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Kinetic and wet oxidation of phenol catalyzed by non-promoted and potassium-promoted manganese/cerium oxide

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Abstract

The wet oxidation of organic compounds to CO_2 and H_2O has been shown to be a very efficient technique in the outflows treatment. This work focuses on the interaction of the chemical element potassium with the catalyst MnO_2–CeO_2 in the wet degradation of phenol. The reaction has been carried out in an autoclave with a controlled system of agitation, pressure, temperature and sampling of the liquid phase. The experiments were performed in the presence of the catalysts MnO_2–CeO_2 and K–MnO_2–CeO_2 in the following operational conditions: temperature of $130\,^{\circ}C$, $P = 20.4$ atm, catalyst concentration in the range 1.5–5.0 g/L, initial phenol concentration of 0.5 g/L, initial pH varying between 6.8 and 8.5, and percentage of potassium in the catalyst MnO_2–CeO_2 ranging between 0% and 10%. Curves indicating the profile of conversion of total organic carbon show that the phenol degradation is favored when the potassium quantity is reduced. This behaviour is confirmed by BET analysis, whereby the catalyst presents larger specific area when compared to the percentages of other components. Regardless of the catalyst used in the phenol oxidation, the kinetic constant of reaction had the same order of magnitude for two parallel stages proposed by a first-order kinetic model.
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1. Introduction

Over the last decades, environmental problems have become more critical and frequent. The contamination of natural waters has been pointed out as one of the largest problems of the modern society. Phenol compounds have been object of investigations in face of the growing demands of the society regarding the quality of water resources. The high toxicity levels and unpleasant odors render these compounds highly risky to human health and preservation of the ecosystem.

Several techniques, used for the outflows treatment, have been efficiently applied to the degradation of phenol. In general, the biological processes are able to oxidize the poisonous outflow entirely, since the microorganisms present are fully adapted to its concentration and toxicity conditions. However, outflows containing phenol in high concentrations can be inadequate to biological treatment. The catalytic wet oxidation has been proven to be a useful and important technique for the treatment of organic pollutants contained in wastewater streams. Several researchers have been seeking new and efficient catalysts able to degrade poisonous outflows at low temperature and reduced cost. The oxidation processes that use heterogeneous catalysts allow for easier catalyst separation than processes containing homogeneous catalysts.

Besides, the catalysts used in the oxidation processes exhibit a loss in the activity due to the deposition of polymeric compounds in the surface of the active sites, requiring, therefore, the development of new catalysts as well as others that can act along with specific promoters and minimize the deactivation process. Alkaline and alkaline-earth metals, such as sodium and potassium, have actually been indicated by Hussain et al. [1] and Masende et al. [2] as more active promoters and less susceptible to products that are deposited at the catalytic sites and provoke deactivation in a very short reaction time. Furthermore, the addition of these metals enables the reaction to be selectively redirected towards the formation of the desired products, maintaining the stability and the performance of the catalyst for a significantly larger period of time.

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Luna [3] used two types of catalysts (Ru/Ce, MnO_2/CeO_2) in the phenol degradation. Their work showed that the reactions of catalytic wet oxidation of the phenol in the presence of the catalyst MnO_2/CeO_2 were better accomplished at 130 °C. Variations in pressure demonstrated little influence on changing of the residual fraction of phenol.

The main objectives of this work are to synthesize and to test a catalyst of the type MnO_2/CeO_2 impregnated with potassium in the wet oxidation reaction of phenol, aiming to selectively degrade the phenol to CO_2 and, as a result, minimizing the production of intermediary compounds which poison the active sites of conventionally used catalysts. This intends to provide, with the best purpose, an interpretation of the results obtained via the development of a kinetic model.

