

p-Nitrophenol abatement by the combination of electrocatalysis and activated carbon

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Abstract

A novel process combining electrocatalysis and activated carbon (AC) in fluidization mode was presented for *p*-nitrophenol (PNP) abatement. The synergetic effect was found by comparing with the individual electrocatalysis and AC adsorption, and the synergetic factor (*f*) was calculated to be 139%. Such a one-step process could almost completely remove the PNP of initial concentration of 150 mg L⁻¹ in no more than 30 min. The mechanism of synergetic effects was due to the formation of AC microelectrodes under the electric field. Activated carbon microelectrodes in fluidization mode could largely improve the PNP degradation adsorbed on the surface of AC. Activated carbon played the double role of adsorbent and catalyst. Furthermore, AC adsorption capacity could be partly regenerated during the electrocatalysis. Sparged with O₂, the removal rate of PNP was almost enhanced to 150%, compared with N₂ sparged at 10-min degradation. Activated carbon amount, liquid flow rate, current, run batches, initial PNP concentration, and sparged gas were investigated to find out the factors affecting PNP abatement. The combined process showed potential application for environmental remediation.

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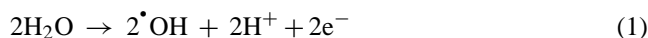
Keywords: *p*-Nitrophenol; Electrocatalysis; Activated carbon; Regeneration; Synergetic effect

1. Introduction

Nitrophenols have been widely used as important raw materials for production of pesticides, insecticides, herbicides [1], explosives, and various synthetic compounds such as dyes [2]. They are typical biorefractory organic compounds and considered to be one of the 114 priority toxic pollutants by US Environmental Protection Agency (EPA). The ever-increasing discharge of these compounds into the environment has caused various problems in water and wastewater treatment systems because they can not be effectively treated by traditional technologies such as biological degradation [3], solvent extraction [4], and adsorption [5]. Accordingly, it is of critical environmental importance to seek for sound technologies for treatment of these kinds of wastewater. Recently, advanced oxidation processes (AOPs) producing high oxidation potential hydroxyl radicals are more often investigated

acting as either pretreatment or mineralization process for such kind of wastewater treatment.

Apart from the well-known AOPs such as Fenton reaction, ozonation, and photocatalysis, electrocatalysis seems to be an increasingly interesting way for wastewater treatment. Electrocatalysis on high oxygen over-potential electrodes such as PbO₂ and SnO₂ is also called advanced electrochemical oxidation processes (AEOPs), in which the mineralization or oxidation of organics is principally achieved by the hydroxyl radical that is electrogenerated on the surface of the electrodes as follows [6–8]:



However, complete mineralization of organic compounds by electrocatalysis would not be economic due to intensive energy consumption. In our previous work, partial degradation of phenol by electrocatalysis for subsequent biological process was attempted to achieve cost-effectiveness of the process [9]. One disadvantage of this combined process was the requirement of pH adjustment before wastewater was

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discharged into the biological unit, which may raise the operating cost.

Adsorption, a well-established technique that is frequently employed on advanced treatment of wastewater, may be one alternative after the first-step treatment by electrocatalysis. Activated carbon (AC) was preferred as the adsorbent due to its low energy requirement, simple performance and wide spectrum of applicability. However, the second-step treatment by the AC adsorption was supposed to be an environmentally incomplete system, and further, the economics of the whole process would be related to the regeneration of the exhausted activated carbon. Recently, activated carbon regeneration by electrochemical method was reported to be a promising approach [10,11]. Thus, based on such consideration, the whole process for *p*-nitrophenol (PNP) abatement could be simplified to be one-step process combined with activated carbon adsorption and electrocatalysis in one reactor. Polcaro et al. tried similar research using carbon pellets in a fixed bed mode for destruction of chlorophenols, and found the process was mass transfer controlled [12]. Mass transfer limited the adsorption and the degradation of pollutants from the well-mixed dilute solution. In view of this, the activated carbon performed in a fluidization mode mass transfer could be improved.

The purpose of this study was to investigate *p*-nitrophenol degradation by the simultaneous operation of activated carbon and electrocatalysis in a single reactor sparged with O₂. The advantages expected from this combined process were (1) to enhance cost-effectiveness of the whole process by reducing equipment and flow, and (2) “in situ regeneration of AC partly” to minimize fresh AC supply. Operating parameters such as current, amount of AC, liquid flow rate, initial PNP concentration and sparged gas type were explored.

