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Anodic oxidation process for the degradation of 2, 4-dichlorophenol in aqueous solution and the enhancement of biodegradability

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ABSTRACT

Degradation of 2, 4-dichlorophenol (2, 4-DCP) in aqueous media by anodic oxidation using Ti-based oxide electrode has been studied. Additionally, the influence of anodic oxidation on the biodegradability of 2, 4-DCP solution was investigated. It was found that alkaline media was suitable for the anodic oxidation of 2, 4-DCP, while acidic media tended to cause more 2, 4-DCP volatizing. The poor degradation of 2, 4-DCP was ascribed to the direct anodic oxidation at lower anodic potential, while the indirect anodic oxidation was responsible for the better degradation at higher anodic potential with a high power consumption. The variation of COD and the characteristic of UV-vis spectra indicated that some organic intermediates were produced during the course of the degradation of 2, 4-DCP. The obvious inhibition of microbial activity was observed when 2, 4-DCP concentration was about 100 mg/L. The anodic oxidation process was able to enhance the biodegradability of 2, 4-DCP solution and this enhancement became greater with the extension of anodic oxidation treatment. This work suggests that the anodic oxidation with the Ti/IrO₂/RuO₂/TiO₂ electrode generally applied in chemical industry is a promising alternative for the pretreatment of the wastewaters containing chlorophenols.

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1. Introduction

Among the various organic wastes, chlorophenols are significantly harmful environmental pollutants due to their high toxicity, recalcitrance, bioaccumulation, and persistence in the environment. The increasing contamination of industrial wastewaters containing chlorophenols refractory to conventional methods has attracted much attention, which promoted the development of new technologies able to degrade these contaminants. In the last two decades, many methods have been investigated for the degradation of chlorophenols including biological processes, active carbon adsorption, incineration, liquid membrane and permanganate oxidation. Though biological processes cost less than other technologies, they are ineffective in treating chlorophenols at higher concentration because of the inhibition of microbial activity caused by chlorophenols, while other conventional technologies like adsorption, incineration, etc., are either economically unfeasible or environmentally incompatible. In recent years, several advanced oxidation processes (AOPs) such as electrochemical anodic oxidation [1,2], electro-Fenton oxidation [3,4], Fenton oxi-

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dation [5] and photochemical oxidation [6] have been proposed for the degradation of chlorophenols.

As one of popular AOPs, anodic oxidation does not require the addition of large amounts of chemicals to wastewater; moreover, there is no tendency to produce secondary pollution and fewer accessories are required [7]. These advantages make the anodic oxidation more attractive than other oxidation processes. This method has been thoroughly investigated in the treatment of organic waste waters using various anodes such as stainless steel, graphite, glassy carbon, carbon fiber, Pt, Ti/Pt, Ti/RuO2, Ti/IrO2, Ti/PbO2, Ti/SnO2 and conductive diamond films [8-11]. Unfortunately, until now none of these materials can be applied extensively taking account of their activity, stability and price. Among these anodes, though conductive diamond can present a high current efficiency, its price is unacceptable. While the current efficiencies obtained from the rest anodes are much lower due to the oxidation of water generating O₂, which results in a high energy consumption [12,13]. For instance, Rajkumar et al. investigated the anodic degradation of mixed phenolic compounds using Ti/TiO₂-RuO₂-IrO₂ electrode in the presence of chloride. The results showed when COD removal was 83%, the energy consumption of 1 kg COD removal reached to 191.6 kWh [14]. Therefore, from an economical point of view, since electrochemical oxidation process is fairly expensive in comparison with biological treatment, the former should not be considered as a single treatment for a real waste but as: (a) a finishing stage in a combined process for advanced treatment or (b) as an auxiliary

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unit to enhance the biodegradability of waste waters followed by biological treatment.

According to the present results, though the Ti-based oxide electrodes coated with IrO₂, RuO₂ and TiO₂ have been used in some electrochemistry industries, little is known about their application in the degradation of chlorophenols. On the other hand, the possibility to couple photocatalytic and biological methods has attracted the attention of many researchers in recent times [15,16]. Although it may be feasible to enhance the biodegradability of wastewaters by electrochemical oxidation, few attempts have been made to couple electrochemical and biological methods for wastewater remediation. Vlyssides et al. reported that the biodegradability of textile dye wastewater was improved evidently after treated by the anodic oxidation of Ti/Pt [17]. Nevertheless, until now the results about using anodic oxidation process to enhance the biodegradability of chlorophenols in water solution almost cannot be found in literature. Hence, in this work, the degradation of 2, 4-DCP by anodic oxidation using Ti/IrO₂/RuO₂/TiO₂ anode was carried out. In addition, the influence of anodic oxidation on the biodegradability of 2, 4-DCP in water solution was also investigated.