2. Experimental procedure

2.1. Catalyst synthesis

The catalyst MnO_2–CeO_2 was synthesized by the co-precipitation method using oxides of manganese(IV) and cerium(IV). The corresponding procedure is presented as follows:

- Preparation of 100 mL of a mixing solution of manganese(II) and cerium(III) chlorides with a total concentration of 150 g/L and nominal molar fraction of 7:3.
- Addition of a 3 M sodium hydroxide solution under constant agitation.
- Separation by filtration of the precipitate followed by washing cycles with distilled water for chloride withdrawal (always verified with silver nitrate), drying at 100 °C for 4 h and finally grinding until a fine dust was attained.
- The final stage consisted on calcinations and oxidation of the catalyst at $T = 350$ °C during 3 h in the presence of oxygen.

2.2. Methodology of impregnation

In order to promote the impregnation of potassium in the catalyst (MnO_2/CeO_2), the following steps were taken:

- Weighing of 10 g of MnO_2/CeO_2.
- Addition of 100 mL of ethanol.
- Weighing of 5.1 g of KOH and addition of the catalyst solution under agitation.
- Allowing the solution thus prepared to rest on a warm plate at 70 °C, until complete evaporation occurs and a powder forms.
- Washing of the dust with distilled water and filtration until complete removal of the excess hydroxide.
- Drying of the precipitate at 100 °C for 5 h.
- Calcinations and activation of the catalyst ($dp = 0.1$ mm) under air flow at $T = 400$ °C during 4 h.

2.3. Catalysts characterization

This stage aimed to determine the specific area as well as the essential characteristics of the catalysts prepared, which were

Table 1
Catalysts characterization (BET analysis)

Catalyst	Surface area (m^2/g)
MnO_2/CeO_2	117.0
1% K–MnO_2/CeO_2	81.84
4% K–MnO_2/CeO_2	82.88
7% K–MnO_2/CeO_2	76.66
10% K–MnO_2/CeO_2	56.85

related to its performance in the degradation reactions. Although not shown in the present work, the isotherms of adsorption (BET) were obtained after an air output procedure under vacuum, using nitrogen at 77 K as adsorptive species in a NOVA-2000 instrument-version 6.10. The results of the analyses are shown in Table 1.

2.4. Experimental setup

The experimental device used in the wet oxidation of phenol is schematically represented in Fig. 1. The stainless has a volume of 500 mL and is connected to a system that controls temperature, pressure, agitation speed and liquid phase sampling. The reaction was processed in closed system for the liquid (300 mL of phenol solution) and solid (catalytic particles) phases and half-open when high-purity oxygen is used (the feeding is continually provided by a cylinder as the oxygen is consumed by the reaction), so that the total pressure in the system, equal to 20.4 atm, remains constant during the reaction. The reactor is closed and submitted to a mechanical agitation of 900 rpm (according to Larachi et al. [4]; Araújo [5] and Luna [3], this value undoubtedly allows the external diffusional resistance to be minimized). In the beginning of the reactor heating procedure, the liquid and solid (catalyst) phases are saturated with nitrogen, followed by
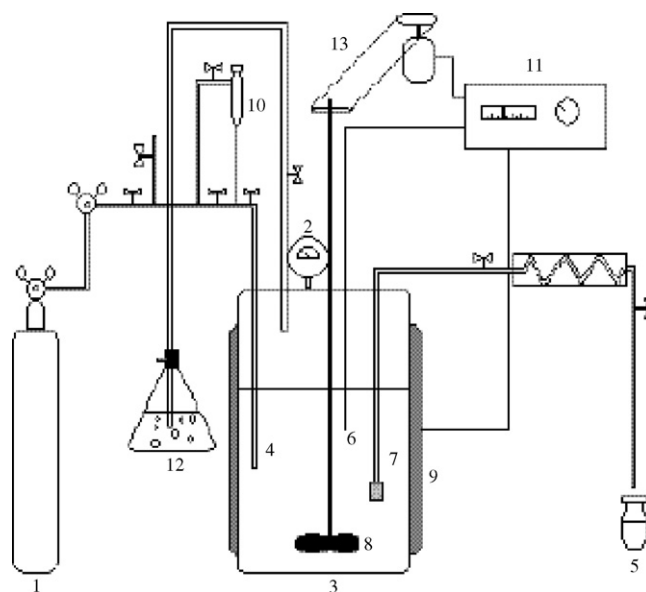