2. Experimental

2.1. Chemicals and materials

All chemicals used were of analytical grade, without further purification. High-purity (>99.9%) gas (O₂, N₂) was used. The activated carbon, provided by Shanghai Reagent Co., China, was crushed and screened and those with particle size of 30–35 meshes were selected. Prior to use, they were

washed several times by deionized water and dried for 24 h to constant weight at 105 °C.

2.2. Set-up

The schematic diagram of the experimental setup is shown in Fig. 1. A known quantity of activated carbon was introduced into annular reactor before startup. The simulated wastewater containing a certain amount of PNP and supporting electrolyte (5 g L⁻¹ Na₂SO₄), adjusted at initial pH 3.0, was pumped into the inlet of the electrocatalytic cell in the bottom and passed through a hydraulic distributor bar, an annular cell, and finally flowed back down to a reservoir. The volume of the solution was about 1.5 L. The anode used here was a β-PbO₂ anode (250 cm² surface), which was modified by fluorine resin to improve resistance against corrosion in the wastewater. The anode and the cathode of stainless steel net (grid 1 mm × 1 mm) were concentrically assembled into the electrolytic reactor. The anodic compartment was separated from the cathodic one by a membrane. A flow meter was used to measure the flow rate of the wastewater in reasonable range to achieve AC fluidization. Gas (N₂, or O₂) was sparged from the bottom of the electrochemical reactor. The reservoir was placed into a water bath under controlled temperature. At appropriate time interval, each sample of about 3 mL in volume was taken from the sampling port.

2.3. Analysis

All samples were immediately analyzed to avoid further reaction. The determination of PNP and its oxidation products was carried out on high-performance liquid chromatograph (HPLC, Gilson, France) by comparing the retention time of the standard compounds. Aliquots of 25 μL were injected to the HPLC to determine the concentration of PNP and degradation products, running with mobile phase of acetonitrile/water/concentrated H₃PO₄ (v/v/v) at 58/42/0.2. The separation was performed using an ODS-18 reversed phase column at the flow rate of 1.5 mL min⁻¹ and column temperature of 25 °C. An UV detector was used with the wavelength set at 254 nm. The decay of PNP and its degradation intermediates were also monitored by HPLC (Hewlett-Packard Model 1100)–Mass Spectrometry (Bruker-Esquire system). Analyses by HPLC were performed under the same operating

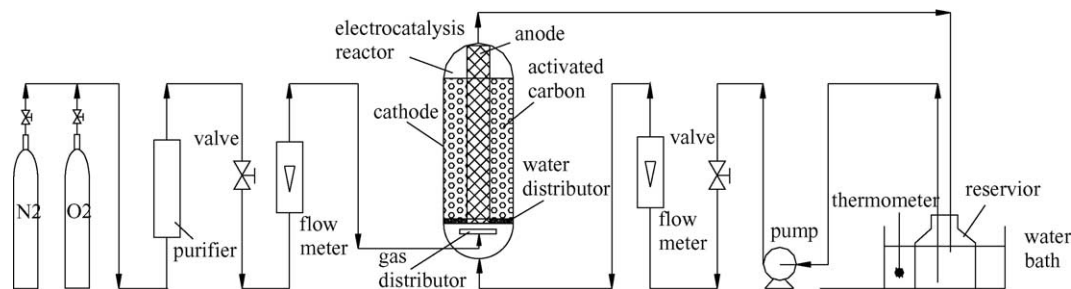


Fig. 1. The schematic diagram of the experimental setup.

conditions as described above. Electron source of ESI was used. Organic acids and anions were determined by ion chromatography (Techcomp IC 1000) with DS-plus™ auto suppressor (Alltech, USA).

