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Synergetic effects for *p*-nitrophenol abatement using a combined activated carbon adsorption-electrooxidation process*

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Abstract: A novel fluidized electrochemical reactor that integrated advanced electrochemical oxidation with activated carbon (AC) fluidization in a single cell was developed to model pollutant *p*-nitrophenol (PNP) abatement. AC fluidization could enhance COD removal by 22%–30%. In such a combined process, synergetic effects on PNP and COD removal was found, with their removal rate being enhanced by 137.8% and 97.8%, respectively. AC could be electrochemically regenerated and reused, indicating the combined process would be promising for treatment of biorefractory organic pollutants.

Key words: Electrochemical reactor, *p*-nitrophenol, Activated carbon fluidization, Wastewater treatment, Synergetic effect
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INTRODUCTION

Good technologies for treatment of biorefractory polluants are of critical environmental importance since they cannot be treated by conventional biological methods. Advanced oxidation processes (AOPs) producing high oxidation potential hydroxyl radicals are often investigated on their role in pretreatment or mineralization process of wastewater treatment. Apart from the well-known AOPs such as Fenton reaction, ozonation and photocatalysis, electrocatalysis seems to be an increasingly popular way for wastewater treatment (Bunce *et al.*, 1997; Jüttner *et al.*, 2000; Zhou *et al.*, 2001). Intensive research to improve electrochemical treatment efficiency focused on two areas. One area is development of better performance stable anodes with high catalytic activity, and high oxygen over-voltage anodes such as PbO_2 and boron doped diamond electrode which had been found to be very effective (Tahar and Savall, 1998; Wu *et al.*, 2002; Perret *et al.*, 1999). The other area is exploration of novel processes such as partial degradation process (Wu and Zhou, 2001), Electro-Fenton process (Alberto and Pletcher, 1999), and Photoelectro-Fenton process (Brillas *et al.*, 1998). There are few researchers who intend to develop and optimize electrochemical reactor to further promote treatment efficiency. In many practical cases, especially when the organic compound concentration is relatively low, mass transfer would certainly become important or even the controlling step (Sudoh *et al.*, 1986).

In order to improve mass transfer and enlarge specific electrode area, the fluidized bed cell is an alternative option (Jüttner *et al.*, 2000). If activated carbon (AC), one widely used adsorbent in water purification, is introduced into an electrochemical cell, operating in a fluidized mode, then the reactor

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is actually a fluidized electrochemical reactor where adsorption and electrochemical oxidation are integrated in one process. To our best knowledge, there are no related reports in literature on biorefractory organic pollutants treatment by this method.

This work is aimed at verifying to what extent AC fluidization can improve organics abatement and exploring if there exist synergetic effects in such a combined process. *p*-nitrophenol (PNP), a biorefractory compound and the priority toxic pollutants by U.S. EPA, was selected as the model pollutant due to its wide presence in wastewater such as pesticides and dyes wastewater.

MATERIALS AND METHODES

Chemicals

All chemicals used were analytical grade without further purification. High purity (>99.9%) gas (O_2, N_2) was used. The activated carbon (AC), provided by Shanghai Reagent Co., China, was crushed and screened and AC with particle size of 30–35 mesh was selected, and before use, was washed several times with deionized water and dried for 24 h to constant weight at 105 °C.

Set-up

Fig.1 showed the schematic diagram of the experimental setup. The electrochemical reactor was cylindrical, and the anode was a modified β-PbO_2 (250 cm^2 surface) proved capable of effectively degrading phenol (Zhou *et al.*, 2002). Such an anode and the cathode of stainless steel net (grid 1 mm×1 mm) were concentrically assembled into the electrolytic cell. The anodic compartment was separated from the cathodic one by a membrane. A known mass of activated carbon was introduced into the reactor before startup. The simulated wastewater (1.5 L) containing 150 mg/L PNP and supporting electrolyte (10 g/L Na_2SO_4), 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 to the cylindrical cell, and finally flowed back down to a reservoir immersed in water bath to control solution temperature at (25±0.5) °C. Constant current density (around 2 mA/cm^2) was maintained at the desired level with only minor adjustments of the applied voltage (cell voltage was around 4.5 V). A flowmeter was used to keep the flow rate of the wastewater in reasonable range to achieve AC fluidization. Gas (N_2 or O_2) was sparged from the bottom of the electrochemical reactor. At appropriate time, about 3 ml in volume sample was taken from the sampling port.

