ACTIVATED CARBON USED AS CATALYST FOR THE CATALYTIC WET AIR OXIDATION OF PHENOL

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Introduction

Since the Industrial Revolution until nowadays, the access to clean water is becoming more and more difficult. The increase of industrial activities, specially those of chemical nature, yearly generates tons of hazardous wastewater. Among them, aqueous effluents polluted by phenolic compounds mean an important percentage. Thus, effective wastewater treatments are mandatory in order to assure a future water supply. Activated carbon (AC) has been typically used as adsorptive material to remove organic compounds from air and water due to its unique textural properties of high specific surface area, yet, it posses other interesting properties. Depending on the raw material used for the carbon fabrication, different mineral content and surface functional groups can be obtained. Activation conditions can be selected in order to manufacture materials with excellent performances in adsorption uses (Rio et al., 2005a; Rio et al., 2005b; Lorenc-Grabowska et al, 2004). Moreover, AC can act as direct catalyst for several reactions (Stuber et al., 2005; Figueiredo et al., 1999).

In recent years, catalytic wet air oxidation (CWAO) has demonstrated to be an effective treatment for biorefractory compounds because it offers the advantage of operating at mild conditions of pressure and temperature. AC can be used as catalyst for the CWAO of phenolic compounds (Fortuny et al., 1998). However, the performance of different AC's can be significantly different (Santiago et al., 2005), which suggests that catalytic activity relies on some specific characteristics not yet well identified. The aim of this work is to study the effect of iron content on the catalytic activity of a commercial activated carbon that has already been successfully used as catalyst in phenol oxidation. In one experiment, the iron content was decreased by acid wash under mild conditions. In another set of experiments, after nitric or sulfuric acid wash, iron was supported on the AC surface by the ion-exchange method. The modified ACs were then tested for CWAO of phenol.

Experimental

Materials and analyses

A commercial activated carbon from Merck (ref. 2514) in form of 2.5 mm pellets was used. Prior to use, the activated carbon was crushed and sieved and the 25-50 mesh size particle range was separated. The above fraction was repeatedly washed to remove all fines and oven-dried overnight at 105ºC. This carbon was labeled as ME.

Crystallized phenol was purchased from Panreac (ref. 144852.1211, 99.9 % purity). HCl and NaOH solutions used for the Boehm method were standard tritation solutions, whereas Na_2CO_3, $NaHCO_3$ have 99.9% purity and were supplied by Sigma Aldrich. Sulphuric and nitric acid, sodium acetate and iron chloride were also supplied by Sigma Aldrich. Deionized water (DI) from a millipore system was used to prepare all the solutions and for measuring pH. Air and nitrogen was supplied by Carburos Metálicos, S.A. with a purity over 99.995%

Phenol concentration in samples from CWAO and adsorption experiments was measured by High Liquid Pressure Chromatography (HPLC). The HPLC was performed in an Agilent Technologies 1100 Series chromatograph, with a C18 reverse phase column (Hypersil ODS, 5 μm, 25 x 0.4 cm). The mobile phase was a 35/65 v/v mixture of methanol and deionised water, acidified at 1.41 with H_2SO_4, at a flow rate of 1 ml/min. The detection of phenol was made with the UV absorbance method at a wavelength of 254 nm.

The Total Organic Carbon (TOC) is measured in a TC Multi Analyser 2100 N/C equipment from Analytic Jena with a non-diffractive IR detector. TOC is performed by chemical oxidation of the sample in a high temperature furnace with the presence of a platinum catalyst. The carbon dioxide produced during the oxidation is measured by means of an infrared detector. Sample acidification and aeration prior to analysis eliminates errors due to the presence of inorganic carbon.

Modification of AC

ME was partially demineralized in 1 l of 0.1 N HCl solution stirred for 24 hours. The mass concentration was 4%wt of AC. The HCl solution was then replaced and stirred for another 24 hours. This carbon was labeled as ME-D.

Nitric acid wash was conducted in a rotavapor at 80ºC. The HNO_3 concentration was 65% and 170 ml were used with 35 g of ME. AC was in contact with acid for 3 hours. Then, it was washed with distillated water until neutral pH and dried overnight at 105ºC. This thus treated AC is labeled as ME-N.