2.4. Methodology

Adsorption–equilibrium experiments were conducted by placing 0.2 g carbon and 200 mL of PNP solution with initial concentration of around 50 mg L⁻¹, 100 mg L⁻¹, 150 mg L⁻¹, 250 mg L⁻¹ and 500 mg L⁻¹ into 0.5 L flasks. The flasks were tightly sealed with rubber and shaken in a temperature-controlled shaker for sufficient period of time. The amount of each solute adsorbed on the carbon at equilibrium was calculated from the mass balance of solute between carbon and solution as

$$q = \frac{V}{M}(c_0 - c_e) \quad (2)$$

where c_0 and c_e denote the initial PNP concentration and the equilibrium PNP concentration in the bulk solution, respectively. q is the solid-phase loading of PNP, measured as milligrams of PNP per gram of active carbon. V is the volume of solution and M is the mass of activated carbon that was added into the solution.

3. Results and discussion

3.1. Activated carbon adsorption

The adsorption equilibrium between the *p*-nitrophenol and activated carbon was studied at 25 °C. As shown in Fig. 2, the adsorption isotherm fits well to the Freundlich equation

$$\ln q_e = \ln K + \frac{1}{n} \ln c_e \quad (3)$$

The parameters obtained by Eq. (3) (K and $1/n$) were estimated graphically as 51.88 and 0.34, respectively.

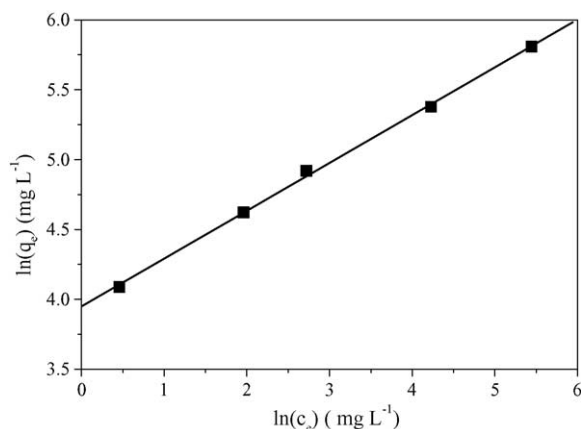


Fig. 2. PNP adsorption isotherm on activated carbon at 25 °C.

3.2. Synergetic effects of the combined process

To evaluate the feasibility of the presence of activated carbon in the electrocatalysis process, PNP abatement was compared in the individual adsorption process, electrocatalysis and their combined process in the same reactor, as shown in Fig. 3. PNP removal by activated carbon adsorption was rapid and it was nearly saturated after treating for 1 h. Under electrocatalysis, PNP concentration steadily decreased with time and after degradation of 1 h, it began to be less than that of by adsorption. It was evident that the combined process had a synergetic effect in enhancing PNP conversion in comparison with the individual ones. For example, after treatment of 10 min, the PNP conversion for the combination process (66%) is around 12% higher than the sum of those for the adsorption (31%) and electrocatalysis (23%). In the combined process, PNP of initial concentration 150 mg L⁻¹ was almost completely removed in no more than 30 min.

PNP abatement by above three processes in the first period of 30 min was tried by the following apparent first-order equation,

$$\ln\left(\frac{c_0}{c}\right) = kt \quad (4)$$

where k is the apparent first-order reaction rate constant. It was well fitted and the data are listed in Table 1. For close examination of this synergetic effect, the apparent rate constant has been chosen as the basic kinetic parameter, since it is independent of the concentration for the system under investigation.

For convenience, k_1 , k_2 and k_{12} presented the k value in the electrocatalysis, adsorption and the combined process, respectively. It was observed that k_{12} was much larger than the addition of k_1 and k_2 , indicating synergetic effects existed

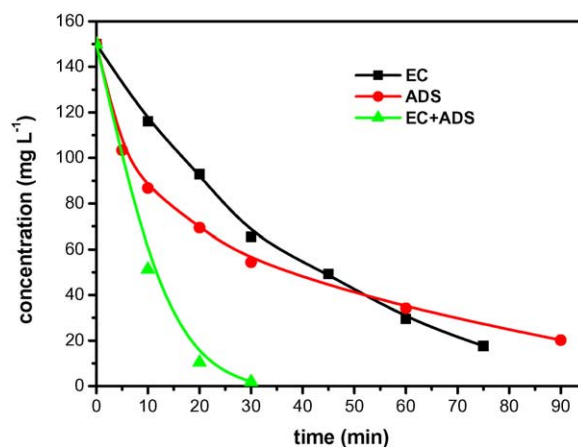


Fig. 3. Comparison of PNP degradation by electrocatalysis, adsorption and their combined process. The operating conditions in the combined process were: current 0.5 A, activated carbon 2 g L⁻¹, wastewater flow rate 3.75 L min⁻¹, temperature 25 °C, initial PNP concentration 150 mg L⁻¹. These conditions are adopted in individual electrocatalysis other than activated carbon addition, and in the individual AC adsorption process without current applied.

