

Electrochemical Investigation of Phenol Oxidation by a TiO₂/GAC Based Packed-Bed Electrode Reactor

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In this work, TiO₂/GAC was prepared by sol-gel method and employed as particulate electrode for efficient phenol oxidation. The X-ray Diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis reveal the titanium dioxide loaded on GAC exists in anatase TiO₂ state. Compared to the GAC electrode, the TiO₂/GAC can enhance feedback current and catalytic-oxidation ability, which could be obtained through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. Furthermore, the excellent electrochemical performance of TiO₂/GAC is validated by the increase of phenol and chemical oxygen demand (COD) removal and obvious decrease of the power consumption during bulk electrolysis of phenolic wastewater.

Keywords: phenol; TiO₂/GAC; packed-bed electrode reactor; catalytic-oxidation performance

1. INTRODUCTION

During the past several decades, electrochemical processes with unique features of simplicity, robustness and high operation efficiency have been introduced into treating wastewater containing different organic pollutants [1-3]. The dimensionally stable anodes (DSAs) are usually employed due to their strong ability in producing reactive hydroxyl radicals ($\cdot\text{OH}$) which are responsible for effective electro-oxidation. To further improve the electrode performances, a three dimension structure equipped with granular activated carbon (GAC) is developed to expand electrode area via GAC bipolarity in the electric field [4-6]. However, this kind of framework is still restricted by excessive oxygen evolution of carbon material and cost-efficient goal toward electro-oxidation is difficult to be achieved through this way. As known that usage of the metal oxide e.g. SnO₂ [7, 8] and PbO₂ [9, 10] could effectively

increase the oxygen evolution potential (OEP) of anodes, maybe employment of such oxides supported GAC particles also would be a feasible approach for enhancing current efficiency and decreasing power cost during organic wastewater treatment.

In this work, GAC loaded TiO_2 (TiO_2/GAC) was prepared by sol-gel method and employed as particulate electrode for phenol degradation. The phase composition of the TiO_2/GAC was detected by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) techniques. Electrochemical tests i.e. cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) conducted on an electrochemical workstation by using three-electrode system were carried out to investigate electrode performances of the prepared TiO_2/GAC . In addition, GAC together with TiO_2/GAC based packed-bed reactor for phenolic wastewater treatment were performed to verify the oxidation enhancement of the TiO_2/GAC particulate electrode via chemical oxygen demand (COD) removal efficiency, current yield and power consumption.

2. EXPERIMENTAL

2.1. *Chemicals and materials*

Phenol (Merck, in 99.5% pure) and sodium sulfate (Na_2SO_4) in analytical pure were used to prepare the raw solution. Others reagents such as ethanol, hydrochloric acid, acetic acid and tetrabutyl titanate were also obtained in analytical pure.

PbO_2/Ti anodes with 2×2 cm and 10×10 cm dimension, which were used for electrochemical tests and phenol oxidation, respectively, were provided by Qixin Company (China). GAC particles having an average particle size of 5 mm, a specific weight of 752 g L^{-1} and a specific surface area of $826 \text{ m}^2 \text{ g}^{-1}$ according to BET method were employed for construction of a GAC based packed-bed electrode reactor and preparation of TiO_2/GAC particulate electrode.

2.2. *TiO_2/GAC preparation and performances characterization*

Prior to experiments, GAC particles were washed several times by deionized water to remove the fines and ashes and dried in an oven at 105°C for 24 h to a constant weight. The TiO_2/GAC was achieved by the sol-gel method which contained three steps: (1) preparation of the precursor reagents including solutions A (35 mL ethanol, 32 mL distilled water and 0.6 mL hydrochloric acid) and B (70 mL ethanol, 23 mL acetic acid and 35 mL tetrabutyl titanate); (2) aged stage: pour A to B using a separating funnel at speed of 4 mL min^{-1} with stirring (500 r min^{-1}) and put the GAC particles into the mixture solution and try to make them well-distributed and then it should be aged for 2 days; (3) baked process: the prepared solution with GAC was moved into an oven to be dried at 105°C under nitrogen protection for 7 h, and then baked according to the following procedure: increase the temperature from 0°C to 200°C in 30mins and maintain 200°C for 1 h, raise temperature from 200°C to 500°C in 40 mins and then maintain 500°C for another 2 h.