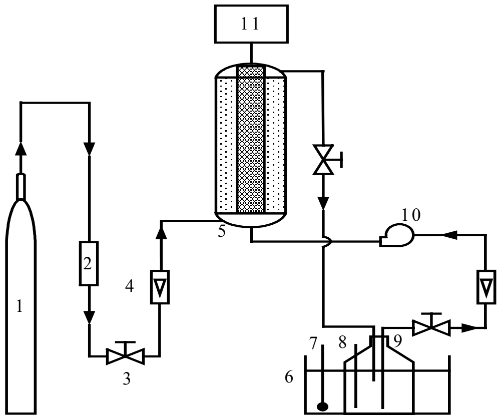


Fig.1 The schematic diagram of the set-up
1: Gas holder; 2: Gas dryer; 3: Valve; 4: Flowmeter; 5: Electrocatalysis reactor; 6: Water bath; 7: Thermometer; 8: Sampling port; 9: Reservoir; 10: Pump; 11: Power

This electrochemical reactor was also used for individual electrocatalysis (EC) or AC adsorption (ADS). In the individual EC process, no activated carbon was introduced into the reactor, while other operating conditions were all the same as those in the combined process (EC+ADS). In the individual ADS process, no current was applied in the system while other conditions were all the same as those in the combined process.

Analysis

The determination of PNP was carried out on high-performance liquid chromatography (HPLC, Gilson) by comparison with the retention time of the standard compound. Aliquots (25 μl) were injected into the HPLC to determine the concentration of PNP, running with mobile phase of acetonitrile/water/concentrated H_3PO_4 (v/v/v) at

58/42/0.2. The separation was performed using an ODS-18 reversed phase column at flowrate of 1.5 ml/min and column temperature of 25 °C. An UV detector with the wavelength set at 254 nm was used. The COD concentration was measured by standard method (APHA *et al.*, 1995). The COD or PNP removal efficiency (η) is defined as:

$$\eta(\%)=(C_0-C)/C_0\times 100 \tag{1}$$

where, C_0 and C denote PNP or COD concentration at initial time and given time t, respectively.

RESULTS AND DISCUSSION

To evaluate the advantages of adding AC into the electrocatalysis process, PNP and COD removal by adsorption (ADS), electrocatalysis (EC) and their combined process (EC+ADS) were compared in the same reactor, respectively.

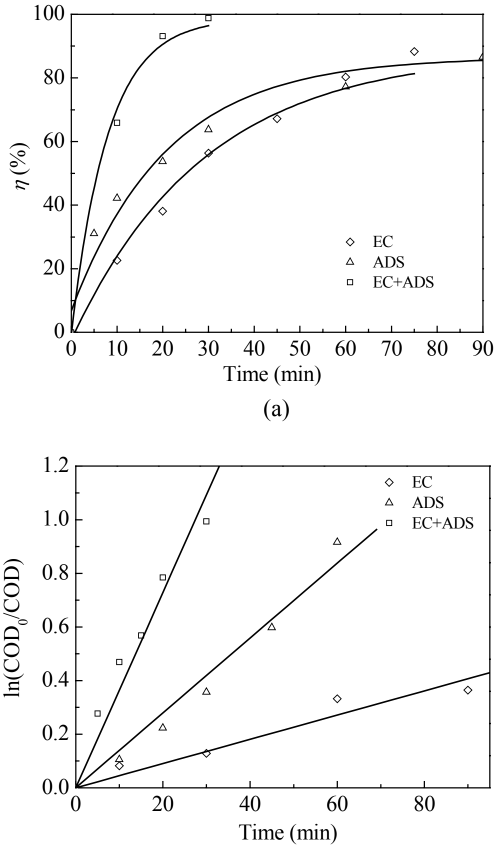
As shown in Fig.2, the tendency of PNP and COD concentration can be fitted well by the following apparent first-order kinetics,

$$\ln(C_0/C)=kt \tag{2}$$

where, k is the apparent first-order reaction rate constant. The k values of the three different processes can be obtained from the data-fitting in Fig.2 and are listed in Table 1. The reaction rate constants in the combined process were found larger than that of the sum of two individual processes, indicating existence of synergetic effects in the combined process. For convenience, k_1, k_2 and $k_{1,2}$ represent the k value in the electrocatalysis, adsorption process and the combined process, respectively. The enhancement factor (f) in the combined process for PNP and COD was as high as 137.8% and 97.8%, using the following calculation

$$f=(k_{1,2}-k_1-k_2)/(k_1+k_2)\times 100\% \tag{3}$$

Such a combined process obviously possesses advantages over using electrocatalysis or adsorption alone for eliminating organic compounds.