Table 1
Comparison of first-order reaction rate constants by the three processes

Process ^a	k (min ⁻¹)
EC	0.0265
ADS	0.0373
EC + ADS	0.1523

Conditions: activated carbon 2 g L⁻¹, wastewater flow rate 3.75 L min⁻¹, temperature 25 °C, initial PNP concentration 150 mg L⁻¹.

^a "EC" and "ADS" refer to PNP degradation by electrocatalysis and adsorption, respectively.

in the combined process. To evaluate the enhancement on PNP conversion, the synergetic factor (f) was calculated to be 138.7% using the following definition,

$$f = \frac{(k_{12} - k_1 - k_2)}{(k_1 + k_2)} \times 100\% \quad (5)$$

Consequently, it can be inferred that using the process combination with electrocatalysis and adsorption simultaneously provided a distinct advantage over electrocatalysis alone for elimination of organic compounds. Hence, it deserved consideration for future wastewater treatment, and it was also essential to explore the mechanism of synergetic effects, which should be clearly related with the added activated carbon.

3.3. Mechanism study of the combined process

PNP degradation intermediates by single electrocatalysis such as phenol, hydroquinone, benzoquinone (BQ), *p*-nitrocatechol, 5-nitropyrogallol, hydroxyquinol, fumaric acid and oxalic acid were confirmed as the principal ones in our previous work [13], which were very similar to that of work of Oturan, where PNP was destructed by electro-Fenton method [14]. The disappearance of such intermediates was observed in three stages: (1) hydroxylated compounds such as *p*-nitrocatechol, hydroquinone, and BQ were formed first, (2) associated with increase of these products till maximum, ring-opening reactions to form aliphatic carboxylic acids such as fumaric acid and oxalic acid, and (3) slow mineralization of organic acids to carbon dioxide.

In the combined process, PNP degradation intermediates are very similar to those in the single electrocatalysis. However, both the numbers and area of peaks in chromatograms were found to decrease evidently, which implies that some early intermediates of oxidation were trapped by the AC before they had a chance to undergo further oxidation for initiation of the mineralization process. Thus, in the combined process, the AC adsorption played an important role.

Activated carbon was reported as catalyst for organic wastewater treatment by wet air oxidation [14,15]. In electrochemical system, carbon black was also proved as a catalyst for 4-chlorophenol oxidation [16]. It was considered that some charged species were adsorbed on the surface of the AC particles and the AC microelectrodes were formed under the electric field. The AC microelectrodes in fluidization mode could largely improve the degradation of the pollutants on

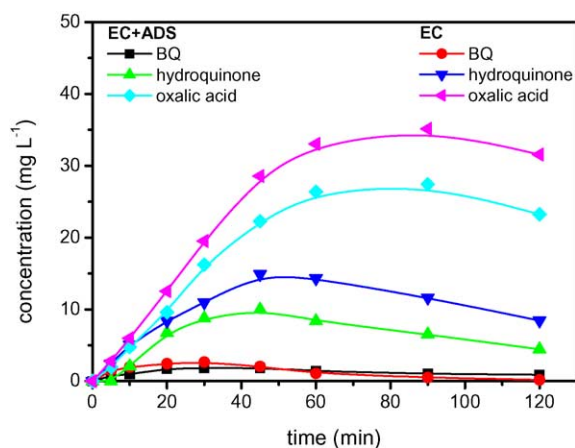


Fig. 4. Comparison of intermediates degradation. Conditions: PNP 150 mg L⁻¹, current 0.5 A, pH 3, flow rate 3.75 L min⁻¹, T 25 °C.

the surface of the AC. As shown in Fig. 4, degradation intermediates in the combined processes of electrocatalysis and the AC declined faster than that in individual electrocatalysis. Therefore, the PNP was destructed much more rapidly and the degradation of intermediates disappeared faster, leading to the ring-opening reaction in the combined processes of electrocatalysis and activated carbon.

