Catalytic wet air oxidation of caffeine by using a Pt based-catalyst supported on a lignocellulosic activated carbon

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INTRODUCTION

Wastewater usually contains a great variety of hazardous organic compounds, being of special concern the so-called *emerging compounds*. Among these substances, the priority compounds are considered as especially toxic, showing most of them endocrine disruption effects.

In recent years it is recognized that pharmaceuticals and toiletries personnel present in wastewaters are the most problematic compounds in regard to disposal, within the so-called emerging contaminants. Such substances are not removed completely by conventional methods of purification, moreover, are bioaccumulated and therefore may present a potential risk to human health. For total or near-complete elimination of these contaminants are developing new treatment technologies, known as tertiary treatments; among others, adsorption, membrane processes, supercritical oxidation or Fenton processes. One of the substance considered as emerging contaminant with greater presence in urban and industrial wastewaters is caffeine, and its metabolite, paraxanthine. It is an alkaloid of the methylxanthine family, which appears as crystalline solid, white and bitter taste, and that is commonly used as a stimulant.

Advanced oxidation processes (AOPs) constitute a promising technology for the treatment of wastewater containing organic refractory compounds, as a pre-treatment step to the conventional biological treatment. Among AOPs, wet air oxidation (WAO) has already been applied successfully to treat effluents from printing and dyeing industry. A wide range of products have been treated successfully due to the capacity of this process to eliminate products with low solubility such as polymers or fatty acids. The main disadvantages of WAO are the high requirements of temperature (200-320 °C) and pressure (20-200 bar) which results in high operation costs. The use of a catalyst strongly improves the degradation of organic pollutants by using milder conditions of temperature and pressure (Herrero et al., 2012; Jurado et al., 2012; Melero et al., 2009).

On the other hand, the most organic materials rich in carbon, mainly coals, wood, coconut shell, peat, agricultural by-products such as fruit stones, seeds hulls, straw and stalks, lignite, coal, petroleum, coke, etc. can be used as precursor materials for activated carbon preparation . The selection of the material is based mainly on (i) low in inorganic matter; (ii) availability and cost; (iii) low degradation upon storage and (iv) ease of activation. The most common processes of activation are physical and chemical. The physical activation involves a first step of carbonization and then the controlled gasification of a carbon precursor with a gas stream (O_2, CO_2, steam water, etc.) at high temperatures. In the chemical activation, the raw material is impregnated using a chemical agent (H_3PO_4, $ZnCl_2$, H_2SO_4, H_3BO_3, KOH, NaOH, etc. solutions) and then is washed and heated at lower temperatures than in physical activation. Some previous works report several conditions using different precursors and chemical activating agents (Gomes et al., 2008; Giles et al., 1960; Gómez et al., 2007).

Lignocellulosic materials constitute the more commonly used precursor and account for around 45 wt% of the total raw materials used for the manufacture of activated carbon. Low contents of inorganic materials are important in the preparation of activated carbons with low ash content, but relatively high volatile content is also needed for the control of the carbon porosity. Both characteristics are common to most of lignocellulosic materials used for the production of activated carbons. These cellulose-type materials such as wood, sawdust, nutshells and fruit stones are mainly used for chemical activation method.

Chemical activation method involves lower temperatures than physical activation and the porosity is generated through dehydration reactions in the carbonaceous structure. Earlier studies have shown that chemical activation using phosphoric acid at moderate temperatures generates, in some lignocellulosic materials, a high surface area and a balanced degree of micro and mesoporosity, useful for a wide range of applications as catalysts or adsorbents. The development of surface area appears to be greatly dependent on the heat treatment temperature in the chemical activation process. We have selected peach stones because of their availability and desirable physical characteristics as activated carbon precursor.

The objective of this work was to evaluate the removal of caffeine from water by catalytic wet air oxidation (CWAO), using a Pt based-catalyst supported on a lignocellulosic activated carbon (based on peach stones). The effect of the operation conditions, e.g., pressure, temperature and weight of catalyst on the removal of the contaminant and Total Organic Carbon was studied.

