

CATALYTIC WET AIR OXIDATION OF PHENOLIC COMPOUNDS AND MIXTURES OVER ACTIVATED CARBON: CONVERSION, MINERALIZATION AND CATALYST STABILITY

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Summary

CWAO over activated carbon (AC) has been investigated in a semi-batch autoclave to better understand the influence of AC properties on their catalytic efficiency and stability. For this purpose, phenol, 4-nitrophenol, 4-chlorophenol and 4-hydroxybenzoic acid have been chosen as model compounds. The performance of CWAO has also been evaluated on synthetic mixtures comprising two to four of the aforementioned molecules to evaluate synergy or competition effects. The amount of pollutant(s) (re-)adsorbed on AC during a preliminary adsorption step, the pollutant conversion and mineralization yield obtained during CWAO as well as the AC stability upon recycling are compared for each case.

Keywords

Water purification and reclamation. Multiphase and particulate reactors.

1. Introduction

The search for alternative wastewater treatment technologies has been intensified due to a growing public concern about health and related environmental issues.

Phenol and phenolic compounds are among the most prevalent organic pollutants found in industrial wastewaters, due to their extensive use in petrochemical units, oil refineries, polymer and pharmaceutical industries. Inhibitory effects of phenol on microbial activity have been reported for concentrations larger than 500 ppm^{1,2}. Therefore high loaded phenolic effluents require additional solutions to conventional biological treatment. Catalytic wet air oxidation (CWAO) over activated carbon (AC) has been successfully tested for the remediation of phenol and some substituted phenols³⁻⁵. Real wastewaters generally contain a range of different pollutants, therefore the need to treat synthetic mixtures in order to evaluate possible synergy and/or competition effects between the pollutants.

The oxidation of four phenolic compounds (phenol, 4-nitrophenol, 4-chlorophenol and 4-hydroxybenzoic acid) and corresponding mixtures comprising two to four compounds is thus investigated in a batch reactor. The aim is to compare the amount of pollutant(s) (re-)adsorbed on the AC during the preliminary adsorption step, the pollutant conversion and mineralization yield achieved during oxidation and the AC stability upon recycling.

2. Experimental

In a standard experiment, 200 mL of aqueous solution containing 1 g/L of each phenolic compound (separate or in mixture) and 2 g of AC (dp=0.8-1.0 mm) are mixed in a stirred autoclave to saturate the AC with the pollutant(s) over night (under nitrogen at 150 °C). Prior to the experiment, a liquid sample is taken to measure the initial concentration(s). Then oxygen is provided, with a partial pressure of 3.5 bar (total air pressure of 20 bar). All experiments are performed batchwise for the liquid phase, whereas air is continuously fed at a flow rate of 60 L/h. The stirrer speed is set at 800 rpm. In these conditions there is no external mass transfer limitation.

Liquid samples are analyzed via high-performance liquid chromatography, using a C18 reverse-phase column and a diode array detector. The closed reflux colorimetric method is employed to determine COD values.

ACs from different precursor materials (carbon L27 from wood, S23 from coconut shell and F22 from coal) are characterized and used as catalysts for phenol oxidation. Subsequently, one of these carbons has been selected to investigate the remediation of other phenolic compounds.

3. Results and discussion

AC screening: Phenol is best adsorbed on S23, which is the most microporous and basic carbon (pH_{PZC} = 9.7).

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Conversely, the adsorption of phenol is clearly hindered by the presence of acidic groups, as the lowest phenol uptake is obtained with acidic L27 ($pH_{pZC} = 6.2$) despite its higher surface area (1860 m^2/g for L27 compared to 1230 and 985 m^2/g for S23 and F22, respectively). The initial oxidation rate observed for the carbons increases in the following order: L27 < F22 < S23, suggesting a correlation between the AC activity and its adsorption capacity (Fig. 1). When recycling ACs, a steep decrease of phenol conversion is observed between the first two runs, before the time-concentration profiles in the liquid phase become stable after three or four cycles. This behaviour can be related to the loss of AC surface area caused by the deposit of high-molecular weight organic compounds. Both porosity measurements and thermogravimetry analysis of spent ACs have confirmed the decrease in surface area. As this deactivation is especially significant for S23 and L27 is too friable for long-term recycling experiments, F22 has been selected for further investigation. After stabilization, the reaction rate is found to be first order with respect to the pollutant concentration from plotting the logarithm of the concentration in the liquid phase as a function of time.

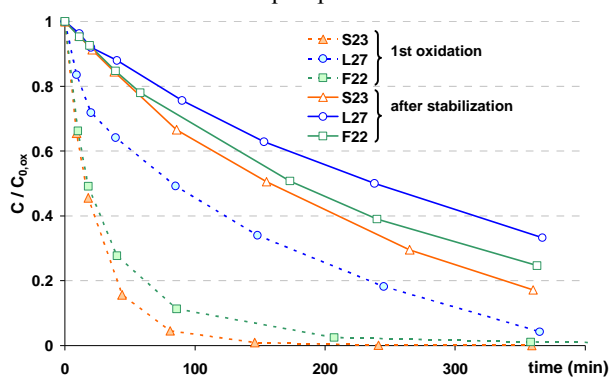


Figure 1 – Time-phenol concentration profiles during the first oxidation and after recycling the AC (stabilized activity). $C_{0,ox}$ refers to the concentration after adsorption.

Remediation of phenols and mixtures: The initial adsorption capacity of the fresh carbon is slightly higher for substituted phenols than for phenol due to the electron withdrawing character of the substituents. However, after several adsorption-oxidation cycles, the re-adsorbed amount is different for each pollutant, depending on both its oxidability (AC regeneration efficiency) and the surface modification of AC (occurring during regeneration). The reactivity of the different phenols is indeed very different resulting in oxidation rate constants, which vary in a ratio of 1 (for 4-nitrophenol) to 10 (for 4-chlorophenol) after AC stabilisation. On the other hand, AC properties are best preserved with the least reactive pollutant. The contribution of intermediates to the remaining COD is also larger with 4-chlorophenol.

In mixtures, the difference between the oxidation rates of the phenols becomes smaller: 4-chlorophenol and phenol are less reactive, while the most refractive compounds (4-nitrophenol and 4-hydroxybenzoic acid)

are better degraded (Fig. 2). Moreover, in terms of global molar concentration, the four-compound mixture is found to behave as the sum of each pollutant taken separately.

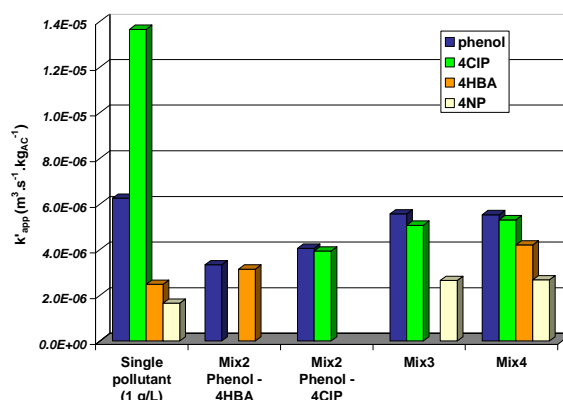


Figure 2 – Apparent oxidation rate constants (k'_{app}) calculated according to $R_{pol,app} = k'_{app} C_{pol}$ for the different compound mixtures studied.

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