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Three-phase reactors for environmental remediation: catalytic wet oxidation of phenol using active carbon

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Abstract

Wet oxidation of phenol aqueous solutions was carried out in a fixed bed reactor operating in trickle flow regime. Mild conditions of temperature (140°C) and oxygen partial pressure (1–9 bar) were used. Three active carbons and one commercially available supported copper catalyst were tested as catalytic material. Previous studies demonstrated that active carbon gives higher phenol conversion than conventional oxidation catalysts, although significant loss of active carbon due to combustion was also found. In the present study, the combustion of the active carbon during the process is highly reduced by lowering the oxygen partial pressure from 9 to 2 bar, maintaining an acceptable phenol conversion. The comparison of the performance of three different active carbons shows that their physical and chemical characteristics largely influence on the phenol conversion achieved.

Keywords: Phenol; Waste water; Oxidation catalyst; Carbon(active); Trickle bed

1. Introduction

The production of phenol has continuously grown for the last decade until reaching 1900 millions of kilograms in 1995 for the USA alone [1]. Phenols and homologous compounds are used as raw material in many petrochemical, chemical and pharmaceutical industries. However, wastes containing phenol are specially toxic towards the aquatic environment. Moreover, even at very low concentration, the chlorination of water contaminated by phenol renders chlorophenols which impart a very disagreeable odour and taste to the water [2]. The above industries produce waste water that usually contains phenolic compounds, which prevent the waste water to be biologically treated by conventional methods due to their bactericide properties [3]. Since regulations about discharge of these compounds are becoming increasingly restrictive, the demand for improved methods of treatment is growing.

At present, oxidation of these aqueous effluents is basically conducted by four different ways: wet oxidation (WO) in subcritical [4] or supercritical [5] conditions; chemical oxidation using an oxidant other than oxygen [6]; or specially designed biological treatments [3]. WO in subcritical conditions permits the treatment of a wide variety of industrial and urban effluents. In this process, the contaminated aqueous stream is oxidised using air (or oxygen) at temperatures from 150°C to 300°C and pressures from 5 to

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20 MPa. Catalytic wet oxidation (CWO) enhances the possibilities of the WO technology by using dedicated metal-supported catalysts, which permits to work at lower temperature and pressure. Thus, CWO appears as an economically and ecologically promising technique to convert refractory organic compounds, such as phenol, into carbon dioxide or harmless intermediates at mild pressure and temperature conditions [7].

On the other hand, active carbons (AC) show good properties as adsorbent for both phenol and oxygen [8]. Moreover, it is well known that AC can perform as true catalyst for different reactions [9] but also as support for other oxidation catalytic species [10]. In addition, the regeneration of spent AC can be successfully conducted by WO [11,12]. However, if only CWO processes are considered, AC has been referenced very few times as support for active metals [13] or direct catalytic matter [14,15].

A comparison between the performance of a commercial oxidation catalyst and an AC was previously reported for CWO of dilute aqueous phenol solutions [15]. The results showed that AC could be efficiently used as catalyst in CWO processes, and similar level of phenol consumption was obtained when compared with those found using supported catalysts. Nevertheless, a substantial consumption of AC was observed during the process, which makes unable, unless reduced, its implementation at larger scale.

In this work, the study of the conditions at which the consumption of active carbon is lowered and even eliminated is presented. Moreover, a comparative study of three active carbons with different ash composition and physical and chemical surface characteristics is included.

2. Experimental

2.1. Materials

Analytical grade phenol (Ph) used as reagent was obtained from Merck. High purity synthetic air was used as oxidant. Three commercially available active carbons from different carbonaceous sources were tested. Two active carbons are hereafter designated as PJ and GH (PJ 20 and GH-12132, Warwick Benbassat, Barcelona, Spain). The other active carbon is referred to as ME (Merck Ref. #2514). Table 1 summarises some characteristics of these active carbons. In addition, a commercial oxidation catalyst was also used as reference. This catalyst (Harshaw Cu0803 T1/8 manufactured by Engelhard, Houston, USA), hereafter referred to as Cu0803, was provided by Chemison, SA (Barcelona, Spain). The main chemical and physical characteristics of this catalyst are listed in Table 2.