MATERIALS AND METHODS

Materials and synthesis of catalysts

The tested catalytic support was based on a mesoporous activated carbon synthesized from peach stones by chemical activation using H_3PO_4 solution. The active phase of the catalyst was platinum with a metallic content of 3%, using $H_2PtCl_6x6H_2O$ as precursor. The metal was incorporated to the support by incipient wetness impregnation. The textural and morphological properties of the catalyst were explored. The tested operation conditions were the total pressure (20-40 bar), temperature (120-180 ºC) and the weight of catalyst (0.005-0.4 g). The sample analysis were carried out by using HPLC technique.

WAO and CWAO experiments

Continuous experiments were carried out in a Microactivity-Reference unit (PID Eng & Tech, model MA-Ref), which is an automated and computer-controlled continuous-flow trickle-bed laboratory reactor. Concentrations of the fed aqueous solutions ranged from 20 to 40 ppm. A fixed-bed tubular reactor in Hastelloy C-276 was heated with a reactor furnace and integrated within the hot box. Liquid and gaseous flows were introduced into the hot box system, which includes an electric forced convection heater which permits the process route to be preheated and kept at temperatures up to 190ºC. The liquid reactant was introduced into the unit using a HPLC positive alternative displacement pump (Gilson, model 307). The oxygen source in these experiments was air, which was fed to the system through an electronic mass-flow controller. The preheated gas and liquid streams merge in a T-joint and are then introduced to the top of the reactor through a 10 mm sintered 316 stainless-steel filter (another is located at the outlet of the reactor, which protected the arrangement from possible catalyst fines). A porous (2 mm) plate made of Hastelloy C-276, supported on a 316 stainless-steel pipe, was placed inside and near the middle of the reactor tube to support the fixed bed composed of 0-0.4 g of catalyst placed over inert spherical glass beads. The reaction temperature was measured by a thermocouple, which was inserted through the upper end of reactor and was in contact with the catalyst bed. The thermocouple was regulated from the pre-set temperature by a PID temperature controller (TOHO, model TTM-005). The gas and liquid phases, which passed the catalytic bed in a co-current down flow mode and flowed out at the bottom of the reactor, were separated in a high-pressure liquid-gas (L/G) separator cooled with a Peltier cell. The L/G separator equipped with a micrometric servo-controlled valve and capacitive level sensor provides an efficient liquid discharge from the unit.

RESULTS AND DISCUSSION

Table 1 summarizes the operating conditions used in the experiments carried out in the installation.

N_2 adsorption-desorption isotherm of the catalyst can be classified as IV-type, characteristic of mesoporous solids. The specific surface area of the catalyst was of 1100 $m^2.g^{-1}$. BET area decreased after the CWAO process until 900 $m^2.g^{-1}$, probably due to the formation of a carbon deposit on the catalyst surface.

Table 1. Operation conditions in WAO and CWAO experiments.

	Run	**T (ºC)**	**P (bar)**	**C_0 (mg/L)**	**Catalyst load. (g)**
WAO	1	150	20	30	0
	2	180	20	30	0
CWAO	3	150	20	30	0,4
	4	150	20	30	0,2
	5	150	20	30	0,1
	6	150	20	30	0,05
	7	120	20	30	0,05
	8	170	20	30	0,005
	9	150	20	30	0,005
	10	130	20	30	0,005
	11	150	30	30	0,005
	12	150	40	30	0,005
	13	150	20	20	0,005
	14	150	20	50	0,005

Reaction 1 is carried out without catalyst, the concentration of caffeine in this reaction does not decrease, it is almost constant. However, in reactions 4, 6 and 7, in presence of catalyst the concentration initially decreases sharply and throughout the remainder of the reaction is almost constant (may decrease in some cases). The 10 reaction was performed in the presence of a small amount of catalyst. In this case, initially reduces the concentration of caffeine. CWAO reaction obtains good conversions in Caffeine, TOC and TN removal. The N-compounds detected in the effluents corresponds mainly to ammonia, with only traces of nitrates. It can be seen that the conversion is enhanced when the temperature increases (Centi et al., 2001).