For sulfuric acid wash, a carbon sample was boiled for 1 hour in 96% H_2SO_4. The weight to weight ratio of acid to dried AC was 9:1. Then, it was washed with distillated water until neutral pH and dried overnight at 105ºC.The obtained AC is labeled ME-S.

Iron impregnation was performed by the ion-exchange method. AC samples were immersed for 2 days in $FeCl_2$ solution at 2%wt Fe concentration in an orbital shaker. This impregnation was conducted on ME, ME-N and ME-S. The iron impregnated AC's are labeled correspondingly as ME-Fe, ME-N-Fe and ME-S-Fe.

At the end of these treatments, all samples were recovered and washed with distillated water until neutral pH and dried overnight at 105ºC. All iron impregnated AC's were subsequently carbonized in an horizontal furnace under nitrogen atmosphere at a heating rate of 20ºC min^{-1} up to 1000ºC and then let to cool until room temperature.

Characterization of activated carbon

Surface area and porosity of the AC's were determined from nitrogen isotherm at 77 K using a Micromeritics 2010ASAP instrument. Samples were outgassed at 250ºC for 24 hours before the analysis. Surface area was determined from BET equation, total pore volume from the near saturation uptake (at the relative pressure of 0.98), mesopore and micropore volume was estimated according to BJH (Barret et al., 1951) and Horwath and Kawazoe theories (Horwart et al., 1983), respectively.

Mass titration method was used to determine the point of zero charge of each sample. 5%wt carbon slurries in deionized water were prepared, then shaken for 24 h and the final pH of the slurry was measured and taken as the pH_{pzc}.

For measuring the iron load, samples were digested in concentrated nitric acid by a microwave digestion equipment. Dilute solutions were analyzed by atomic absorption spectrophotometry. No significant amount of metals other than iron was detected.

SEM analysis was also conducted in order to determine possible textural changes. An XPS coupled to the SEM microscope was used in order to identify particles observed on carbon surface.

Boehm titration was applied to determine the acidic surface functional group content of the samples. Solutions of $NaHCO_3$, Na_2CO_3 and NaOH (0.05 N) were used. The number and type of acidic sites were calculated by considering that NaOH neutralizes carboxylic, lactonic and phenolic groups, Na_2CO_3 neutralizes carboxylic and lactonic groups, and that $NaHCO_3$ neutralizes only carboxylic groups. Carboxylic groups were therefore quantified by direct titration with $NaHCO_3$. The difference between the groups titrated with Na_2CO_3 and those titrated with $NaHCO_3$ was assumed to be lactones and the difference between the groups titrated with NaOH and those titrated with Na_2CO_3 was assumed to be phenols. Each determination was performed by triplicate.

Experimental procedures

Phenol adsorption isotherms were obtained at 20ºC (± 2ºC) in oxic conditions. Solutions with phenol concentrations ranging from 0.5 to 7 g/l were used to evaluate the adsorption capacity at high concentrations. 0.25 g of AC was allowed to equilibrate with 50 ml of phenol solution at different concentrations. They were stirred for approximately 2 hours, and left 0.5 hour to let the AC to settle. The final concentration of samples was measured by HPLC.

CWAO experiments were carried out in a trickle bed reactor in downflow co-current. The reactor containing the AC packed bed consists of a titanium tube (20 cm long and 1.1 cm i.d.), which is placed in a controlled temperature oven (±1ºC). Typically, 7.0 g of AC was loaded into the reactor. The air flow rate was held constant at 2.4 STP ml/s. The liquid space velocity was set to 8.2 h^{-1} which is equivalent to a space time of 0.12 h, according to the weight of the catalytic bed. Phenol feed concentration was always 5 g/l. The experimental conditions were fixed at a temperature of 140ºC and 2 bar of oxygen partial pressure, giving a total working pressure of 13.1 bar. The experiments were run for 55 hours. Liquid samples were periodically withdrawn and then analyzed to determine phenol conversion (X) and TOC abatement (X_{TOC}). Also pH was measured in all the samples.