XRD patterns were obtained on a XRD diffractometer (type: D8 Advance Bruker Corp) with CuK α radiation at tube voltage/current 40 kV/30 mA, and λ of 1.5406 Å. XPS (ESCALAB 250Xi, ThermoFisher Corp) was conducted with AlK α X-ray source of energy 1253.6 eV at a power of 240 W. The pressure in the analysis chamber was maintained below 2×10^{-9} mbar during the measurements.

The performances of GAC and TiO₂/GAC particulate electrodes were carried out on an electrochemical workstation (Zahner Corp, IM6) with 0.25 M Na₂SO₄ and 0.01 M phenol solution by a three-electrodes system composed of PbO₂/Ti anode (2×2 cm), Pt counter electrode (4×4 cm) and saturated calomel electrode (SCE) as a reference electrode at temperature of 25 °C. The scanning rate for CV test was 50 mV s⁻¹ and the EIS cures were obtained at open circuit potential of 0.53 V.

2.3. Electrochemical reactor and phenol bulk oxidation

The electrochemical process for bulk electrolysis was composed of eight cells constructed by polymethyl methacrylate plastics and a D.C power modeled KZN-1540D. Each cell was equipped with PbO₂/Ti and Ti electrodes (10 cm×10 cm) with inter-electrode distance of 5 cm and a peristaltic pump. The cells were packed with GAC or TiO₂/GAC and the detailed information for the cell and process were provided elsewhere [11]. Synthetic phenolic wastewater (0.01 M phenol and 0.25 M Na₂SO₄) was oxidized at flow rate of 0.6 L h⁻¹ and current density of 100 A m⁻² under continuous mode.

2.4. Analytical methods

A Spectrophotometer UV-visible (UV-1800, Shimadzu) was used to detect phenol concentration and COD of each sample was determined by the standard method [12]. The average current efficiency (ACE, %) and power consumption (E_{sp} , kWh kg⁻¹ COD) were calculated according to the following equations, respectively [13].

$$\text{ACE} = F\xi V \frac{(\text{COD}_0 - \text{COD}_t)}{8It} \times 100\% \quad (1)$$

$$E_{sp} = \frac{3600UI}{q(\text{COD}_0 - \text{COD}_t)} \quad (2)$$

where F is Faraday constant (96,485 C mol⁻¹), ξ the porosity of the packed-bed electrode cell (here its value is about 0.42), V the volume of each cell (L), t the residence time (s), I the current (A), U the applied voltage (V), q the flow rate (L h⁻¹), COD₀ and COD_t (g L⁻¹) the initial COD and COD at time t , respectively.

3. RESULTS AND DISCUSSION

3.1. Surface composition of TiO₂/GAC

Fig. 1 shows the XRD patterns of the TiO₂/GAC and GAC particles. From this figure, strong diffraction peaks at angles of 25.363°, 37.008°, 37.862°, 38.625°, 48.095°, 53.944°, 55.110°, 62.166°,

62.743° , 68.814° , 70.345° , 75.103° and 76.090° are observed, which are indexed to anatase TiO_2 phase according to JCPDS no. 65-5714; while the diffraction peaks of GAC are located at angles of 21.004° , 22.890° , 26.522° , 36.026° , 43.310° , 50.493° and 60.153° (JCPDS no. 50-0927). In addition, the regular distribution of these peaks illustrates the TiO_2 crystal is even loaded at the surface or into the mesopore/micropore of GAC particles, which could be interpreted by crystallite parameter calculated from the peaks and half-height of lattice planes (101), (103), (004), (112), (200), (105), (211), (204), (116) and (220) using the Scherrer equation [14]; these results are given in Table 1.