3.4. Optimization of operating parameters

3.4.1. Continuous run of the reactor

As stated above, AC adsorption played an important role in the combined process. It is vital to evaluate the batches of running the reactor because of the deterioration of AC capacity after several times of reuse. Without changing the activated carbon (3 g), the reactor was repeated five times for fresh PNP (150 mg L⁻¹, 1.5 L) degradation, every run lasting for 1 h. For comparison, another test under same conditions other than in the absence of electrocatalysis, i.e., single adsorption, was carried out.

As listed in Table 2, in the combined process, PNP conversion was slightly changed from about 100% to 86% with the batch number reached 5. While in the adsorption process alone, PNP conversion declined remarkably from about 80% to 8%, indicating the capacity of AC was near saturation after operation of batch 5. As mentioned above, the contribution of

Table 2
PNP degradation in the combined process and adsorption in five continuous batches

Batch no.	PNP conversion (%)	
	ADS	EC + ADS
1	80.2	99.9
2	44.7	94.8
3	20.0	92.0
4	12.8	89.4
5	8.1	86.8

Conditions: PNP 150 mg L⁻¹, AC 2 g L⁻¹, pH 3, flow rate 3.75 L min⁻¹, T 25 °C.

adsorption on PNP conversion would be greater than that of electrocatalysis in the first period of 1 h (see Fig. 3). Thus, the significant decrease of adsorption on PNP conversion would certainly lead to the reduction of PNP conversion in the combined process. But practically, it only dropped within 15% in 5 runs. This fact confirmed that partly recovery of AC capacity was achieved in the combined process, i.e., regeneration of the consumed AC, which had been noticed by some works as the promising approach for AC regeneration [10,11]. The regeneration mechanism was proposed to be electrodesorption, where the organics adsorbed would firstly desorb from the activated carbon surface, and shifted to the surface of the anode to be further oxidized by electrochemical oxidation [10,17]. In this way, partial regeneration of spent activated carbon was fulfilled in the combined process. Under these conditions, no decay on performance was found after five batch runs.

3.4.2. Effect of activated carbon amount

The effects of the activated carbon amount on PNP conversion are shown in Fig. 5. More activated carbon would certainly promote PNP degradation. However, AC amount of 2 g L^{-1} was found sufficient because no significant enhancement on PNP conversion was observed when the amount of AC was increased from 2 g L^{-1} to 5 g L^{-1} .

BQ was reported as the typical intermediate in phenolic compound degradation under chemical oxidation, and was known as a rather persistent byproduct due to the difficulty in ring-opening [18,19]. Therefore, the study of BQ evolution will reveal the synergetic effect in the combined process. If activated carbon acted as the only adsorbent, BQ generation should be totally attributed to electrocatalysis. In other words, BQ formation would be similar at two different AC amounts due to the same electrocatalysis conditions. Plus the adsorption effect, BQ concentration in the solution of higher AC amount would be less. However, as shown by Fig. 6 of BQ variation with time at the AC amount of 1 g L^{-1} and 2 g L^{-1} , higher AC amount gave much more rapid formation of BQ, and followed by faster disappearance. This contradic-

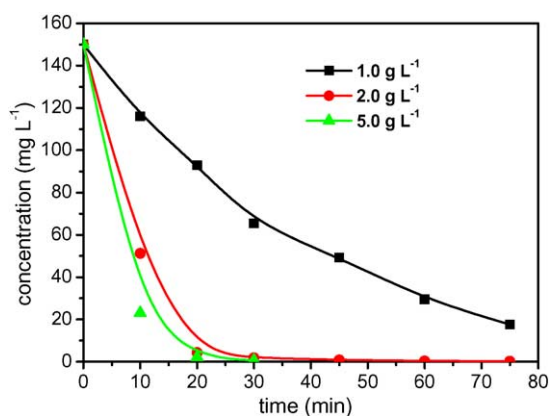


Fig. 5. Effect of AC amount on PNP degradation. Conditions: PNP 150 mg L^{-1} , current 0.5 A , pH 3, flow rate 3.75 L min^{-1} , $T 25^\circ \text{C}$.

