Electrochemical regeneration of activated carbon loaded with *p*-nitrophenol in a fluidized electrochemical reactor

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Abstract

This paper described a novel electrochemical process for the regeneration of activated carbon (AC) loaded with *p*-nitrophenol (PNP), aiming to reduce regeneration time and improve cost-effectiveness of the process by adoption of a novel non-active anode of modified lead dioxide and operation of AC in a fluidized mode. The regeneration parameters such as current density, liquid flow rate, NaCl concentration, pH of the solution and regeneration time were systematically investigated. Under the optimum conditions, the regeneration efficiency of AC could reach 90% in 1.5 h, and no significant declination was observed after five-times continuous adsorption–regeneration cycles, confirming the reuse feasibility of the regenerated AC. The adsorption of organic pollutants was confirmed occurring in the micropore of AC, and AC regeneration was mainly due to the decomposition of organics by the attack of active species such as hydroxyl radical that were generated by electrochemical oxidation. The time-space production for AC regeneration has been greatly improved in the present modified process, indicating this regeneration process is much more potentially cost-effective for application.
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1. Introduction

Due to its large specific surface area and adequate pore size distribution, activated carbon (AC) has been widely employed in water and wastewater treatment. But AC is relatively expensive and readily saturated, thus it would not only be uneconomic but also bring about environmental pollution if the exhausted AC is not effectively regenerated. Therefore AC regeneration methods are urgently required for a wider application of AC in processes [1].

There are many well-established techniques used to regenerate AC including extractive regeneration, thermal regeneration [2], and wet air oxidation [3]. Thermal regeneration may be the most extensively used method in industry, however, this process is of time-consumption, high energy demand and high cost that characterized by 5–15% carbon loss because of oxidation and attrition [1,2]. AC regeneration by wet air oxidation requires high temperature (800–850 °C) and high pressure

(0.2–1.0 MPa), thus it is expensive due to the large cost on equipments and operation [1,3].

Recently, AC regeneration by electrochemical oxidation has been reported to be a promising approach, by which the regeneration efficiency can be reached as high as 80–95% [4–6]. Though AC regeneration mechanism is proposed by electrodesorption, where organics are desorbed on AC surface and further oxidized by electrochemical oxidation [5,8], it is still far from clear because only a few works on organics degradation mechanisms and almost no experimental works related to the change of physico-chemical properties of AC have been carried out. Much more attention has been paid to optimize AC regeneration process [4–7], however, long regeneration time is required to reach high regeneration efficiency (may be as long as 5 h) [4], which certainly influences the economics of the process and thus limits its application. The main reasons are as follows. (1) Active electrodes such as graphite and Pt are adopted; on which oxygen is more likely generated other than active species such as hydroxyl radicals [9]. It has been reported that the performance of the electrochemical oxidation is strongly dependent on the electrode material [10], which are basically divided into two types, active electrode and non-active electrode. And it was

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found that non-active electrodes such as PbO_2 exhibited better performance for organic pollutants degradation than that of the active electrodes such as Pt [11]. Therefore, the AC regeneration is not complete enough due to the relatively low electrochemical oxidation activity. (2) Less attention is paid to the mass transfer during regeneration, which causes the regeneration time being longer. It was reported that mass transfer would become the decisive factor when the pollutant concentration was relatively low [12], which resulted in the degradation of pollutants more likely occurring on the surface of the electrodes rather than the bulk of the solution. So that many degradation intermediates would stay easily on the anode and led to the electrode fouling [13], which reduced the degradation efficiency and thus increased the regeneration time. Therefore, it is urgently necessary to optimize the electrochemical reactor by promoting mass transfer to enhance the time-space efficiency for organic pollutants degradation, so that it could reduce the AC regeneration time.

Bearing these problems in mind, this work made two modifications to enhance the cost-effectiveness of the regeneration process. (1) A novel non-active electrode of the modified PbO_2 electrode was used, which could generate hydroxyl radical effectively and maintain good performance stable for organic wastewater treatment, where its service life was predicted to be 10.4 year in application under $0.1\,A\,cm^{-2}$ current density and strong acidic solutions (maybe as high as $9\,M\,H_2SO_4$) [14]. (2) AC regeneration was performed in a fluidized mode. As reported in our previous work, electrochemical oxidation was found accelerated effectively by improvement of mass transfer in this fluidized electrochemical reactor [15], which might speed up the AC regeneration.

