Improvement of spent activated carbon regeneration by wet oxidation processes

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ABSTRACT

Activated carbons saturated with *p*-nitrophenol were regenerated under subcritical conditions by means of wet oxidation, analyzing the effect of temperature (160–200 °C) and oxygen partial pressure (3–12 bar). The research intended to achieve two main objectives: (a) to restore the carbons adsorption performance and (b) to get insight about the *p*-nitrophenol oxidation process and how it can be influenced by the presence of the adsorbent.

Based on the contaminant oxidation mechanisms, which was defined as a series of radical processes, a kinetic model was developed. The model was created by COMSOL MULTIPHYSICS software, and allowed obtaining characteristical parameters. Further comparison between theoretical and experimental results showed the suitability of the model in the whole range of experimental domain. Subsequent application of this model to regeneration experiments confirmed the need of developing a new model in the latter case, since the presence of carbon involved a significant modification of kinetic parameters, which was related to the catalyzing action of the adsorbent.

It was also found that both temperature and pressure affect the *p*-nitrophenol degradation process as well as porosity regain of the carbons. Values of *p*-nitrophenol regeneration efficiency up to 87% for the highest values of temperature and oxygen partial pressure.

1. Introduction

In spite of the wide use of activated carbons (ACs) for the treatment of organic compounds in wastewater, carbon adsorption is a costly process and this fact has encouraged an increasing research concern into the manufacture of low-priced alternatives to activated carbons, as well as regeneration processes.

Regeneration of ACs by means of aqueous thermal desorption with an oxidizing agent, is a well known and viable alternative in comparison with other regeneration processes such as, solvent extraction, biological treatment, electrochemical methods, microwave, and thermal regeneration [1,2].

Previous works have proved the suitability of wet oxidation regeneration (WOR) processes for wastewater treatment under mild pressure and temperature conditions yielding results that are comparable to those attained with supercritical water [3,4]. In the context of the regeneration of ACs saturated with organic compounds, WOR oxidation has also proved to be very effective, with high regeneration efficiencies.

By WOR processes, the spent carbon, within an aqueous solution, is subjected to heating (150–200 °C) and simultaneously oxygen is fed to the bulk of the solution at moderate pressures (usually in the interval 10–50 bar). When the saturated adsorbent comes into contact with warm water, part of the adsorbate begins to desorb. The oxygen fed to the water then proceeds to oxidize the desorbed adsorbate modifying the desorption equilibrium and promoting the migration of more adsorbate molecules within the liquid phase.

Wet oxidation of organic pollutants as well as WOR of adsorbents saturated with hazardous organic compounds has attracted the interest of researchers due to its fast reaction rate, which easily allows the decomposition of the molecules in the aqueous solution to other less-toxic ones. For instance, Joglekar et al. carried out wet air oxidation (WAO) of aqueous solutions of phenol and substituted phenols, and their results showed efficiencies of phenol removal greater than 99.9% [5]; Quesada et al. investigated the catalytic wet air oxidation of paracetamol on activated carbon as a water treatment technique using an autoclave reactor. They found that the use of adsorbent in several cycles showed a drop in both BET surface area and catalyst performance [6]; Delmas et al. [7] worked with a blend of two model pollutants in a fixed bed reactor, they found out that AC acted as a catalyst of its own regeneration. Also, catalytic

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wet oxidation (CWO) of phenol and derivates have been studied in several occasions [8–10].

In general, the pieces of research concerning the study of WOR of organic loaded ACs are focused on the analysis of the influence of variables, such as temperature, pressure or heating ramp. However, although in most of these works the stages of desorption as well as the oxidation of the organics on the liquid phase are addressed, the process is not quantitatively analyzed.

To the best of the authors' known, the estimation of the oxygen that is actually consumed in the bulk phase and that oxidizes the adsorbate within the porous network of the adsorbent has not been made before.

In a previous work [11], this research group studied the regeneration of ACs saturated with *p*-nitrophenol (PNP) by desorption in water under subcritical conditions, and achieved values of regeneration efficiencies up to 80%. Using an oxidant agent such as oxygen in the process might improve these results provided the oxygen fed can react with the PNP difficult to remove by simple desorption which is presumably adsorbed by strongest bonds. As a continuation of this previous studies, this work is targeted to improve the cited studies in terms of regeneration efficiency, at the same time that it aims to investigate the influence of the carbon presence on the adsorbate oxidation.

In this way, the (PNP) oxidation process was separatively investigated in the systems PNP–O_2 and AC–PNP–O_2. In both cases, the study was firstly made experimentally and then complemented with a modellization using COMSOL MULTIPHYSICS SOFTWARE. From it, different energetic and kinetic parameters were estimated.