The purposes of this work were to gain a better insight into the application of anodic oxidation to the degradation of 2, 4-DCP and the enhancement of biodegradability using the anode which has been generally applied in chemical industry. It can present valuable information about the possibility of 2, 4-DCP degradation by anodic oxidation coupled with biological processes.

2. Materials and methods

2.1. Chemicals

 $H_2 IrCl_6 \cdot 6H_2 O$ (purity 99.9%) and RuCl₃·XH₂O (purity 99.95%) were supplied by Shanghai Jiuling Chemical Co., Ltd. Other chemicals were either HPLC or analytical grade from Shanghai. All solutions were prepared with high-purity water with conductivity $<6\times10^{-2}\,\mu S/cm$ at 25 °C. The pH values of solutions were adjusted using H_2SO_4 or NaOH.

2.2. Preparation of electrodes

The electrodes were of 20 cm^2 ($2 \text{ cm} \times 10 \text{ cm}$) visible surface area and were prepared by thermal decomposition of appropriate mixtures of precursor salts dissolved in isopropanol. Firstly, the titanium sheets were subjected to surface pretreatment by 5% hot Na₂CO₃ solution for 60 min, followed by 10% hot H₂SO₄ solution pickling for 90 min and then they were washed by de-ionized water. The precursor solution of RuCl₃, H₂IrCl₆ and TiCl₃ in isopropanol was manually painted on the pretreated titanium sheets, and the solvent was evaporated in air at 80 °C. Then the sheets were fired at 450 °C for 15 min in a muffle furnace with a low and continuous flow of oxygen. The above two steps were repeated until the coating of IrO₂, RuO₂ and TiO₂ reached the following loading: the contents of Ru, Ir and Ti were 0.20, 0.85 and 0.40 mg/cm² respectively on 1# electrode, while on 2# electrode they were 1.10, 1.20 and 0.55 mg/cm^2 respectively. Finally, the coating was annealed at 450 °C for 60 min to obtain a complete oxidation.

2.3. Experimental procedures

2.3.1. Voltammetry experiments

Electrochemical measurements were obtained using a threeelectrode cell in conjunction with a computer-controlled electrochemical analyzer (LK98B α , Tianjin, China). Ti/IrO₂/RuO₂/TiO₂ electrodes (1.20 cm²) were used as the working electrode and the counter electrode, saturated calomel electrode (SCE) as a reference. The experiments were performed in the unstirred solutions containing 2, 4-DCP (80 mg/L) and Na₂SO₄ (0.05 mol/L) at pH 9.0 within a potential range of -1.5 to 1.5 V, with a sweep rate of 20 mV/s.

2.3.2. Investigation on the volatizing behavior of 2, 4-DCP

The 100 mL solution containing 2, 4-DCP (80 mg/L) and Na_2SO_4 (0.05 mol/L) was fed into a 100 mL beaker, followed by pH adjustment, and then a stirring of 400 r/min was provided by a magnetic stirrer. The samples were drawn for the analysis of 2, 4-DCP at the desired time to learn its volatizing behavior.

2.3.3. Procedure of anodic oxidation treatment

An electrochemical cell composed of a 100 mL beaker with 3 electrodes was employed for the anodic oxidation of 2, 4-DCP. The Ti/IrO₂/RuO₂/TiO₂ electrode (2#) was used as anode, the Ti/IrO₂/RuO₂/TiO₂ electrode (1#) as cathode, and saturated calomel electrode as a reference. The distance between anode and cathode was 15 mm, and the height of electrodes dipped into the electrolyte solution (100 mL) containing 2, 4-DCP (80 mg/L) and Na₂SO₄ (0.05 mol/L) was about 32 mm. Electrolysis was carried out under potentiostatic condition with a stirring of 400 r/min provided by a magnetic stirrer. During the course of electrolysis, current values were recorded by the computer system, and samples were drawn at the desired time for water quality measurements. All the experiments of this work were performed with a constant anodic potential at room temperature (25 ± 2 °C).

