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Catalytic removal of phenol from aqueous phase using oxygen or air as oxidant

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Abstract

A preliminary study of specific catalysts used to oxidize organic compounds which are hazardous to the environment is presented. The catalytic oxidation of phenol in an aqueous solution using commercially supported copper oxides was studied in a continuous trickle-bed reactor at three temperatures (120, 140 and 160°C) and under three partial pressures of oxygen (0.6, 0.9 and 1.2 MPa) using molecular oxygen or air as oxidation agents. The influence of various parameters is presented. Over the range of conditions used, the oxidation kinetics are first order with respect to phenol and COD (chemical oxygen demand) reduction and half order with respect to the partial oxygen pressure. The results are similar when using air or oxygen as an oxidizing agent. Activation energies for phenol oxidation and COD conversion were found to be 85 and 76 kJ/mol.

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1. Introduction

The chemical industry generates waste-water that contains organic products hazardous to the environment and, especially, to natural water resources. Therefore, this waste-water needs to be treated before its release. Phenol (or homologous compounds) is one of the most serious pollutants, because it presents problems under conventional treatments and because it is widely used in the chemical industry. Thus, conventional biological treatments are inefficient due to the antibiotic properties of this kind of compound. On the other hand, liquid–liquid extraction processes [1,2] are only favourable for very high concentrations of phenol. Thus, for effluents of middle or low concentrations, a chemical pretreatment is necessary. As a step in the direction towards low-cost solutions, we suggest in this work the use of oxidation supported catalysts in continuous reactors. This technology has not yet been industrially applied because of the absence of suitable active heterogeneous catalysts capable of stable operation in the liquid phase oxidation of organic compounds. Other technological approaches reported, capable of reducing hazardous organic contamination in aqueous effluents such as: wet oxidation [3–5], processes in supercritical conditions [6,7] or burning, need more drastic thermodynamic conditions.

Batch and semi-batch approaches have been studied previously [8–13] but the applicability of the results to a continuous process and the suitability of the phases in contact makes the use of the reported results difficult.

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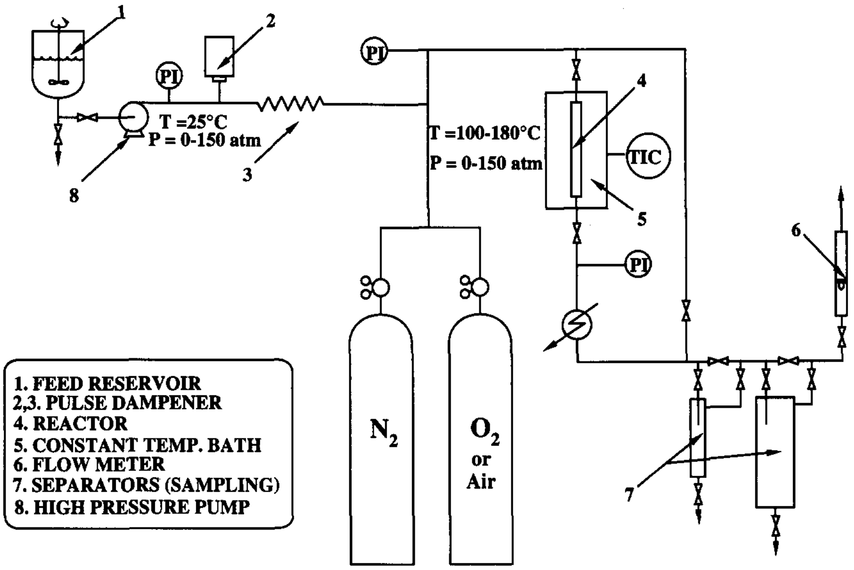

Fig. 1. Experimental apparatus for catalytic oxidation studies.