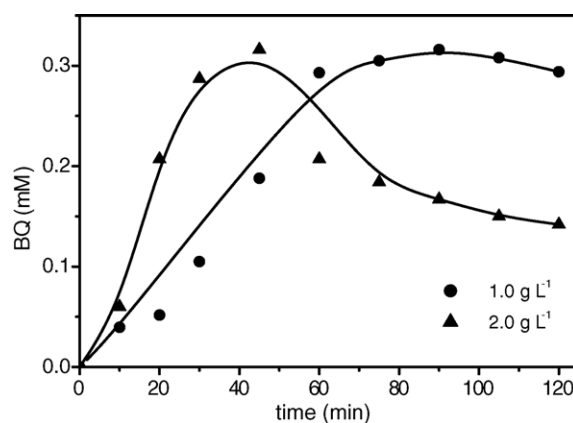


Fig. 6. BQ evolution at AC amount of 1.0 g L^{-1} and 2.0 g L^{-1} . Conditions: PNP 150 mg L^{-1} , current 0.5 A , pH 3, flow rate 3.75 L min^{-1} , $T 25^\circ \text{C}$.

tion confirmed that the AC acted not only as an adsorbent but also as a catalyst.

3.4.3. Effect of liquid flow rate

Liquid flow rate was an important parameter and could largely affect mass transfer. It was found that fluidization mode could largely improve mass transfer and accelerate the removal of PNP [20]. The enhancement was 30% in fluidization mode comparing with that in fixed bed mode. 3.75 L min^{-1} was considered to be the optimal liquid flow rate [21].

3.4.4. Effect of initial concentration of PNP

To investigate how the initial PNP concentration affected the application possibility of this combined process, different initial PNP concentrations (150 mg L^{-1} , 300 mg L^{-1} , and 500 mg L^{-1}) were examined, as shown in Fig. 7. The reaction rate constants calculated by Eq. (4) are listed in Table 3. Eq. (4) could be rewritten as

$$\ln \frac{c_0}{c_0 - \Delta c} = kt \quad (6)$$

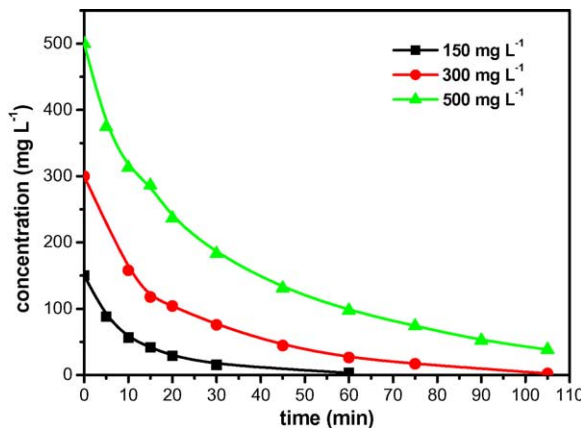


Fig. 7. Effect of initial PNP concentration on PNP removal. Conditions: current 0.5 A , AC 2 g L^{-1} , pH 3, flow rate 3.75 L min^{-1} , $T 25^\circ \text{C}$.

Table 3
Reaction rate constants of different PNP concentrations

PNP concentration (mg L ⁻¹)	<i>k</i> (min ⁻¹)
150	0.0696
300	0.0438
500	0.0261

where, Δc is the absolute PNP removal concentration. Thus, the absolute PNP removal can be calculated by the following equation

$$\Delta c = c_0(1 - e^{-kt}) \quad (7)$$

In Table 3, it could be observed that a high initial concentration would lead to the slight decrease of PNP removal rate. However, according to Eq. (7), the absolute PNP removal is correlative to c_0 and k , in which c_0 is the crucial factor. The absolute PNP removal should be favored at higher initial PNP concentration. This can be also confirmed from Fig. 8. For example, after treatment of 30 min, the absolute PNP removal of initial concentration 500 mg L⁻¹ was almost 200 mg L⁻¹ higher than that of initial concentration 150 mg L⁻¹. In view of that, this process would be much more effective for the treatment of higher concentration pollutants.

3.4.5. Effect of current

Current is an important factor in a usual electrocatalysis process, as in the previous works, where the phenol degradation rate was promoted at higher current [9]. To our surprise, little change on the PNP conversion was observed at different currents in the combined process. This phenomenon was also obtained by others [22], where they found no change of phenol with an applied current of between 10 A and 20 A in the presence of 1.5 g carbon black in an electrochemical cell. This makes the current less critical for PNP removal. However, it is more important to an environmental process, because the contribution of adsorption on PNP conversion would be different. This was confirmed by the variation of the typical intermediate, BQ.