2.3.4. Enhancement of biodegradability by anodic oxidation process

In this study, oxygen consumption curves were used to evaluate the biodegradability of the 2, 4-DCP solutions before and after anodic oxidation treatment. The anodic oxidation treatment of 200 mg L^{-1} 2, 4-DCP solution was carried out according to the procedure presented in Section 2.3.3.

The quantity of oxygen consumption was obtained by the following steps: (a) the activated sludge from a municipal sewage treatment plant was aerated with air for 360 min in order to make microorganisms in endogenous respiration phase, then it was condensed to a concentration of 5500 mg/L (MLSS) by a settlement process; (b) the sample of 200 mL before or after anodic oxidation treatment, was fed into a jar of 250 mL, then the aeration with air was supplied to saturate the solution with dissolved oxygen (DO), followed by the addition of 50 mL condensed sludge. After the above steps, aeration was stopped and the jar was sealed immediately by a rubber plug with DO probe (a small amount of mixture was allowed to overflow for the sake of emitting out gas bubbles). The values of DO were manually recoded at the desired time until the concentration of DO was lower than 1.0 mg/L. In these experiments, a stirring of 400 r/min was presented; (c) to calculate the quantity of oxygen consumption at different times according to the variation of DO, then oxygen consumption curves could be drawn.

2.4. Analytical methods and instruments

The concentration of 2, 4-DCP was determined spectrophotometrically by 4-amino antipyrine method (GB7490–87, China). The absorbance was measured at 510 nm in a 752 spectrophotometer. The content of COD was measured by dichromate method (GB11914–89, China). The concentration of DO was measured with a JPB-607 DO meter. pH was measured with a pHS-25C acidity meter. The UV–vis spectrum during the degradation of DCP was measured at 200–600 nm using a TU-1901 UV–vis spectrophotometer (Beijing, China). The morphologies of electrodes were scanned with a JSM-6700F field emission scanning electron microscope (Japan).



Fig. 1. SEM morphologies of Ti-based oxide electrodes (×2000).



Fig. 2. Cyclic voltammograms obtained in the solution of 80 mg/L 2, 4-DCP+0.05 mol/L Na₂SO₄ at pH 9.0 using Ti/IrO₂/RuO₂/TiO₂ as working electrode.

3. Results and discussion

3.1. Morphologies of Ti-based oxide electrodes and cyclic voltammetry

The two electrodes were prepared according to the procedure presented in Section 2.2. The SEM images of the two electrodes are shown in Fig. 1. It can be seen that 1# electrode had a smooth surface with approximately uniform cracks, while 2# electrode had a dense oxides coating with a not so smooth surface. The morphology difference between the two electrodes was ascribed to the fact that 2# electrode had a higher loading of oxides than 1#.

The cyclic voltammograms with Ti/IrO₂/RuO₂/TiO₂ electrodes obtained in the solution containing 80 mg/L2, 4-DCP and 0.05 mol/L Na₂SO₄ at pH 9.0 are shown in Fig. 2. As can be observed, the two electrodes had a similar potential window of -0.9 to 1.1 V. The compound (2, 4-DCP) exhibited strong electrochemical stability at 1# electrode with 2# as the counter electrode because neither its oxidation nor its reduction took place in the potential window of 1# electrode. However, in the potential window of 2# electrode, a weak oxidation peak can be observed at about 0.4-1.0V, which indicates the presence of direct electron transfer between 2, 4-DCP and 2# electrode surface, namely the direct oxidation of 2, 4-DCP at 2# electrode can take place. The different loadings of oxides and morphologies were responsible for the above different electrochemical behaviors. In the subsequent experiments of electrolysis, 2# electrode was used as anode and 1# electrode as cathode.

3.2. Influences of pH and anodic potential on the degradation of 2, 4-DCP

Since 2, 4-DCP is a volatile organic compound, in the study of its degradation using anodic oxidation process, the removal by volatizing must be considered. The volatizing removal efficiencies of 2, 4-DCP under different pH conditions with a stirring of 400 r/min, are presented in Fig. 3a. As can be seen, the volatizing removal efficiencies were very low and remained almost unchanged at pH 12, but with the decreasing of pH the efficiency increased significantly. In the aqueous medium of pH < pK_a (pK_a = 7.85, the dissociation constant of 2, 4-DCP), it mainly exists in the form of molecules, while in the aqueous medium of pH > pK_a, it mainly exists in the form of ions, this is the reason why the lower pH tends to cause more 2, 4-DCP volatizing. Though the volatizing of 2, 4-DCP is



Fig. 3. Influences of pH on 2, 4-DCP volatizing (a) and anodic oxidation degradation at 1.8 V (b).