2. Experimental section

The experimental equipment, shown in Fig. 1, consists of a stirred tank of 1 litre connected to a high-pressure metering pump that works in a flow-rate range of 10–150 ml/h. This pump feeds a triphasic tubular reactor (1.1 cm internal diameter and 20.0 cm in length), operating in a trickle-bed regime, heated by an external flow of oil coming from a thermostatic bath equipped with a temperature control system. The reactor was filled with catalyst, previously ground and sieved in the range 25–50 mesh. The oxygen or air was directly fed from a high-pressure gas cylinder after reaching the desired value. The products of the reaction were rapidly cooled, before separating the liquid and gas phases. This separation was carried out in two vessels, the smallest one being used for liquid sampling. The gases were measured with a flow-meter that also acted as a gas flow controller. Both the feed and the different reaction products were analysed by COD and high-performance liquid chromatography to determine respectively the phenol conversion to carbon dioxide and water, and the disappearance of phenol.

This work presents the results obtained for the catalytic removal of phenol in the aqueous phase. In particular, the results of the catalytic oxidation of an aqueous solution of 5 g/l in phenol, using oxygen or air as oxidant, are summarised. Firstly, an activity test of three typical oxidation catalysts was carried out. In this step, two commercial catalysts (Harshaw Cu-0803 and Topsøe LK-821), and a modified one were used. This third catalyst was a mixture of cement and of Topsøe LK-821 to improve its mechanical strength. The temperature was equal to 140°C and the gas flow-rate was 2.3 ml/s. The liquid flow-rate was 35.4 ml/h, working at 0.41 h of inverse WHSV (weight hourly space velocity). The partial oxygen pressure was maintained at 0.9 MPa. The particle diameter of the catalyst was 25–50 mesh and 14.52 g of catalyst was loaded in the reactor. In the second part, the kinetic results of catalytic oxidation, using air or oxygen as oxidant, of an aqueous solution of 5 g/l in phenol, were obtained. In this case the best catalyst resulting from the results of the first part (Harshaw Cu0803 T1/8 10% CuO on γ-Al_2O_3) was used. Temperature was varied between 120 and 160°C, the partial oxygen pressure was varied between 0.6 and 1.2 MPa and the

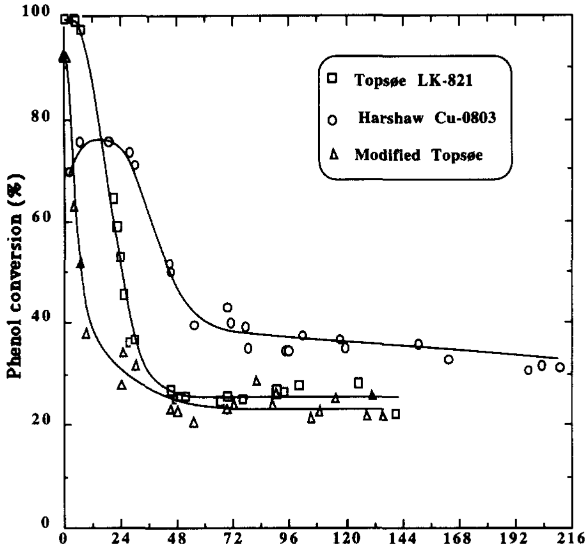

Fig. 2. Phenol conversion changes during the activity test of the catalysts.

reciprocal of WHSV was varied between 0.1 and 1 h.

3. Results and discussion

Fig. 2 presents the experimental results of phenol removal activity at times ranging up to 214 h for the three catalysts studied. The behaviour of phenol conversion versus time of operation shows a different trend during the first 48 h than for 48 h onwards for all the catalysts tested. This fact is surprising because it has not been previously reported, although some authors [8,10], working with batch and semi-batch conditions, indicate a different activity for consecutive runs with reused catalyst.

It has been also observed that all these catalysts present a good performance at the beginning of the run but the phenol conversion rapidly decreases, tending to a plateau. After approximately 48 h, the phenol conversion becomes stabilised. Some problems of plugging were encountered during reaction with the two commercial catalysts, mainly with the Topsøe LK-821 catalyst. These problems, owing to catalyst decomposition, may be attributed to the interaction between the catalyst and the water because these commercial catalysts are made for gas phase reactions. A liquid phase oxidation catalyst must be refractory to the influence of water, having high mechanical strength, chemical and hydrolytic stability and hydrophobicity. In this way, the third catalyst, modified Topsøe LK-821, avoids these problems, although its initial activity is lower because it contains less active metal than the original Topsøe catalyst. In conclusion, the most initially active catalyst is the Topsøe LK-821 sample, reaching the highest phenol conversion of 100% but, unfortunately, its decline of activity is also the highest and this catalyst shows a residual activity of only 25%. In contrast, the Harshaw Cu-0803T sample reaches 80% conversion but shows the highest residual activity, approximately 40%. The modified Topsøe sample does not present plugging problems in the reactor and its behaviour is similar to the original Topsøe LK-821 solid.