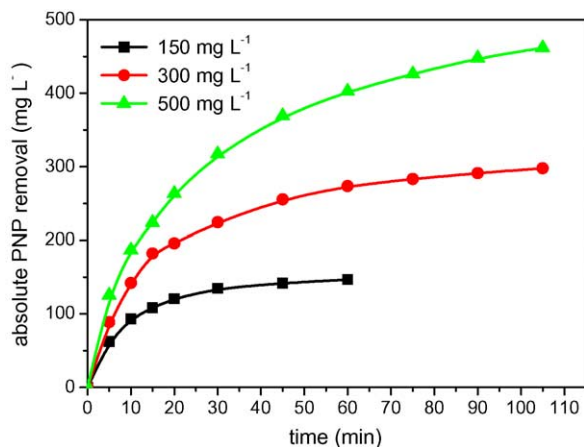


Fig. 8. Effect of initial PNP concentration on absolute PNP removal. Conditions: current 0.5 A, AC 2 g L⁻¹, pH 3, flow rate 3.75 L min⁻¹, *T* 25 °C.

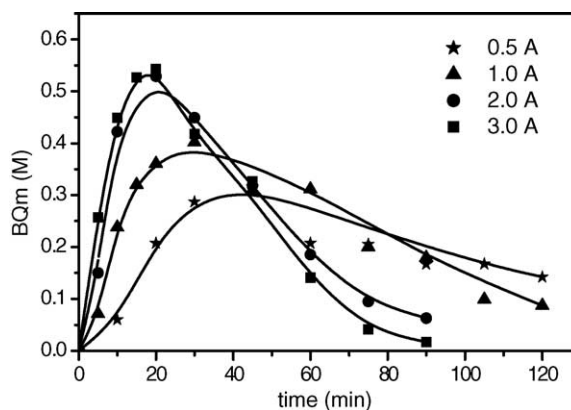


Fig. 9. Effect of current on BQ evolution. Conditions: PNP 150 mg L⁻¹, AC 2 g L⁻¹, pH 3, flow rate 3.75 L min⁻¹, *T* 25 °C.

As shown in Fig. 9, BQ evolutions under different current were compared. The results showed that under all currents BQ concentration increased firstly, and then decreased after reaching maximum concentration. With the increase of current, much more BQ generated in less time, and they disappeared much rapidly. The faster formation of BQ demonstrated that much more PNP was degraded other than phase transfer by adsorption. The rapid vanish of BQ led to fast mineralization of intermediates to little weight organic acids, which was favorable to regeneration of activated carbon capacity. This was verified by comparison of the regenerated AC adsorption capacity at different currents. At this point, higher current promoted AC regeneration efficiency. In the work of Zhang, the regeneration efficiency increased linearly with current intensity [11]. However, in our work, current of 2 A would be better account for economics because no greater changes were found on BQ evolution when applied current of 3 A.

3.5. Enhancement of sparged gas

Under the sparging gas, the reactor turned into a real three-phase electrochemical reactor. As shown in Fig. 10,

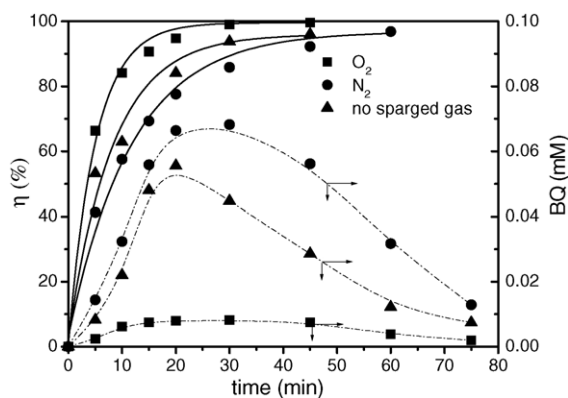


Fig. 10. Effect of gas (O₂ and N₂) sparging on PNP conversion and BQ evolution. Conditions: PNP 150 mg L⁻¹, current 0.5 A, AC 2 g L⁻¹, pH 3, flow rate 3.75 L min⁻¹, *T* 25 °C.