Table 1
Characteristics of the active carbons

Active carbon	ME	PJ	GH
Source	Wood	Mineral	Coconut
Ash (%)	4	15	3
Surface area (m^2/g)	990	960	810
Average pore diameter (Å)	14	16	15
Pore volume (cm^3/g)	0.55	0.60	0.41

Table 2
Characteristics of the catalyst Cu0803

Support	γ-Al_2O_3
Active metal	10% CuO
Surface area (m^2/g)	130
Average pore diameter (Å)	95
Pore volume (cm^3/g)	0.31

Twenty five to fifty mesh size particles were used for all the experiments. Thus, all these materials were previously crushed, sieved, and the above particle size range was then selected. This fraction was thoroughly washed to remove all fines, then dried at 110°C overnight, allowed to cool and finally stored under inert atmosphere in a desiccator until use. Physical characterisation of both catalyst and active carbons was performed by nitrogen adsorption (Micromeritics Model ASAP 2000) using the BET isotherm method.

2.2. Experimental set-up

An aqueous phenol solution is contained in a 5 l stirred glass tank connected to a high-precision metering pump (Eldex AA-100-S2, Napa, CA, USA) that performs in a 10–150 ml/h flow rate range. This pump feeds a packed bed reactor that consists of a stainless steel tube (20 cm length and 1.1 cm i.d.) filled with catalytic matter. The reactor is placed in a controlled temperature oven (±1°C). A high pressure tank provided with a pressure regulator, which allows to work at constant pressure, supplies the air used as oxidant.

The liquid and gaseous streams are mixed, preheated at the reaction temperature, and then cocurrent downflows through the reactor. The outlet effluent is collected in two vessels to separate the gaseous and liquid phases. One of them is also used as sampler. At the gas vent of the above separators, a gas rotameter provided with a needle valve permits to measure and control the air flow rate. A detailed scheme of this system can be found elsewhere [16].

2.3. Experimental procedure

Two hundred and fourty hours tests were completed for each one of the catalytic substances tested. In all the experiments, an aqueous phenol solution of 5 g/l was fed to the reaction system, which was always operated at 140°C. The system pressure was varied from 1 to 9 bar of oxygen partial pressure, while the air flow rate was held constant at 2.4 ml/s measured in standard conditions. In the test with Cu0803, the liquid weight hourly space velocity (WHSV) was kept constant at 2.4 h^{-1}, i.e. a space time of 0.42 h. However, this parameter was set at 8.2 h^{-1} for the active carbons, i.e. a space time of 0.12 h. Therefore, the liquid flow rate was fixed according to the weight of the catalytic bed. Outlet liquid samples were periodically withdrawn and then analysed. When active carbon was used, this was collected at the end of the test and then dried at 400°C under a nitrogen flow in order to remove any adsorbed phenol. Subsequently, the active carbon was weighed to calculate the loss of carbon during the test. A reference test, performed with an inert material (carborundum) instead of any catalyst, showed no significant phenol consumption, less than 2%, at 140°C and 9 bar of oxygen partial pressure. Phenol adsorption isotherms of each active carbon were obtained at 20°C (±2°C) in oxic conditions following a standard protocol [17].

2.4. Product analysis

The phenol concentration was determined by HPLC (Beckman System Gold, San Ramon, CA, USA). A C_{18} reverse phase column (Spherisob ODS-2) was used to separate the phenol from the partial oxidation products. The mobile phase was a mixture of 35% methanol and the balance distilled water, the flow rate being 1 ml/min. UV absorbance at wavelength 254 nm allowed phenol to be detected and measured. Then, Phenol conversion (X_{Ph}) was defined as

$$X_{Ph}(\%) = \frac{[Ph]_{in} - [Ph]_{out}}{[Ph]_{in}} \times 100, \quad (1)$$

where $[Ph]_{in}$ and $[Ph]_{out}$ denote inlet and outlet reactor phenol concentration, respectively. In addition, some selected samples were analysed in order to determine their total organic carbon (TOC).