For calculations of X and X_{TOC} the following general expression was used:

$$X(\%) = \frac{C_o - C_e}{C_o} x100$$

where C_o is the inlet concentration and C_e the concentration in the exited effluent.

Results

The results shown in Table 1 indicate that the acid wash treatment followed by the impregnation and carbonization does not significantly change the original textural properties as they show basically the same surface area and micropore volume. An increase in the mesopore volume is observed due to the pore widening effect of the acid wash. However, all samples are predominantly microporous carbon, having more than 75% of their porosity in the micropore range.

Table 1. Properties of parent and modified AC.

Sample	A_{BET} (m^2/g)	$V_{micropore}$ (cm^3/g)	$V_{mesopore}$ (cm^3/g)	V_{total} (cm^3/g)	pH_{pzc}	NaOH uptake (meq/g)
ME	1206	0.483	0.029	0.569	7.36	0.208
ME-D	1272	0.484	n.m.	0.592	6.90	0.239
ME-N	1149	0,459	0.068	0.577	3.22	1.07
ME-S	1261	0.499	0.092	0.653	2.37	1.20
ME-Fe	1119	0.448	0.072	0.567	8.55	0.104
ME-N-Fe	1085	0.431	0.082	0.562	7.99	0.372
ME-S-Fe	1147	0.453	0.087	0.599	8.27	0.143

The pH_{pzc} values indicate that carbonization at 1000ºC under nitrogen removes the surface acid groups expectedly created during the acid treatment. However, these values should be higher considering that at 1000 ºC no acidic oxygen functionalities should remain on the AC surface. Also NaOH uptake reveals an unexpected acidity on the carbon surface. This could be due to the presence of acid after the washing step that neutralizes part of the NaOH, resulting in a higher amount of oxygen functionalities when calculations are done based in the Boehm technique. However, iron itself can contribute to the total acidity of the AC with supported iron.

Figure 1 displays the iron content of each AC prepared. In addition, the iron content after use is shown, which will be used in the further discussion. The demineralization procedure was capable of halving the original content. Also the ion-exchange impregnation method was demonstrated to be effective for increasing up to four times the original iron content, specially in the sample previously washed with sulfuric acid. As Figure1 demonstrates, the acid wash step helps the subsequent iron impregnation. In the case of ME-Fe, where the impregnation was conducted on ME without previous acid treatment, the final iron content is only 20% higher than the original, showing that the impregnation was not so effective over this AC.

The phenol adsorption isotherms are depicted in Figure 2. According to the adsorption capacity encountered, only a slight increase of about 15%, compared to the original ME, was achieved with samples ME-Fe and ME-D. In contrast to previous studies (Dastgheib et al. 2004), the heat treatment under nitrogen did not considerably improve the phenol uptake due to the expected enhancement of the π–π interaction as the surface oxygen groups are removed. Probably, the iron acidity offsets this effect. In the case of ME-D, the results show that demineralization increased the phenol uptake probably due to a reduction in the overall surface polarity and hydrophilicity by eliminating iron oxygenated compounds from the carbon surface.