The behaviour of Harshaw Cu-0803T catalyst has been studied at three temperatures (120, 140 and 160°C) and under three partial pressures of oxygen (0.6, 0.9 and 1.2 MPa), using oxygen or air as the oxidizing agents. To obtain comparable results, tests were carried out in the time domain of constant catalytic activity (72–144 h). If C and C_0 are respectively the phenol concentration in the reactor effluent and in the feed, the phenol conversion corresponds to $1 - C/C_0$. Examples of the results obtained are presented in Figs. 3 and 4.

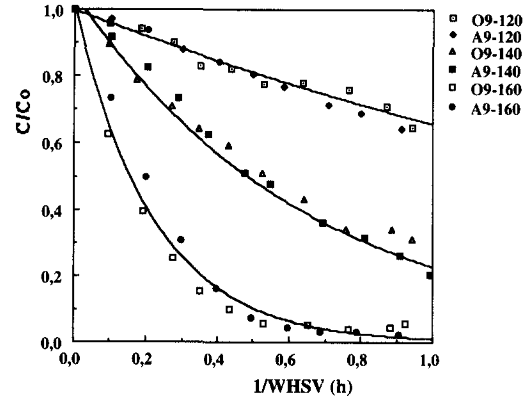

Fig. 3. Influence of temperature and oxidation agents on phenol conversion.

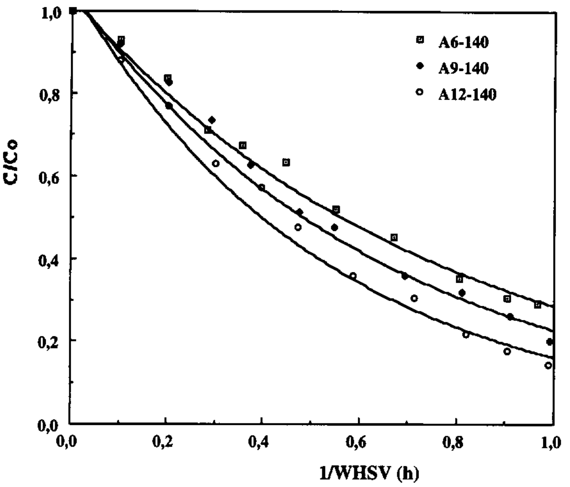

Fig. 4. Influence of pressure on phenol conversion.

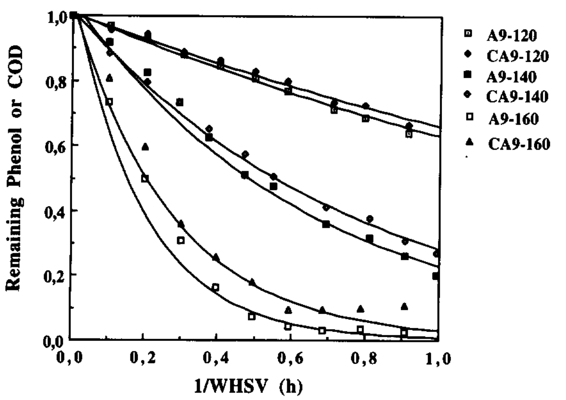

Fig. 5. Variation of phenol and COD reduction at different temperatures.

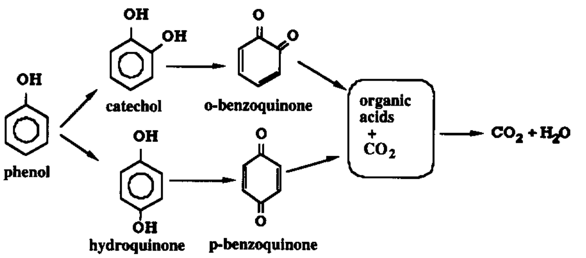

Fig. 6. Simplified reaction scheme for the oxidation of phenol.