The study was structured as follows;

- In the first place, the oxidation of PNP under different temperatures and oxygen pressures was evaluated. A model was created to simulate the process, based on the reaction mechanisms taking place, which are widely documented.
- Then, this model was applied to WOR data, with the aim of elucidating if the kinetics of PNP oxidation might be influenced by the presence of the AC.
- Finally, a new model was built for the system AC–PNP–O_2, and the differences between kinetics parameters were evaluated.

2. Experimental

2.1. Material

PNP was obtained from Sigma and used without further purification.

The adsorbent used in this work is carborb (CB) a commercial activated carbon provided by Chemviron (microporous material, specific surface area 930 m^2 g^{-1} and point of zero charge of 10.2) [12]. Prior to use, the adsorbent was repeatedly washed with boiling distilled water and dehydrated at 110 °C for 48 h. Finally the adsorbate was stored in a dessicator at room temperature.

The saturation of the spent carbon was made as follows: a mass of 2.4 g of CB carbon was added to 1 L of PNP solution (3 g L^{-1}). The system was then left to equilibrium under a thermostated temperature of 298 K for 72 h, since these conditions guarantee the complete saturation of the carbon and the adsorption equilibrium [13].

2.2. PNP oxidation

PNP oxidation tests were performed in a 500 mL stainless steel autoclave equipped with a mechanically driven stirrer. The experimental installation used is described elsewhere [11]. Temperature was modified in the range of 160–200 °C using an electric jacket and the oxygen partial pressure was varied in the range of 3–12 bar. A stirring speed of 600 rpm and an average heating rate of 2.8 °C min^{-1} were used in all cases. Once the selected temperature was reached, the oxygen was introduced in the reactor, this moment is taken as zero time.

For all experiments a volume of 433 mL of 0.1 g L^{-1} PNP solution was added in the reactor, since previous calculations showed that these conditions allow the previsible expansion of liquid water, as well as its conversion to vapor, under the experimental conditions used.

The concentration of adsorbate in aqueous solution was measured by an ultraviolet spectrophotometer (Heλios-α), at different time intervals, at the wave length of 225 nm.

The experimental series were denoted as Ox(oxidation)/*T*/*P* where *T* and *P* stand for the temperature and oxygen partial pressure of each oxidation process, respectively.

2.3. Regeneration of activated carbons

The experimental installation and procedure for WOR processes are the same as in the case of oxidation processes, also using the same experimental conditions; 0.5 g of spent carbon was introduced in the reactor with 433 mL of distilled water and once the target temperature was reached, the oxygen was introduced in the reactor, this moment was considered as zero time. The concentration of desorbed compound was measured spectrophotometrycally at different periods of the time.

After regeneration, the ACs were weighted and kept in a dessicator for subsequent analysis.

The regenerated adsorbents were denoted as WOR (wet oxidation regeneration)/*T*/*P*, where *T* and *P* stand, respectively, for the temperature and oxygen partial pressure of each regeneration process.

2.4. Characterization of activated carbons

The porosity of pristine, spent and regenerated ACs was studied by N$_2$ adsorption at 77 K (AUTOSORB-1, Quantachrome); before analysis, all samples were outgassed at 120 °C for 12 h.

Adsorption data were used to calculate typical textural parameters by means of suitable models [14]. In particular, the following parameters were calculated: (a) the value of the BET specific surface (S_{BET}), (b) the external surface (S_{EXT}) by the α_s-method using a suitable reference non-porous solid [15], (c) the volume of micropores through the Dubinin–Radushkevich equation (V_{DR}), and (*d*) the volume of mesopores (V_{me}), as the difference between the pore volume at $P/P_0 = 0.95$ and $P/P_0 = 0.10$.

The suitability of the regenerated samples as PNP adsorbents was checked by PNP adsorption isotherms, under the conditions defined in previous works [12]; briefly, a carbon mass of 0.05 g was added to 10 mL of 3 g L^{-1} PNP solution, and kept under stirring conditions (600 rpm) for a period of time of 120 h. The concentration of the supernatant solutions was measured spectrophotometrically at 225 nm (Heλios-α spectrophotometer), as previously indicated. The amount of PNP adsorbed was calculated from the difference between initial and final concentration.

The regeneration efficiency (R.E, %) was calculated by means of Eq. (1), which was used with two adsorbates: N$_2$ at 77 K (taking the adsorbed quantity as that corresponding to a partial pressure of 0.95), and PNP in aqueous solution at 25 °C (taking the adsorption quantity as the difference between the solution initial and final concentration).

$$\text{R.E.}(\%) = \frac{\text{Adsorption capacity after regeneration}}{\text{Adsorption capacity of fresh AC}} \times 100 \quad (1)$$