3. Results and discussion

Phenol adsorption data of each active carbon was fitted to the Freundlich equation

$$\frac{x}{m} = kC^{1/n}, \quad (2)$$

where C is the concentration of unadsorbed phenol left in solution, i.e. in equilibrium with the active carbon, and x/m is the amount of phenol adsorbed per unit weight of active carbon. Table 3 shows the Freundlich parameters estimated in each case.

It should be noted that these adsorption capacities were obtained in oxic conditions, which could influence on the results. It has been reported [18] that the presence of dissolved oxygen promotes phenol polymerisation by oxidative coupling. This would give a larger adsorption capacity if compared with that obtained in anoxic conditions.

It was observed that both PJ and GH become saturated at a phenol concentration much lower than the reactor feed solution concentration, i.e. 5 g/l. Only for ME, the saturation concentration is around 5 g/l. Fig. 1 shows (open circles) the time needed to completely saturate the active carbon (ME) bed, i.e. apparent phenol conversion turns zero. This experiment was performed at 140°C by flowing a 5 g/l phenol solution through the reactor filled with active carbon under nitrogen atmosphere. Typically, 6.6 g of ME were loaded in the reactor. So, according to the

Table 3
Freundlich isotherm constants for phenol adsorption at 20°C

Active carbon	ME	PJ	GH
k (mg/g)(l/mg)$^{1/n}$	49	44	62
$1/n$	0.24	0.23	0.17
Maximum capacity (mg/g)	370	310	260

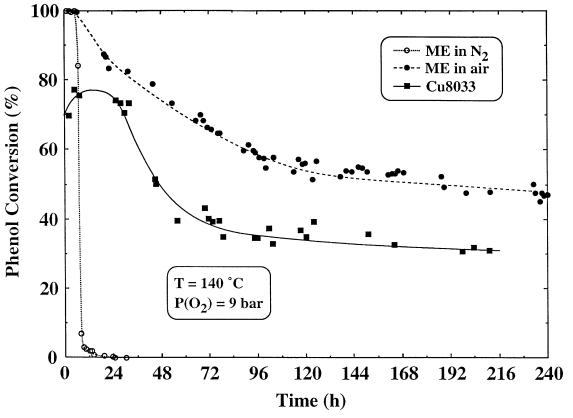

Fig. 1. Evolution of the phenol conversion during the activity test for ME (in air or N_2) and Cu0803.

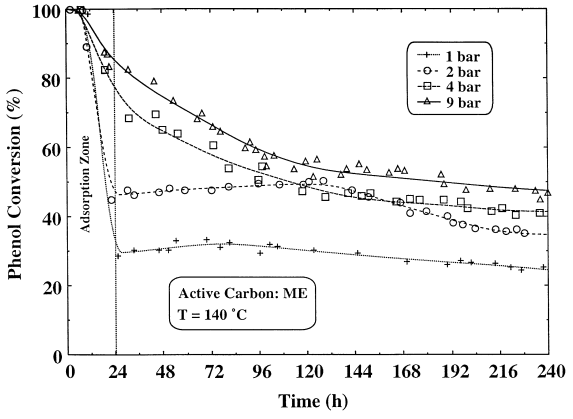

Fig. 2. Phenol conversion dependence on the oxygen partial pressure using ME.

maximum capacity of this active carbon and the liquid flow rate used, the saturation time at 20°C is about 9 h. This mostly agrees, within the experimental error, with the experimental saturation time found at 140°C, which shows no significant mass transfer restrictions in the phenol adsorption step during the continuous process.