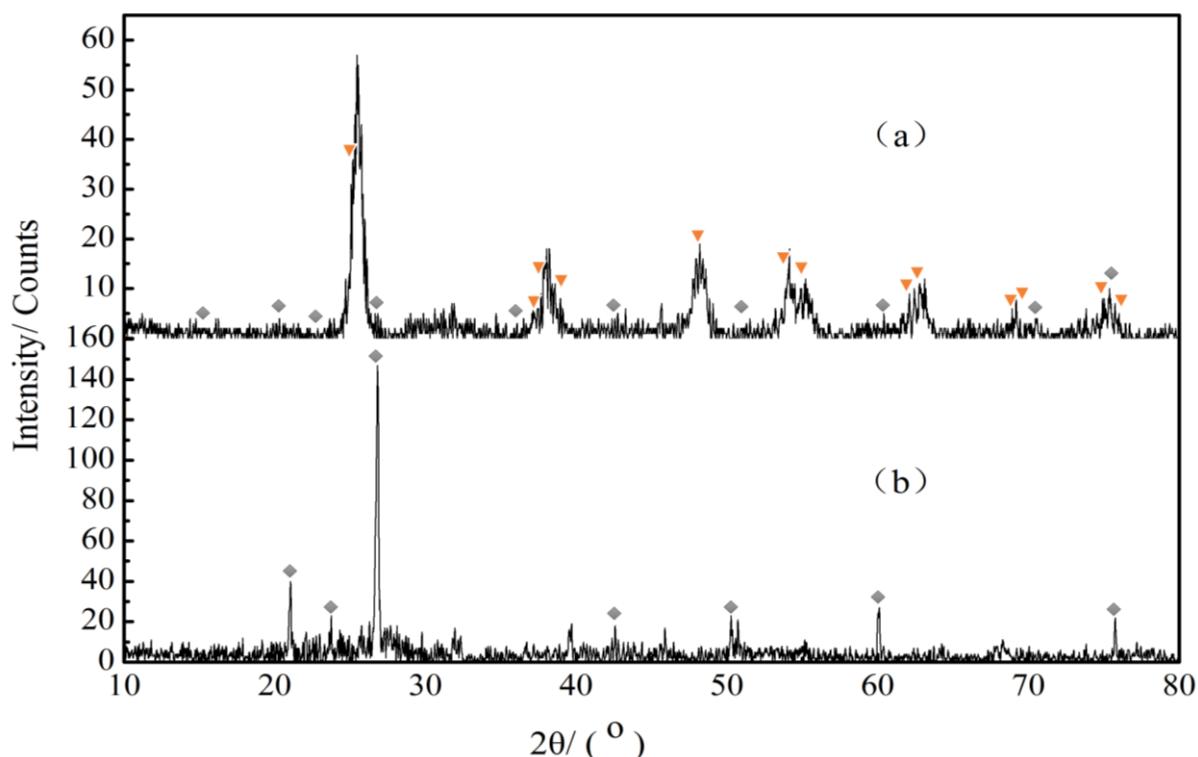


Figure 1. XRD patterns of TiO_2/GAC (a) and GAC (b). Phases: \blacklozenge , C; \blacktriangledown , TiO_2

Table 1. Theoretical and experimental crystallite parameters of the prepared TiO_2/GAC

Lattice planes (hkl)	101	103	004	112	200	105	211	204	116	220
Theoretical [15]	0.3510	0.2424	0.2379	0.2334	0.1890	0.1699	0.1664	0.1480	0.1362	0.1339
Experimental	0.3513	0.2315	0.2376	0.2321	0.1820	0.1532	0.1664	0.1482	0.1269	0.1324