Catalyst deactivation may be caused by the formation of a carbonaceous deposit onto the catalyst surface, as no Ni leachates were detected. The catalyst recovered after the reaction recovers the structure of the Pt/AC precursor. After the recovery the catalyst is reduced at 350ºC in order to employ it in a new reaction.

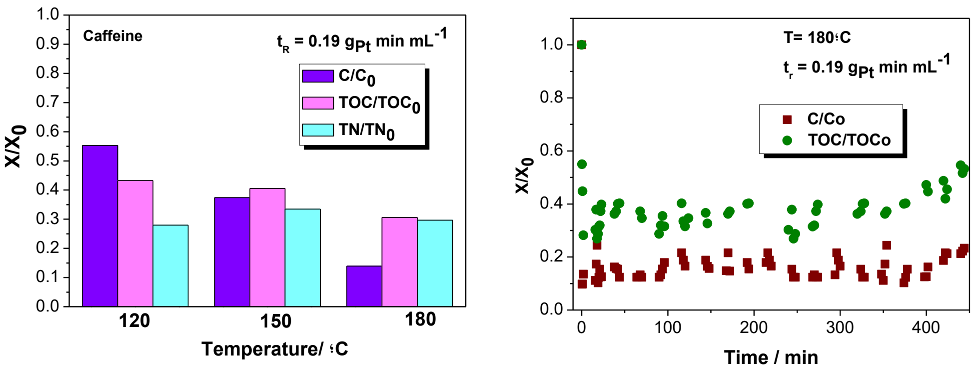

Figure 1. Conversions obtained at different temperatures and evolution of caffeine and TOC with reaction time.

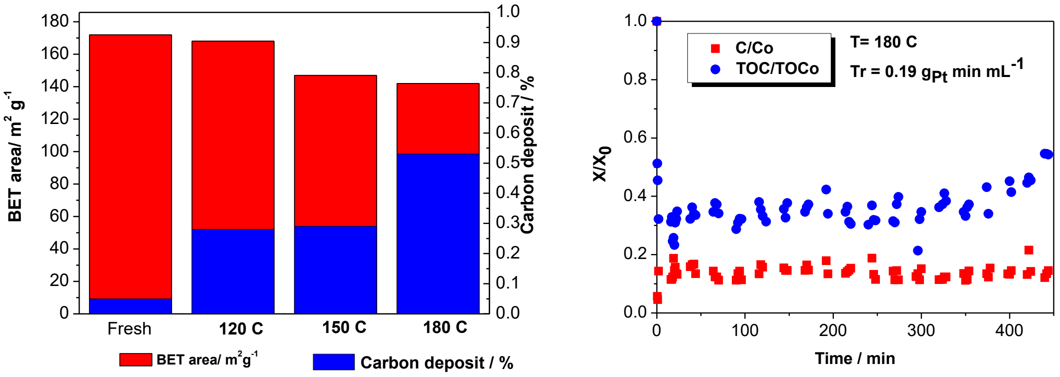

Figure 2. Catalyst deactivation by the formation of a carbonaceous deposit onto the catalyst surface, and caffeine and TOC removal after reduction of catalyst used.

After the reduction the catalyst can be employed in a new reaction with conversions similar to those obtained by the fresh catalyst. This is due to the regeneration after the reduction treatment.

CONCLUSIONS

The results of the study showed that CWAO of caffeine and TOC in water was successfully carried out using Pt(3%)/activated carbon as catalyst at the tested conditions. This material provides an efficient removal of caffeine, a trace compound of the domestic wastewater pollution in a continuous system. The calcination of the catalyst recovered after the reaction allows its reutilization with performances very similar to those obtained for the fresh catalyst.

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