A comparison between the performance of ME (filled squares) and Cu0803 (filled circles) in typical WO conditions is also shown in Fig. 1. Even though the WHSV for ME is almost 3.5 times higher than for Cu0803, ME proved to perform better in terms of phenol conversion. In case of comparable WHSV, phenol removal would be at least three times higher for ME than for Cu0803. This speaks for a very high activity of ME in aqueous phase oxidation processes.

The deactivation of the supported catalyst Cu0803 in the course of the test is attributed to the progressive leaching of the copper active species due to the acidic reaction medium [16,19]. Unlike Cu0803, the decreasing phenol conversion observed for ME is due to the loss of active carbon by combustion [15]. At the end of the test, it was found that a 33% of the active carbon initially loaded had been consumed. However, it was also proved that ME keeps the catalytic activity and the decreasing phenol conversion observed is only due to the decreasing true space time as a result of the combustion of the active carbon.

Therefore, a new set of tests was conducted using ME and progressively lowering the oxygen partial pressure from 9 to 1 bar in order to minimise the loss of active carbon. The rest of experimental conditions was kept constant. Recently, one half reaction order with respect to the oxygen partial pressure was reported for the catalytic wet oxidation of phenol in a trickle bed system [16] so the decrease in phenol conversion should not be dramatic. Fig. 2 illustrates the effect of the oxygen partial pressure showing the evolution of the phenol conversion throughout the tests.

It should be noted that, at first, the process is largely influenced by the adsorption step and the equilibrium phenol concentration is only reached beyond 24 h. In the first hours, all the phenol is either retained by adsorption or destroyed by oxidation giving an apparently complete phenol consumption. At 24 h, when the active carbon consumption is still negligible for any pressure, the ratios between phenol conversion obtained at the different pressures mostly agree with those expected according to the oxygen partial pressure dependence, i.e. one half reaction order. Beyond 24 h, for 9 and 4 bar, the phenol conversion considerably decreases in the course of the test, which means that there is a significant carbon consumption. On the contrary, an almost constant phenol conversion was found at 1 and 2 bar, which indicates a low active carbon consumption during the test. This is illustrated by the loss of active carbon, Table 4, which was measured in each case at the end of the test. As can be seen, no apparent improvement in carbon consumption is obtained by working at oxygen partial pressures below 2 bar. The negative consumption found between

Table 4
Influence of the oxygen partial pressure on the carbon consumption

$P(O_2)$ (bar)	1	2	4	9
Consumption (%)[a]	−18	−3	16	33

[a] With respect to the initially active carbon loaded.

1 and 2 bar can be explained by the presence of adsorbed phenol-based polymers, which cannot be removed during the desorption process at 400°C. These polymers are formed by oxidative coupling of phenol [16] and could be only eliminated at temperature higher than 400°C. At this elevated temperature, an important consumption of active carbon would also be expected, so the change of weight due to the polymers removed or the carbon burned out would become indistinguishable.

As expected, the final phenol conversion falls as the oxygen partial pressure decreases. Thus, the phenol conversion goes from 45% obtained at 9 bar to 25% found at 1 bar. However, the phenol conversion obtained at 2 bar is a considerable 35%. Thus, an oxygen partial pressure of 2 bar gives a low consumption of active carbon, simultaneously yielding a reasonable phenol conversion. In order to establish whether or not the oxygen partial pressure affects the selectivity of the oxidation, the final TOC was determined for the four cases shown and then the selectivity to the production of carbon dioxide was calculated as the percentage of phenol destroyed to carbon dioxide. Both parameters are shown in Table 5. As expected, the final TOC is higher at lower oxygen partial pressure, however, the selectivity ranges from 70% to 75%, which reveals a very low dependence of the selectivity, within the experimental error, with respect to the oxygen partial pressure.