The XPS survey spectra in Fig. 2a provide the existence of atomic species on surface of the prepared TiO_2/GAC , which are oxygen, titanium, carbon and chlorine (detection of aluminum is due to system error) and their atomic ratios are 55.83%, 21.76%, 10.18% and 7.03%, respectively. High

accuracy spectrum of Ti2p (Fig. 2b) for Ti2p_{3/2} together with Ti2p_{1/2} at binding energies of 458.8 eV and 465.04 eV indicates there is only one Ti atom in TiO₂, and the difference of binding energy for the two states is 6.24 eV, which is slightly higher than that of other work [16]; this may be caused by error of different instruments. The spectrum of O1s in Fig. 2c validates that most of oxygen atom is bonded with Ti at binding energy of 533.0 eV and 530.8 eV. Hence, these results confirm that titanium dioxide is successfully loaded on the surface of GAC particles.

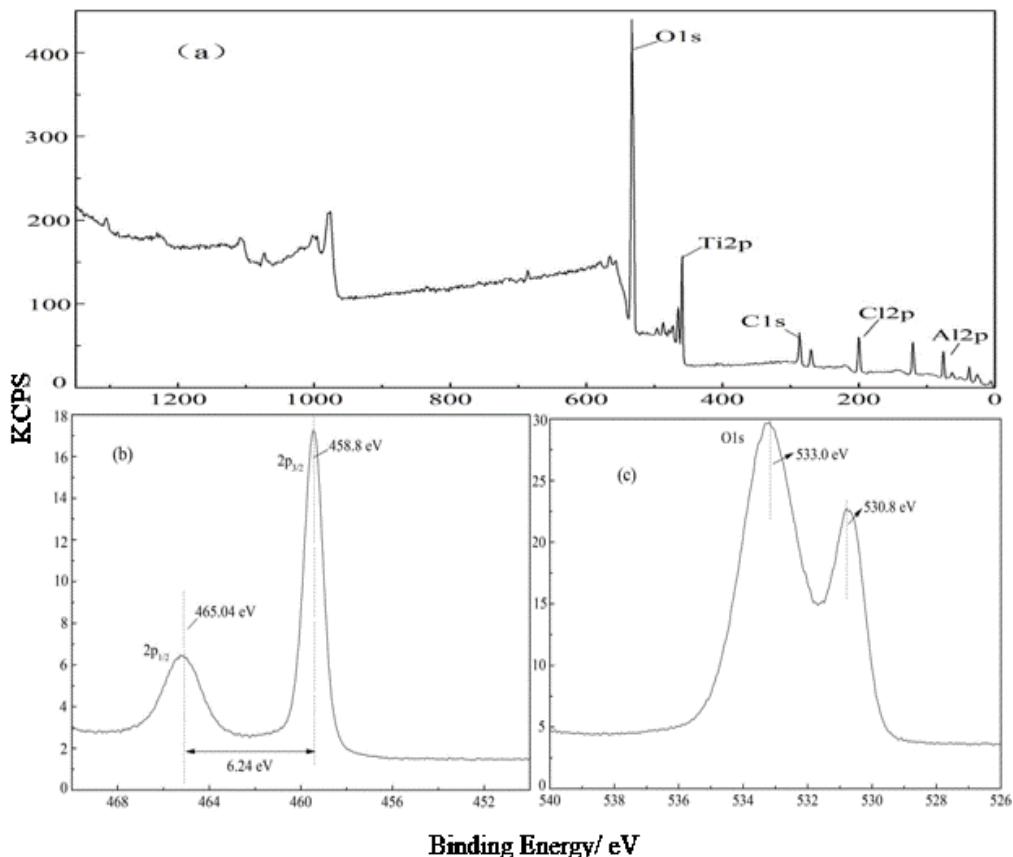


Figure 2. XPS spectra for TiO₂/GAC particulate electrode (a), Ti 2p (b) and O1s (c) peaks