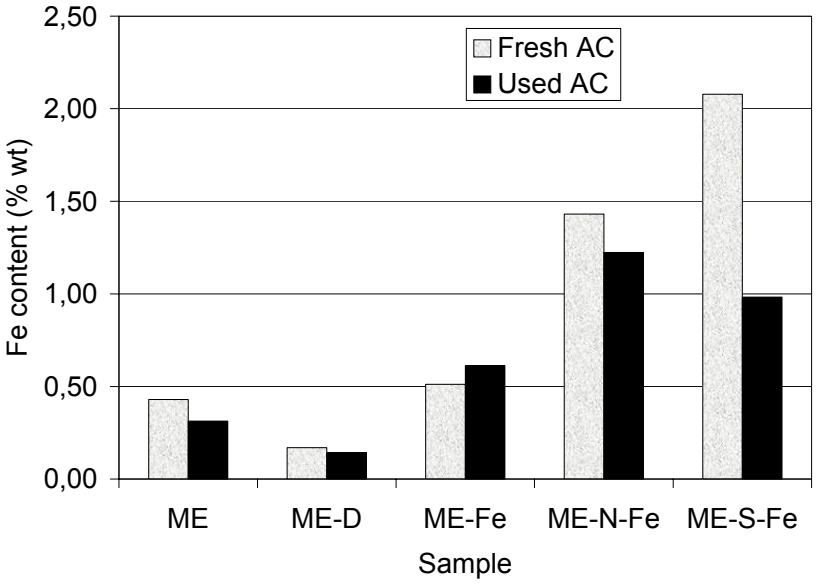

Figure 1. Iron content expressed in %wt of fresh and used in CWAO activated carbons.

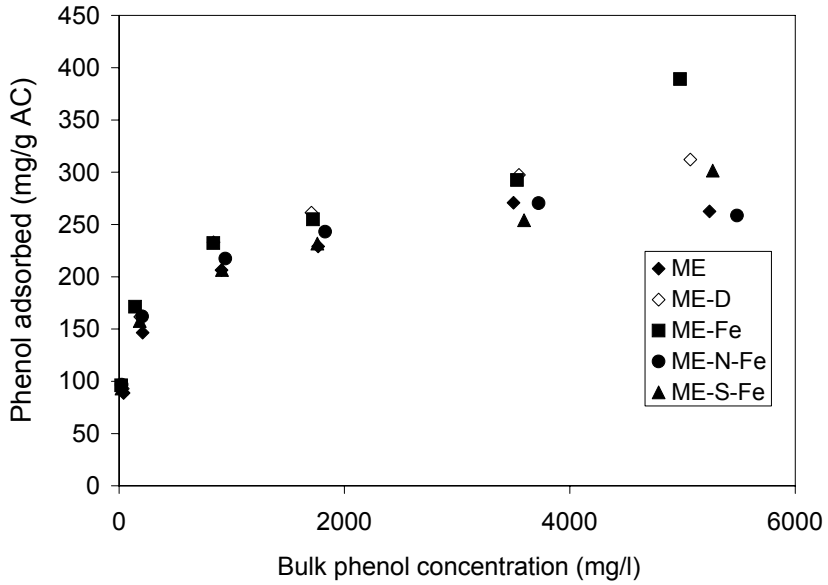

Figure 2. Adsorption isotherms of phenol over activated carbons at 20ºC.

The results of CWAO of phenol in a TBR system are shown in Figure 3. From previous studies (Suarez-Ojeda et al. 2005), it is known that during the first 20 hours, phenol removal rather corresponds to adsorption on the activated carbon. After this transient period, a steady state is achieved. Figure 3 indicates that iron impregnation on ME significantly increases the phenol conversion from 45% to 80%. Also, it must be noted that ME-D gives a conversion of only around 20%, which is less than half of the phenol conversion obtained with the original ME. All these results suggests that iron could be responsible for the catalytic activity shown by the AC, since all AC samples show similar textural properties and approximately same pH_{pzc} and they only differ in their iron content. No distinction between conversion obtained with sample ME-N-Fe and ME-S-Fe is observed, although the iron content is quite different. This suggests that, at the higher content, part of the supported iron could be less active by forming clusters. ME-Fe gives an intermediate phenol conversion between that of the ME and the highest obtained. As ME-Fe only has a slightly higher iron load than the original ME, it only gives an additional 15% phenol

conversion. As it can be seen in Figure 1, all the ACs present iron leaching. Thus, despite ME-S-Fe lost almost half of its original iron content, the phenol conversion in steady state is the same than that given by ME-N-Fe, which only lost 15% of the original iron content. Therefore, the contribution of the homogeneous catalysis should be further assessed.