The objective of this work is to verify the advantages of the modified regeneration process, and to elucidate possible mechanism for AC regeneration by HPLC analysis, N_2 adsorption isotherm, and adsorption isotherm measurement. Much more attention was paid to the optimization of AC regeneration process to improve cost-effectiveness of this modified method, using *p*-nitrophenol (PNP) as the model adsorbent. Nitrophenol was chosen due to its environmental importance: one of priority toxic pollutants and typical biorefractory organic compounds used as raw materials for production of pesticides, insecticides, herbicides, explosives, and various synthetic compounds such as dyes [16].

2. Experimental

2.1. Chemicals and materials

All chemicals used were analytical grade without further purification. The activated carbon (AC, woody), provided by Shanghai Reagent Co., China, were crushed and screened and those with particle size of 0.4–0.5 mm were selected by metallic size sieves. Prior to use, they were washed several times by deionized water and dried for 24 h to constant weight at 105 °C. The AC (virgin or regenerated) used for electrochemical regeneration was previously saturated as follows: 1 g of the dried AC was added to a 1-L PNP solution $(1000\,mg\,L^{-1})$ to adsorption, and the suspension was maintained at room temperature by ther-

mostat and shaken mechanically for 1 day (longer than needed to achieve equilibrium). The residual concentration of PNP in the solution was determined by HPLC analysis (measurement as described below) to establish the adsorption capacity. Then the exhausted AC was filtered out with size sieves and was dried at 105 °C for 12 h. Thereafter, the cooled carbon was weighted and kept in a desiccator for electrochemical regeneration.

2.2. Electrochemical regeneration

Fig. 1 shows the schematic diagram of the electrochemical reactor used in this work. The reactor was cylindrical, and two hydraulic distribution boards were installed on the upper and lower parts of the body, which divided the reactor into three parts from top to bottom, i.e. outlet chamber, electrochemical cell (Ø 75 mm × 180 mm) and inlet chamber. The outlet chamber and electrochemical cell were connected by a flange. The cathode was set surrounding the inert wall of the electrochemical cell (plexiglass), and the anode rod (Ø 45 mm × 200 mm) was set in the centre, among which AC was packed. In this experiment, the cathode was stainless steel net (grid 1 mm × 1 mm), and the anode was a β-PbO_2 ($250\,cm^2$ effective surface) that was modified by fluorine resin. The schematic diagram of the experimental setup and the preparation of the anode could be seen in detail in our previous work [17,14].

Prior to regeneration, a known mass of the prepared exhausted AC was introduced into the electrochemical reactor. The supporting electrolyte of NaCl (1.5 L, concentration of 1–$5.0\,g\,L^{-1}$), adjusted at suitable pH value, was pumped into the inlet of the reactor in the bottom and passed through a hydraulic distributor bar to the electrochemical cell, and finally flowed back down to a reservoir which was placed into a water bath to
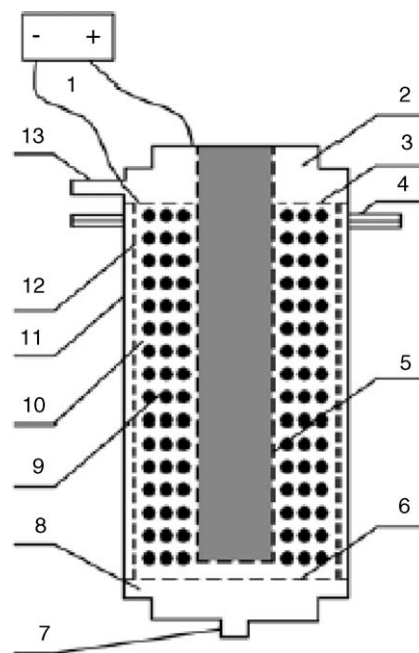

Fig. 1. The schematic diagram of the reactor. 1. Power; 2. outlet chamber; 3 and 6. hydraulic distribution board; 4. flange; 5. anode; 7. inlet; 8. inlet chamber; 9. AC; 10. electrochemical cell; 11. body; 12. cathode; 13.outlet.