Hence, the comparison between the performance of the three active carbons was conducted using 2 bar of oxygen partial pressure. At this pressure, the weight of active carbon at the end of the respective tests was found to be higher than the initial weight. This means that the active carbon consumption was very low or even null for the three active carbons. The evolution of the phenol conversion throughout the tests for each active carbon is shown in Fig. 3. Note that, during the first 24 h, the phenol conversion appears to be almost complete in all the experiments. As in the above set of experiments, this effect is due to adsorption, so phenol is retained in the active carbon rather than destroyed by oxidation. Once the equilibrium phenol concentration is reached, a roughly steady phenol conversion is obtained during the test. It should be pointed out that phenol conversion dramatically depends on the type of active carbon used. Thus, the best performance is given for ME with a 35% of phenol conversion. In contrast to this behaviour, PJ only yields a small 15% and GH renders an insignificant 8%. This proves that the characteristics of the active carbon play a decisive role in its performance as oxidation promoter.

Table 5
Influence of the oxygen partial pressure on the TOC depletion and selectivity to CO_2

$P(O_2)$ (bar)	1	2	4	9
Final TOC[a] (mg/l)	3000	2860	2540	2430
Selectivity (%)	75	71	74	73

[a] Initial TOC: 3825 mg/l.

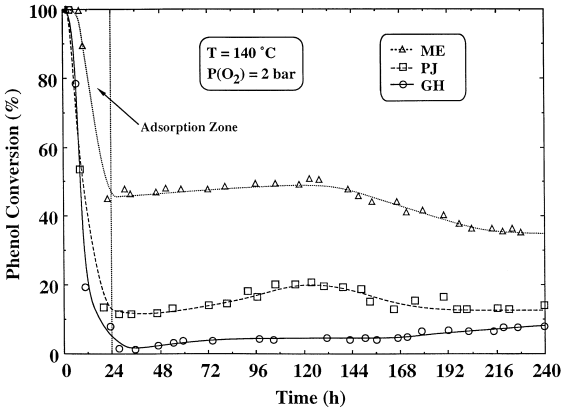

Fig. 3. Phenol conversion profiles using different active carbons.

The correlation between the physical properties of the active carbons, Tables 1 and 3, and the phenol conversion yielded is still unclear. One can speculate that neither the mineral matter content, which is related to the ash content, nor the pore volume are too related to the phenol conversion. Only the surface area and the maximum adsorption capacity fit to a degree with the trends shown by each active carbon. It seems that the higher is the surface area the higher is the phenol conversion. However, no significant phenol conversion was reported [14] for an active carbon with a surface area greater than anyone of those tested in our work.

It is suspected that the chemical characteristics of the active carbon surface strongly influence on its performance. It has been shown that the presence of oxygen-containing groups is a key factor in the phenol adsorption processes [16]. In addition, there is a slight increase in phenol conversion during the test with GH. This could be related to the progressive oxidation of the active carbon surface, which would improve the performance of this active carbon by creating suitable oxygen-functionalities.

4. Conclusions

Active carbon can be efficiently used as a catalyst in CWO processes conducted in trickle bed systems. In addition, its catalytic activity exists without the presence of any active metal. In terms of phenol removal, active carbon is superior to conventional oxidation copper catalysts. Nevertheless, in typical CWO conditions (140°C and 9 bar of oxygen partial pressure), there is a substantial loss of active carbon by combustion.

The active carbon consumption can be reduced by lowering the oxygen partial pressure from 9 to 2 bar. At the latter pressure, the loss of active carbon is negligible whereas the phenol conversion only decreases for a factor of 1.3, giving a steady phenol conversion of approximately 35%, the selectivity to the production of carbon dioxide being of about 75%.

The physical properties and the source of the active carbon can be hardly related to the phenol conversion yielded. This suggests that the catalytic performance of the active carbon is rather related to the chemical surface characteristics, in particular, to the number and type of oxygen-containing groups. Ongoing research is focused to the chemical characterisation of the active carbon surface and also to establish an oxidation reaction mechanism in order to elucidate the different behaviour observed for each active carbon.

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