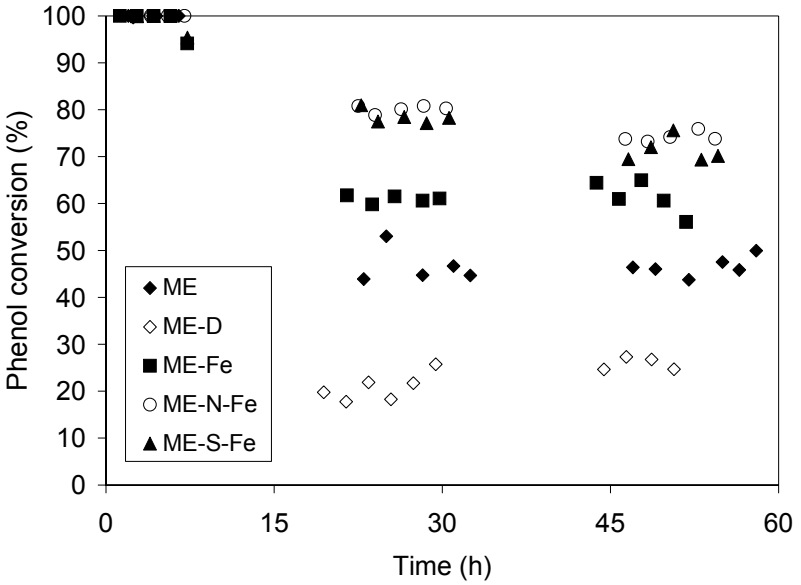

Figure 3. Phenol conversion by different activated carbons in the TBR at 140ºC, 2 bar of oxygen partial pressure and 0.12 h of spatial time.

The TOC abatement is illustrated in Figure 4. Although the general trends are similar to those shown by phenol conversion, for TOC, there is a clear difference between the value obtained with ME-N-Fe and ME-S-Fe, the latter giving the highest conversion. However, except in the case of ME-D, all samples treated by iron impregnation show a better TOC abatement than the original carbon ME. For a better understanding of the iron effect on the biodegradability of the effluent, it is necessary to assess the distribution of the partial oxidation products, which will be completed in the future.

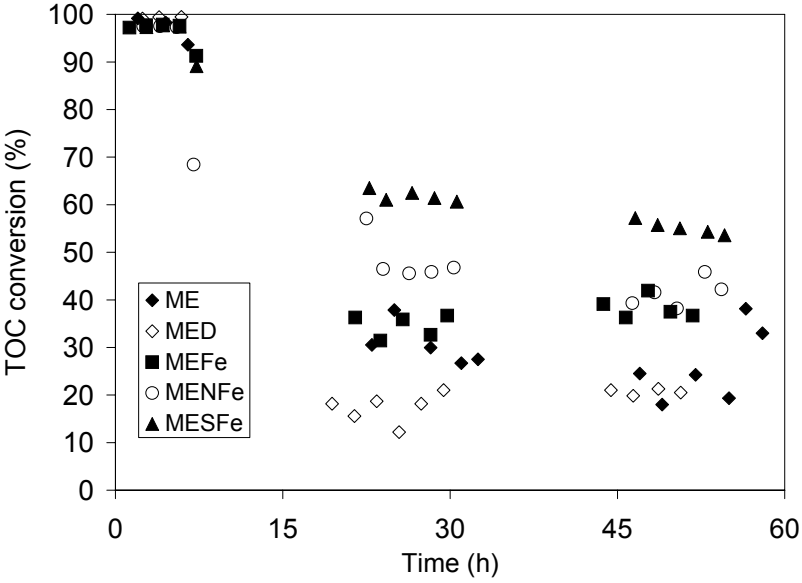

Figure 4. TOC conversion by different activated carbons in the TBR at 140ºC, 2 bar of oxygen partial pressure and 0.12 h of spatial time.

Conclusions

The iron content of the activated carbon is one the main properties responsible for the catalytic activity in CWAO. All samples used in this study have similar textural properties, such as surface area and porosity volume, but differ in their iron content. By decreasing the original iron content of ME, which has proven catalytic activity in the CWAO of phenol, the phenol conversion in steady state halves. In addition, by increasing the iron content, the phenol conversion rises from 45% to 80% in steady state, indistinctively of the previous acid wash treatment. Also the TOC abatement of the exited stream also increases when using an activated carbon with high iron content. However, it is necessary to assess the effect of the homogeneous catalysis, which could appear due to the observed leaching of iron.

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