3.2. Electrode performances

Fig. 3 depicts the CV curves of GAC and TiO₂/GAC coupled with PbO₂/Ti anode conducted in hybrid of 0.25 M Na₂SO₄ and 0.01 M phenol within potential window from 0 to 2.5V (vs. SCE) at 50 mV s⁻¹. The two asymmetrical curves without redox peaks indicate the reactions in the system should be irreversible and phenol could be directly oxidized at surface of the anode and particulate electrodes [17-19]. In addition, compared with GAC, larger feedback current is shown when the TiO₂/GAC is employed, which illustrates the oxidative ability of the particulate electrode could be enhanced by loading TiO₂. Voltammetric charge (Q) is usually used to evaluate active spot of anodes and it could be calculated according to CV curve by the following equation:

$$Q = \frac{\int_{U_1}^{U_2} itdv}{U_2 - U_1} \quad (3)$$

where U_1 and U_2 are the initial and final potential (V), i the feedback current (A) and v the scanning rate (mV s^{-1}). By using Eq. (3), the parameter Q of the GAC and TiO_2/GAC are obtained with values of 0.23 C and 0.38 C, respectively; in this sense, the prepared TiO_2/GAC electrode should possess abilities of enhancing phenol removal efficiency and current yield during bulk electrolysis.

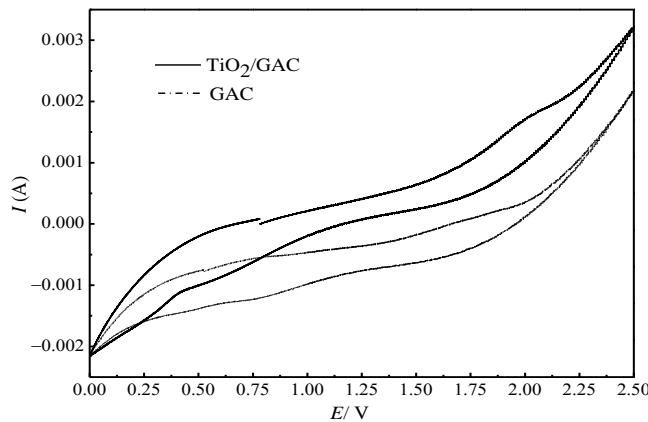


Figure 3. CV curves of GAC and TiO_2/GAC coupled with PbO_2/Ti anode in solution containing 0.25 M Na_2SO_4 and 0.01 M phenol at scanning rate of 50 mV s^{-1}

The Nyquist complex plane impedance spectra of GAC and TiO_2/GAC are presented in Fig. 4. A relatively lower semicircle diameter at high frequency is observed if the TiO_2/GAC is used, which indicates the resistance for charge transfer could be effectively decreased by loading TiO_2 catalyst. The inclined lines approximating to 45° angle demonstrate that better electron-diffusion process is achieved on carbon electrodes regardless of the existence of the TiO_2 [14, 20, 21]. The equivalent electric circuit is provided in Fig. 4b, within which R_e is the electrolyte resistance; C_1 , C_2 and R_1 , R_2 the capacitance and resistance of the surface film formed on anode and carbon electrodes, respectively; C_{fp} and C_p the capacitance formed due to gradually voltage decrease; R_{ct} the charge-transfer resistance and Z_w the Warburg impedance related to the diffusion of electrons into the carbon electrodes. The exchange current density i_0 can be calculated by parameter R_{ct} as follows [22]:

$$i_0 = RT / nFR_{ct} \quad (4)$$

where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T the absolute temperature (K) and n the number of transferred electrons during phenol oxidation (here $n=4$).