From Fig. 3 it can be seen that the temperature greatly influences the phenol removal at similar values of 1/WHSV. At 1/WHSV = 1 h, the conversions obtained are 35%, 80% and 97% for temperatures equal to 120, 140 and 160°C, respectively. An inspection of Fig. 4 shows that pressure has less influence on the conversion of phenol. Results obtained at 1/WHSV = 1 h, at 140°C and under 0.6, 0.9 and 1.2 MPa of pressure show the maximum difference ranging from 50 to 85%. Thus, when the pressure is doubled, the conversion is only multiplied by 1.7, while an increment of only 40°C produces three times more conversion of phenol. These comparisons have been carried out at 1/WHSV where the influence of pressure is maximum. Similar trends could be drawn from the experimental results at 120 and 160°C, these last results being presented in Fig. 7. Fig. 3 also includes the influence of the oxidation agent on the conversion. Through all the results obtained it can be concluded that the use of oxygen or air at identical partial pressure does not affect, within experimental error, the results.

The results presented in Figs. 3 and 4 show that there is a regular trend of conversion versus 1/WHSV at constant temperature and oxygen pressure. A mathematical analysis of these results confirms that the oxidation reaction in phenol is first order. This agrees with results previously reported elsewhere [5–11]. This adjustment permits the calculation of the pseudo first-order kinetic rate constant for each temperature tested. Thus, the apparent activation energy of this reaction was calculated. The activation energy obtained, 85 kJ/mol, reasonably agrees with other values published for experimental discontinuous equipments [13]. On the other hand, a 1/2 kinetic order has been observed to partial oxygen pressure in agreement with most of the values published [7–11]. The results show that our experimental continuous reactor is suitable for studying the treatment of aqueous solutions, with a high pollutant loading, in conditions similar to those used in industry. This continuous reactor presents some advantages when compared to batch or semi-batch reactors, such as the elimination of the induction time of the catalyst and the elimination of interference coming from the polymerisation of reaction intermediates, thus preventing the problem of fouling catalysts.

Fig. 5 includes the results of phenol removal at 120, 140 and 160°C, under 0.9 MPa partial oxygen pressure, the air being the oxidizing agent. These

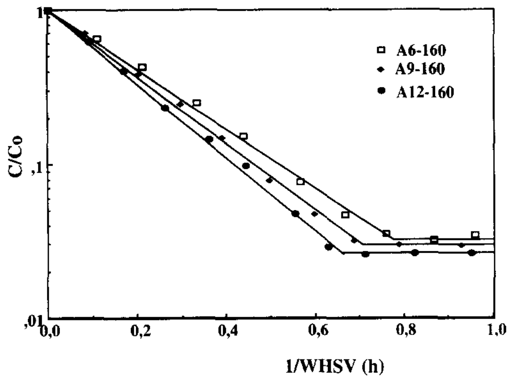

Fig. 7. Influence of pressure at 160°C, in semi-log plot.

results are compared with those of the reduction of COD. The difference between the phenol removal and the reduction of COD is due to the reaction intermediates from phenol. Fig. 6 presents the simplified reaction scheme for the oxidation of phenol in which the important interconnection between the intermediates, the presence of diphenols, quinones and organic acids can be seen. COD analysis indicates the extent of the reaction, that is the amount of eliminated phenol converted into carbon dioxide and water. Experimental results of COD against 1/WHSV show a similar trend to that of phenol removal. Thus, a first-order reaction for COD and a 1/2-order reaction with respect to the partial pressure of oxygen were obtained as well as a value of 76 kJ/mol for apparent activation energy.

Plots showing the removal of phenol at 160°C and at 0.6, 0.9 and 1.2 MPa partial oxygen pressure versus 1/WHSV are presented in Fig. 7 in which the semi-log plots allow us to see a change in the reaction order. It must be noted that the plots of the results change to straight lines with increasingly high values of 1/WHSV, where phenol removal is greater than 95%, changing from this point to other lines with different slopes. This fact was also reported by Willms et al. [11] and was not observed in the other experiments obtained at 120 and 140°C because of the lower conversion of phenol.

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