPLC and TOC (see Fig. 7). Experimental HPLC results show that phenol is quickly oxidized into organic compounds. TOC results also show that the intermediate organic species remain in the solution for a longer time and are eventually mineralized into CO_2 and H_2O . Comparing the HPLC and TOC curves, it is obvious that the organic intermediate species degrade at a much slower rate than that of phenol.

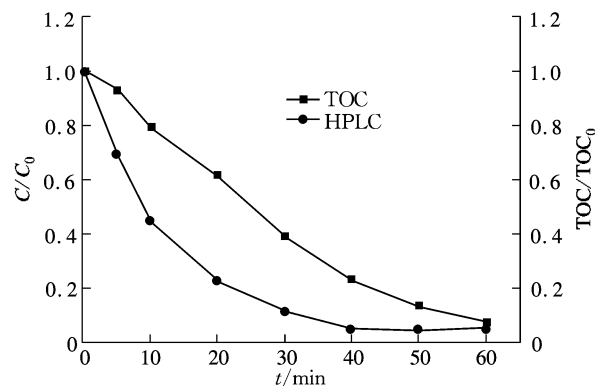


Fig. 7 Degradation of 100 mg/L phenol solution in 50 mmol Na_2SO_4 at 101.91 mA/cm^2 , 25 °C in terms of HPLC and TOC

3 Conclusion

The results of this study show that among all the oxidation processes conducted here, the combination of BDD and TiO_2 treatment has higher efficiency in removing phenol, particularly, the method of electrocatalysis and succedent photocatalysis. It is probably ascribed to the production of $\text{S}_2\text{O}_8^{2-}$ during electrocatalysis which is helpful in the degradation of phenol with the help of TiO_2 . Taking both degradation efficiency and energy conservation into consideration, 25.48 mA/cm^2 is selected to be the most ideal working current density. As for the initial concentration, the removal rate decreases with the increase in the initial phenol concentration though the actual removed amount of high concentration outweighs that of low concentration. Comparing HPLC and TOC, it is obvious that the organic intermediate species degrade at a much slower rate than that of phenol. Kinetic studies of phenol are also investigated in this experiment and it is found that the degradation kinetics fits the pseudo-first order reaction.

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References

- [1] Santos A, Yustos P, Quintanilla A, et al. Kinetic model of wet oxidation of phenol at basic pH using a copper catalyst [J]. *Chem Eng Sci*, 2005, **60**(17): 4868–4880.
- [2] Santos A, Yustos P, Cordero T, et al. Catalytic wet oxidation of phenol on active carbon: stability, phenol conversion and mineralization [J]. *Catal Today*, 2005, **102/103**: 213–218.
- [3] Cañizares P, Lobato J, Paz R, et al. Electrochemical oxidation of phenolic wastes with boron-doped diamond anodes [J]. *Water Res*, 2005, **39**(12): 2687–2702.