The simulated results and calculated i_0 values of the two particulate electrodes are summarized in Table 2. It can be seen that the values of R_e and R_1 are almost equal when GAC and TiO_2/GAC are used, while the values of R_2 and R_{ct} for the two particulate electrode are quite different. In the presence of the TiO_2 catalyst, the R_2 value decreases to 6.84Ω , which is only about one fourth of that for GAC based packed-bed electrode reactor, indicating the electron transfer rate for phenol oxidation would be effectively accelerated. In addition, compared with GAC, R_{ct} values obviously decreases from 329.3Ω to 206.5Ω , resulting into the increase of i_0 values from $1.83 \times 10^{-6} \text{ A cm}^{-2}$ to $2.92 \times 10^{-6} \text{ A cm}^{-2}$. Both the

R_2 decrease and i_0 increase are beneficial to efficient phenol degradation, which directly confirm the employment of TiO₂/GAC as particulate electrode is a better alternative compared with GAC particles.

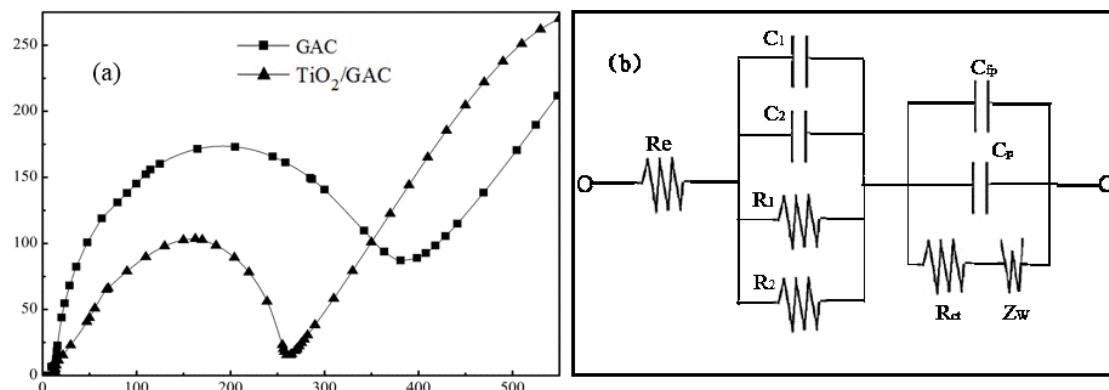


Figure 4. The EIS (a) and equivalent electric circuit (b) of GAC and TiO₂/GAC coupled with PbO₂/Ti anode in solution containing 0.25 M Na₂SO₄ and 0.01 M phenol at the open circuit potential of 0.53 V

Table 2. Summary of the EIS simulated results and i_0 values of the GAC and TiO₂/GAC electrodes

Electrodes	R_e (Ω)	R_1 (Ω)	R_2 (Ω)	R_{ct} (Ω)	$i_0 \times 10^{-6}$ (A cm ⁻²)
GAC	5.88	0.33	29.33	329.3	1.83
TiO ₂ /GAC	4.63	0.35	6.84	206.5	2.92

3.3. Bulk electrolysis

The comparison of the two particulate electrodes for phenol oxidation is shown in Fig. 5. It can be seen from Fig. 5a that both COD and phenol removal efficiency are significantly enhanced if the prepared TiO₂/GAC is used, leading to obvious increase of current yield and decrease of specific power consumption (Fig. 5b). After 224 minutes treatment, the effluent concentrations of COD and phenol by using TiO₂/GAC are 123.6 mg L⁻¹ and 7.1 mg L⁻¹, respectively, which are increased by ratios of 77.3% and 96.2% compared with those of GAC particles (544.2 mg L⁻¹ and 185.6 mg L⁻¹, respectively). Such enhancement is mainly for electrode area expansion and decrease of the oxidation resistance evoked by TiO₂ catalytic performance [23], further validating the excellent oxidation ability of TiO₂/GAC for degradation of organic pollutants.