Fig. 4. Influence of anodic potential on 2, 4-DCP removal (initial pH 9.0).

beneficial to reduce its content in wastewater, how to avoid air pollution in practical engineering is worthy of special attention.

The removal efficiency of 2, 4-DCP by anodic oxidation process with the constant anodic potential of 1.8 V at different pH values, is shown in Fig. 3b. As it can be seen, pH values had a significant effect on the anodic oxidation of 2, 4-DCP. It is clear that at the same reaction time, the removal efficiency increased with the increasing of pH. Under the initial pH conditions of 6.0 and 9.0, a removal efficiency of 100% was obtained at 240 min, but only about 60% for initial pH 3.0. Additionally, taking into account the fact that the acidic medium can lead to more 2, 4-DCP volatizing confirmed by Fig. 3a, hence it can be concluded that the alkaline medium is beneficial to the anodic oxidation of 2, 4-DCP. In the experiments, pH values were measured after the reactions of 360 min, and results showed that the pH values decreased to 2.5, 4.0 and 5.8 from 3.0, 6.0 and 9.0, respectively. The reason of pH value decreasing was presented in the latter section.

Results of Fig. 4 give the influence of anodic potential on the removal of 2, 4-DCP at pH 9.0. It can be observed that at the same reaction time, the removal efficiency increased with increasing anodic potential value and there was only a little difference between the removal efficiencies obtained at 1.0V and 1.4V. The anodic oxidation of 2, 4-DCP at 2# Ti-based oxide electrode can be classified into two actions: direct anodic oxidation and indirect anodic oxidation. According to the cyclic voltammogram of 2# electrode shown in Fig. 2, it can be degraded by direct anodic oxidation at the lower anodic potential (0.4-1.0 V). However, both anodic oxidation and volatizing were responsible for the removal efficiencies presented in Fig. 4, therefore it could be inferred that the volatizing action played an important role in the removal of 2, 4-DCP at lower anodic potential (lower than the onset potential for oxygenevolving) referenced to the results given by Fig. 3a and in this case, the anodic oxidation action was very weak due to the smaller current density. At higher anodic potential, the generation of O₂ by the oxidation of H₂O at Ti-based oxide electrode caused the direct electron transfer between 2, 4-DCP and the anodic surface almost could not take place. Therefore, in the potential region of oxygenevolving, the degradation of 2, 4-DCP was mainly ascribed to the indirect anodic oxidation by hydroxyl radicals (.OH) and/or high valent oxide (MO, M is the Ti-based oxide electrode), which has been well established according to Comninellis' results [7,18]. Both M (•OH) and MO can destruct pollutants by the reactions in Eqs. (3) and (4). In the following schematic equations, R is a fraction of an organic compound.

$$M + H_2O \rightarrow M(\bullet OH) + H^+ + e^- \tag{1}$$

$$M(\bullet OH) \rightarrow MO + H^+ + e^-$$
(2)

Table 1

Variations of 2, 4-DCP degradation, pH and power consumption with anodic oxidation time (1.8 V; initial pH 9.0).

Time (min)	2, 4-DCP (mg/L)	COD (mg/L)	рН	Power consumption for 1 kg 2, 4-DCP removal (kW h)
0	80	98	9.0	
30	45.1	-	-	9.5
60	26.9	95	7.7	14.8
120	12.2	92	6.9	25.0
180	3.1	86	6.4	32.2
240	0	78	6.0	41.6
360	0	48	5.8	

$$M(\bullet OH) + DCP \rightarrow M + R + CO_2 + H_2O$$
(3)

$$MO + DCP \rightarrow M + R + CO_2 + H_2O$$

$$(4)$$

Based on the mechanism of anodic oxidation, the migration or diffusion of 2, 4-DCP to the anode surface is a key step both for its direct anodic oxidation and indirect anodic oxidation. In alkaline medium, 2, 4-DCP mainly exists in the form of negative ion because of its dissociation, and in this case driven by electric field force, 2, 4-DCP negative ions migrate and diffuse toward the anode surface during the course of electrolysis, which is beneficial to the anodic oxidation of 2, 4-DCP. This reason can explain the fact that the removal efficiency of 2, 4-DCP increases with the increasing of pH values.