Table 4
H₂O₂ concentration produced in the process

Process	H ₂ O ₂ (mmol L ⁻¹)
EC	0.14
EC + O ₂	0.52

Conditions: current 0.5 A, sparged dioxygen rate 0.05 m³ h⁻¹, wastewater flow rate 3.75 L min⁻¹, temperature 25 °C.

degradation rates of the PNP under the same flow rate of O₂, N₂ and without sparged gas were compared. PNP conversion by sparging O₂ was much faster than that of PNP by sparging N₂, and even faster than that in absence of gas. The removal rate of PNP was almost enhanced 150% when oxygen was sparged into the reactor at 10-min treatment. Nevertheless, BQ (dot dash line) concentration maintained very low compared with that of BQ under sparging with N₂. In common electrocatalysis, faster PNP degradation rate would certainly lead to the rapid generation of cyclic intermediates, e.g., BQ. This contradiction implied that the sparged O₂ played an important role in the catalytic oxidation of intermediates. The accumulation of the primary intermediates (BQ) under N₂ suggested that O₂ was needed for the degradation of the by-products. Some authors had reported that oxygen could be changed into stronger oxidizing agent H₂O₂ by the two-electron reduction of oxygen [23,24]. In the same electrochemical system (absence of AC), H₂O₂ formation in the presence of air was also verified in our previous work [25,26]. H₂O₂ was quantitatively carried out by the standard titration method of potassium permanganate. As listed in Table 4, the concentration of H₂O₂ generated under oxygen sparging was 0.52 mmol L⁻¹, while it was only 0.14 mmol L⁻¹ in individual electrocatalysis process without oxygen sparging. Thus, we deduced that such a tendency of BQ evolution would be related with O₂ and H₂O₂. AC was not only a good media entrapping low concentration of PNP degradation intermediates, but also a catalyst for the decomposition of H₂O₂ [27]. H₂O₂ generated on the cathode would be transferred to the bulk of the solution or the surface of activated carbon. Thus, these intermediates would be further oxidized by this powerful oxidant on the surface of activated carbon. Someone may argue that it should be attributed to the enhancement of the adsorption capacity of AC, where organics were found undergoing polymerization reactions in the presence of dissolved oxygen [28]. However, no different intermediates especially polymers were found compared to that in the absence of oxygen.

4. Conclusion

The combined processes with electrocatalysis and activated carbon for *p*-nitrophenol abatement in one reactor showed synergetic effect in comparison with the individual ones. The mechanism of synergetic effect was considered to be the formation of AC microelectrodes under the electric field. AC acted not only as adsorbent but also as catalyst. The

electrocatalysis benefits from the catalytic role of AC, and adsorption benefits from the partial electrochemical regeneration of AC adsorption capacity.

Amount of AC, current, liquid flow rate, initial PNP concentration and sparged gas type (N₂ or O₂) were high to affect the performance of the combined process. Activated carbon amount of 2 g L⁻¹ is found to be sufficient in 1.5 L. *p*-Nitrophenol degradation in fluidization mode could be improved 30% at optimal liquid flow rate of 3.75 L min⁻¹. Higher current could lead to the fast decay of intermediates to little weight organic acids. The absolute PNP removal should be favored at higher initial PNP concentration, in view of which this process would be much more effective for the treatment of higher concentration pollutants. By sparging O₂ PNP conversion was much faster than that of PNP by sparging N₂, and even faster than that in the absence of external gas. The sparged O₂ played an important role of catalytic oxidation of intermediates like BQ. The continuous run of reactor showed that five batches run would not lead to much decay on performance and partly regeneration of spent activated carbon was verified in the combined process.

The catalytic characteristic of activated carbon was also confirmed by the following facts: (1) higher activated carbon amount led to much more rapid formation of PNP degradation intermediates (BQ) till maximum and faster disappearance; (2) the introduction of O₂ promoted PNP removal while the formation of H₂O₂ was verified in the same electrochemical system (absence of AC).

In general, the combined process with electrocatalysis and activated carbon adsorption is promising for future environmental remediation. Further study is suggested to probe the change law of the synergetic effect with operating conditions for best performance.

Acknowledgements

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