From the engineering purpose, it is also of great concern the superiority of the TiO₂/GAC based packed-bed electrode reactor in cost-effective property. The experimental results conducted at current density of 100 A m⁻² and flow rate of 0.6 L h⁻¹ show the average current efficiencies of TiO₂/GAC are always higher than those without TiO₂ catalyst together with the decrease of the power consumption at the same reaction time (Fig. 5b). When the reaction time is 224 min, the current yield increases from 30.6% to 38.5% and the power consumptions decrease from 159.6 kWh kg⁻¹ COD to 126.8 kWh kg⁻¹ COD in the absence and presence of TiO₂ catalyst. It is worth noting that the power cost is obviously

lower than three works conducted by using $\gamma\text{-Al}_2\text{O}_3$ particulate electrode for chloramphenicol (CAP) oxidation ($222.7 \text{ kWh kg}^{-1}$ CAP) [24] and modified kaolin particulate electrode for anionic surfactants degradation at (about 816 kWh kg^{-1} COD with COD removal efficiency of 76%) [25]. Therefore, the increase of oxidation rate and decrease of power consumption by the TiO_2/GAC particulate electrode could simultaneously reduce the reactor volume and running cost, making the technology more attractive from an economic point of view.

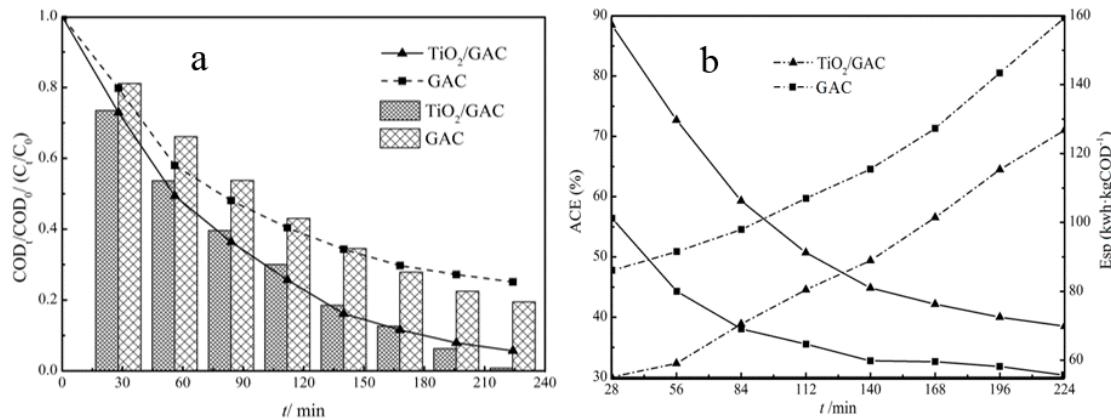


Figure 5. Dependence of COD and phenol concentration (a), ACE and E_{sp} (b) on reaction time during phenolic wastewater treatment at current density of 100 A m^{-2} and flow rate of 0.6 L h^{-1} . Notes: (a) the lines and bars depict the COD and phenol concentration, and (b) ACE and E_{sp} are described by solid and dotted lines, respectively.

4. CONCLUSION

The employment of GAC and TiO_2/GAC prepared by sol-gel method as particulate electrodes coupled with PbO_2/Ti anode was investigated for phenol oxidation in this work. The XRD and XPS results reveal that the anatase TiO_2 exists at surface or in mesopore/micropore of GAC particles. Compared to GAC particles, the voltammetric charge of the prepared TiO_2/GAC is increased from 0.23 C to 0.38 C and oxidation resistance is obviously decreased from 329.3Ω to 206.5Ω , leading to the increase of exchange current density from $1.83 \times 10^{-6} \text{ A cm}^{-2}$ to $2.92 \times 10^{-6} \text{ A cm}^{-2}$ during phenol degradation; moreover, the bulk electrolysis show that the effluent COD and power consumption low to values of 185.6 mg L^{-1} and $126.8 \text{ kWh kg}^{-1}$ COD under conditions of flow rate 0.6 L h^{-1} , current density 100 A m^{-2} and reaction time 224 minutes, which are decreased by ratios of 77.3% and 20.6% to those of GAC particulate electrode, respectively, directly validating the higher catalytic-oxidation ability of the prepared TiO_2/GAC particulate electrode in degradation of organic pollutants.

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