In this study, besides the content of 2, 4-DCP, the variation of COD content was also used to evaluate the progress of 2, 4-DCP degradation. Table 1 gives the variations of 2, 4-DCP, COD, pH and power consumption with electrolysis time under the experimental conditions of 1.8 V and initial pH 9.0. As can be seen, the removal of 2, 4-DCP was rapid and a removal efficiency of 84.8% could be achieved at 120 min, while COD exhibited a trend different from 2, 4-DCP: the reduction of COD was very slow in 120 min, but became rapid after 120 min. Therefore, it could be inferred that in the earlier stage of electrolysis, the main function of anodic oxidation was to oxidize 2, 4-DCP generating organic intermediates characterized by a poor COD removal. However, in the later stage of electrolysis, 2, 4-DCP was completely removed and the further oxidation of organic intermediates gave rise to the relatively significant decreasing of COD.

It can be observed that the pH value decreased obviously with the extension of reaction time. The anodic oxidation of H_2O led to the generation of H^+ by the reactions in Eqs. (1), (2) and (5), which was the main reason for pH value decreasing. Generally, the incomplete degradation of organic compounds by anodic oxidation can result in the generation of carboxylic acid [10,19], which may be another reason for pH value decreasing.

$$M(^{\bullet}OH) \rightarrow M + 0.5O_2 + H^+ + e^-$$
 (5)

Table 1 shows that though 2, 4-DCP was completely removed at 240 min, only a 20% COD removal was obtained with a higher power consumption of 41.6 kW h for 1 kg 2, 4-DCP removal. It is evident that the further reduction of COD requires more power consumption, hence anodic oxidation process should not be considered as a single treatment for the real waste water containing 2, 4-DCP of high content because of the unacceptable power consumption.

3.3. UV-vis spectra change during anodic oxidation treatment

To clarify the changes of molecular and structural characteristics of 2, 4-DCP as a result of anodic oxidation treatment under the experimental conditions of 1.8 V and pH 9.0, representative UV-vis spectra changes of the solution as a function of electrolysis time were depicted in Fig. 5. As can be observed from these



Fig. 5. UV-vis spectral changes with electrolysis time (anodic potential of 1.8 V; initial pH 9.0).

spectra, before the treatment (0 min), the absorption spectrum of 2, 4-DCP in water (80 mg/L) was characterized by three bands in the ultraviolet region with maximum absorption at 220 nm, 260 nm and 305 nm respectively. The peaks at 220 nm and 305 nm were ascribed to the absorption of $\pi\text{-}\pi^*$ electron transition and the absorption of $n-\pi^*$ electron transition, respectively. The absorption peak at 260 nm was caused by the vibration of benzene ring as well as $\pi - \pi^*$ electron transition, which was the typical absorption characteristic of benzene ring. Clearly, the three absorption peaks significantly decreased with electrolysis time and finally disappeared completely at 360 min, indicating a rapid degradation of 2, 4-DCP. The peak at 260 nm decreased rapidly indicating the destructions of benzene ring and resonance double-bond, and as a result, this absorption characteristic disappeared completely even at 240 min. On the other hand, while the absorption peak at 305 nm decreased with electrolysis time, it exhibited a trend of blue shift, which indicated the generation of organic intermediates confirmed by the variations of 2, 4-DCP and COD shown in Table 1.

3.4. Influence of anodic oxidation on the biodegradability

According to the previous discussion, the application of Ti/IrO₂/RuO₂/TiO₂ anode in treating the wastewaters containing 2, 4-DCP at large scale is limited by the difficulty to reduce the power consumption. Additionally, anodic oxidation process is not specific (or almost not) for particular substrates, while the biological method (which is the most common and cheapest process used for wastewater remediation) and is not able to treat bio-recalcitrant or bactericidal substances [10]. Therefore, it may be an alternative to couple the versatility of anodic oxidation with the cheapness of biological methods by the following process: the pretreatment of the waste waters containing 2, 4-DCP is conducted using anodic oxidation to destruct the molecular structure of 2, 4-DCP enhancing the biodegradability, followed by biological treatment to further reduce organic substances. Evidently, the feasibility of the above idea lies in the enhancement of biodegradability caused by anodic oxidation. In this work, the biodegradability of 2, 4-DCP water solutions before and after anodic oxidation was evaluated with oxygen consumption curves.