- [4] Hadj Salah N, Bouhelassa M, Bekkouche S, et al. Study of photocatalytic degradation of phenol [J]. *Desalination*, 2004, **166**: 347–354.
- [5] Brillas E, Sirés I, Arias C, et al. Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode [J]. *Chemosphere*, 2005, **58**(4): 399–406.
- [6] Fujishima A, Rao T N, Tryk D A. TiO₂ photocatalysts and diamond electrodes [J]. *Electrochim Acta*, 2000, **45**(28): 4683–4690.
- [7] Qourzal S, Barka N, Tamimi M, et al. Photodegradation of 2-naphthol in water by artificial illumination using TiO₂ photocatalyst: identification of intermediates and the reaction pathway [J]. *Appl Catal A: Gen*, 2008, **334**(1/2): 386–393.
- [8] Szpyrkowicz L, Kaul S N, Neti R N, et al. Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater [J]. *Water Res*, 2005, **39**(8): 1601–1613.
- [9] Sirés I, Cabot P L, Centellas F, et al. Electrochemical degradation of clofibric acid in water by anodic oxidation comparative study with platinum and boron-doped diamond electrodes [J]. *Electrochim Acta*, 2006, **52**(1): 75–85.
- [10] Guo Z F, Ma R X, Li G J, et al. Degradation of phenol by nanomaterial TiO₂ in wastewater [J]. *Chem Eng J*, 2006, **119**(1): 55–59.
- [11] Colón G, Sánchez-España J M, Hidalgo M C, et al. Effect of TiO₂ acidic pre-treatment on the photocatalytic properties for phenol degradation [J]. *Journal of Photochemistry and Photobiology A*, 2006, **179**(1/2): 20–27.
- [12] Torres R A, Pétrier C, Combet E, et al. Bisphenol A mineralization by integrated ultrasound-UV-iron(II) treatment [J]. *Environ Sci Tech*, 2007, **41**(1): 297–302.
- [13] Torres R A, Nieto J I, Combet E, et al. Influence of TiO₂ concentration on the synergistic effect between photocatalysis and high-frequency ultrasound for organic pollutant mineralization in water [J]. *Appl Catal B: Environ*, 2008, **80**(1/2): 168–175.
- [14] Xu J J, Ao Y H, Fu D G, et al. A simple route to synthesize highly crystalline N-doped TiO₂ particles under low temperature [J]. *J Cryst Growth*, 2008, **310**(19): 4319–4324.
- [15] Gimeno O, Carnajo M, Lopez M J, et al. Photocatalytic promoted oxidation of phenolic mixtures: an insight into the operating and mechanistic aspects [J]. *Water Res*, 2007, **41**(20): 4672–4684.
- [16] Panizza M, Cerisola G. Removal of colour and COD from wastewater containing acid blue 22 by electrochemical oxidation [J]. *J Hazard Mater*, 2008, **153**(1/2): 83–88.
- [17] Skoumal M, Arias C, Cabot P L, et al. Mineralization of the biocide chloroxylenol by electro-chemical advanced oxidation processes [J]. *Chemosphere*, 2008, **71**(9): 1718–1729.
- [18] Michaud P A, Panizza M, Ouattara L, et al. Electrochemical oxidation of water on synthetic boron-doped diamond thin film anodes [J]. *J Appl Electrochem*, 2003, **33**(2): 151–154.
- [19] Louhichi B, Ahmadi M F, Bensalah N, et al. Electrochemical degradation of an anionic surfactant on boron-doped diamond anodes [J]. *J Hazard Mater*, 2008, **158**(2/3): 430–437.
- [20] Zhang X, Wu F, Wu X W, et al. Photodegradation of acetaminophen in TiO₂ suspended solution [J]. *J Hazard Mater*, 2008, **157**(2/3): 300–307.
- [21] Wang Y Q, Gu B, Xu W L. Electro-catalytic degradation of phenol on several metal-oxide anodes [J]. *J Hazard Mater*, 2009, **162**(2/3): 1159–1164.
- [22] Makgae M E, Klink M J, Crouch A M. Performance of sol-gel titanium mixed metal oxide electrodes for electro-catalytic oxidation of phenol [J]. *Appl Catal B: Environ*, 2008, **84**(3/4): 659–666.
- [23] Ollis D F. Contaminant degradation in water [J]. *Environ Sci Tech*, 1985, **19**(6): 480–484.
- [24] Tahar N B, Savall A. Mechanistic aspects of phenol electrochemical degradation oxidation on a Ta/PbO₂ anode [J]. *J Electrochem Soc*, 1998, **145**(10): 3427–3435.

掺硼金刚石电极结合二氧化钛光催化阳极氧化降解苯酚

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摘要: 采用二氧化钛光催化结合掺硼金刚石电催化来提高污染物氧化效率. 以苯酚作为模型废水污染物, 分别比较了采用 BDD 电催化和 TiO₂ 光催化以及两者结合方法的降解过程, 研究了电流密度和初始浓度等条件对降解效果的影响, 并进行了反应动力学讨论. 实验结果表明: 与单独处理相比, BDD 和 TiO₂ 组合处理方法拥有较优的苯酚去除效果, 尤其是先电解后光催化的方式, 其最优工作电流密度为 25.48 mA/cm², 并且随着苯酚初始浓度增加, 去除率随之下降. 动力学研究表明反应符合准一级动力学方程.

关键词: 掺硼金刚石; 阳极氧化; 二氧化钛; 苯酚

中图分类号: TQ150.9