(a)

(b)

Fig.2 Comparison of PNP (a) and COD (b) removal by electrocatalysis, adsorption and their combined process

Table 1 Reaction rate constants for COD and PNP

Processes	k_{PNP} (min^{-1})	k_{COD} (min^{-1})
EC	0.0265	0.0045
ADS	0.0373	0.0139
EC+ADS	0.1523	0.0364

The liquid flowrate significantly influences mass transfer, which in turn affects both the electrocatalysis and adsorption. To explore how the behaviors of AC affect the performance of the combined process, the results of liquid flowrates influence on COD removal are listed in Table 2. At flowrate of 1.25 L/min, AC was almost fixed and it started to fluidize when the flowrate was increased to 1.75 L/min. The enhancement of COD removal by fluidizing was remarkable. For example, COD removal rate was improved by about 16%–22%

when the flowrate was increased from 1.25 L/min to 1.75 L/min. But, when liquid flowrate increased from 3.25 L/min to 3.75 L/min, the enhancement became insignificant. This indicated that COD removal was no longer mass-transfer controlled when the liquid flow was higher than 3.25 L/min. It also implied that optimal flowrate for this reactor was 3.25 L/min, where the enhancement on COD removal was around 22%–30% compared with that of the fixed one.

Table 2 Effects of liquid flowrate on COD removal

Flow rate (ml/min)	30 min	60 min
1.25	39	53
1.75	55	65
3.25	68	79
3.75	71	83

The synergetic effect was apparently related to the addition of AC. It may be argued that the synergetic effect should be attributed to the AC adsorption. To verify it, comparison of PNP abatement by single process (adsorption) and by the combined process was carried out under similar conditions, each was repeated 5 runs, with every run lasting 1 h, as shown in Fig.3.

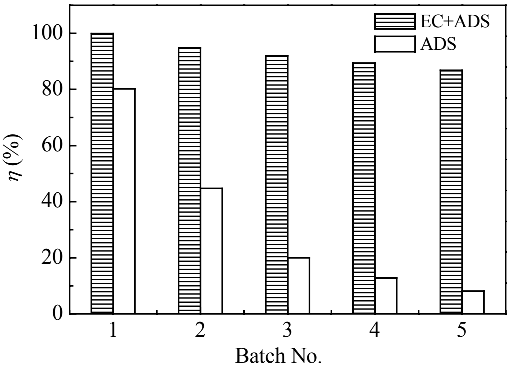


Fig.3 Comparison of PNP abatement in the combined process and single adsorption

In the combined process, PNP conversion slightly decreased from about 100% to 86% with the batch number reached 5. While in the individual adsorption, PNP conversion remarkably decreased from about 80% to 8%, indicating AC capacity was near saturation after 5-time operation. Thus, significant decrease of adsorption capacity 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 partial recovery of AC was achieved in the combined process, i.e., regeneration of the spent AC, which had been noticed by some workers as the promising approach for AC regeneration (Narbaitz and Cen, 1994; Zhang, 2002). They considered the regeneration followed the electrodesorption mechanism, where adsorbed organics would be first desorbed from the AC surface, and then shifted to the anode surface to be further oxidized by electrochemical oxidation. In this way, partial regeneration of spent AC was achieved in the combined process and 5 batches run would not lead to obvious decrease in performance.

From the above preliminary investigation, the advantages expected from this combined process were (1) enhanced cost-effectiveness of the whole process by reducing equipment and flow; (2) in-situ regeneration of AC partly to minimize need for fresh AC supply. Therefore, such a combined process provided a novel alternative for biorefractory compounds abatement. Further work on the effects of parameters and mechanism on the synergetic effect is required.

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