Results of Fig. 6a show the oxygen consumption curves obtained from the solutions of various 2, 4-DCP concentrations before anodic oxidation treatment. The curves A, B and D corresponded to 60, 100 and 160 mg/L 2, 4-DCP solutions respectively, while the curve C was the oxygen consumption of endogenous respiration. The curve A nearly coincided with the curve C in the beginning showing the similar oxygen consumption, however, after 20 min the oxy-



Fig. 6. Influence of 2, 4-DCP concentration on oxygen consumption (a) and influence of anodic oxidation on oxygen consumption (b).

gen consumption values of curve A significantly exceeded those of endogenous respiration, which indicated that for microorganisms, only a short lag phase of 20 min was needed to decompose 60 mg/L 2, 4-DCP. To compare the curves B and C, when 2, 4-DCP concentration was 100 mg/L, the lag phase of microorganisms was extended for 75 min, additionally, after 75 min the oxygen consumption increased slightly, hence in this case, the obvious inhibition of microbial activities could be caused by 2, 4-DCP. The curve D was below the curve C and the two were parallel showing the oxygen consumption values obtained from 160 mg/L 2, 4-DCP always less than those from endogenous respiration, which indicated in this case, 2, 4-DCP had a toxic action on microorganisms.

Results of Fig. 6b shows the oxygen consumption curves obtained from the solutions containing 200 mg/L 2, 4-DCP treated by anodic oxidation under the conditions of 1.8 V and pH 9.0 with various times. As can be seen from Fig. 6b, the curve E obtained from the solution before anodic oxidation treatment, located parallel below the curve D of endogenous respiration showing a toxic action on microorganisms. From the curve C, after a lag phase of 25 min, the oxygen consumption increased rapidly, while according to the curves A and B, the lag phase became shorter with the increasing of anodic oxidation time. It was also observed that the oxygen consumption increased with the increasing of anodic oxidation time. Therefore, the anodic oxidation by Ti/IrO₂/RuO₂/TiO₂ electrode was able to enhance the biodegradability of 2, 4-DCP solution. The reasons of the enhancement in biodegradability by anodic oxidation process are the destruction of 2, 4-DCP molecular structural (the destruction of benzene ring and de-chlorination) and the generation of biodegradable intermediates, which can be partly confirmed by Fig. 5. In a recent study, Chatzisymeon et al. reported that the biodegradability of olive mill wastewater after treated by anodic oxidation using diamond electrode reduced apparently, implying the formation of reaction by-products that are less readily degradable [20]. Hence, it is not always feasible that using anodic oxidation process to enhance the biodegradability of various wastewaters.

4. Conclusions

The composition of Ti/IrO₂/RuO₂/TiO₂ electrode had a significant effect on its voltammetric behavior in 2, 4-DCP solution. At this anode, both direct and indirect anodic oxidation could account for the degradation of 2, 4-DCP in view of various potentials. The direct oxidation was weak because of the smaller current density, while the indirect anodic oxidation with Ti/IrO₂/RuO₂/TiO₂ electrode could rapidly oxidize 2, 4-DCP at higher anodic potential in alkaline medium, but the non-ideal reduce of COD indicated that the degradation of 2, 4-DCP was non-complete. Taking into account the power consumption, it is not a reasonable alternative to treat the wastewater containing 2, 4-DCP of higher content using anodic oxidation as a single method.

According to the oxygen consumption curves, 2, 4-DCP of 60 mg/L only had a slightly effect on microbial activity and 2, 4-DCP of 100 mg/L was able to cause the obvious inhibition of microbial activities, however, 2, 4-DCP of 160 mg/L could have a toxic action on microorganisms. The anodic oxidation rapidly destructed the molecular structural of 2, 4-DCP generating the non-toxic and easily biodegradable intermediates, which led to the enhancement in biodegradability. Moreover, this enhancement became greater with the extension of anodic oxidation treatment. The results of this work indicate using the anodic oxidation of Ti/IrO₂/RuO₂/TiO₂ to enhance the biodegradability of the wastewater containing chlorophenols, followed by biological treatment, is a promising alternative for the degradation of chlorophenols.

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