Fig. 1. Schematic diagram of the slurry reactor. (1) Oxygen cylinder; (2) pressure guage; (3) slurry reactor; (4) distributor; (5) liquid sampler; (6) thermocouple; (7) sampling tube; (8) magnet-driver; (9) heating jacket; (10) reagent injection; (11) temperature controller; (12) sampling of the gas; (13) agitation controller.

the feeding of oxygen under low pressure (3 atm). When the internal temperature of the reactor reaches the desired value of 130 °C ($t = 10$ min, considered as the zero time of reaction), the feeding of the gaseous phase begins until establishing a total pressure of 20.4 atm, necessary for sample collection. A liquid phase sample collector, fixed in the upper part of the reactor, enables sampling ($V = 10$ mL) at consecutive intervals of time. This device comprises a porous filter to impede the passage of catalyst and a system of valves which allows for the collection of the liquid phase in such a way that the level of total organic carbon (TOC-Shimatzu model 5050), present in the reactional medium, is satisfactorily quantified. In the end of the reaction, the gas line is closed and the reactor is immediately cooled down to reach room temperature. Finally the catalyst is recovered and discarded and new tests are accomplished with a fresh catalyst.

3. Results and discussion

The experimental investigation of the influence of potassium content, catalyst concentration, initial reaction pH and deactivation of the catalyst was accomplished in the following conditions: $T = 130$ °C, $P_{total} = 20.4$ atm and $C_{phenol} = 0.5$ g/L. It has been verified, although not presented here, that, at the reaction zero time, the conversion of phenol is insignificant. This can probably be explained by the initial low concentration of oxygen (3 atm) present in the liquid phase at the beginning of the reaction. Before carrying out the reaction (without the presence of oxygen, $t = 10$ min, until the temperature reached the value of 130 °C), the possibility of phenol to be adsorbed in the surface of the catalyst had been considered. The initial TOC value in the phenol solution remained approximately constant during the whole time, showing that it is not adsorbed on the catalyst. The water used to wash out the catalyst was also analyzed, and no significant amount of phenol was detected.

3.1. Catalyst characterization

The results of the BET analyses accomplished with the catalysts MnO_2/CeO_2 and $K–MnO_2/CeO_2$ are presented in Table 1.

Table 1 shows that, when the amount of impregnated metal increases, there is a decrease in the superficial area of the catalyst. A larger amount of potassium seems to entirely cover the active sites of the catalyst. This phenomenon had been observed by Hussain et al. [1], who demonstrated that impregnation with metal excess blocks the pores, reduces the specific surface and the activity of the catalyst, thus reducing its efficiency.

3.2. Influence of potassium content in the catalyst MnO_2/CeO_2

Soon afterwards, experiments were accomplished seeking to investigate the effect of the amount of potassium (0%, 1%, 4%, 7% and 10%) impregnated in the catalyst MnO_2/CeO_2, on the wet oxidation of phenol. The reaction was carried out with a concentration of catalyst equal to 3.0 g/L and a pH of 7.5. The curves of conversion of the substratum as a function of time can be seen in Fig. 2.
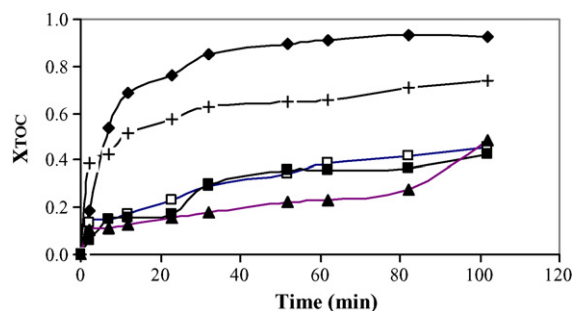

Fig. 2. Effect of the potassium content on the conversion of total organic carbon: (♦) 1%, (+) 4%, (■) 7%, (▲) 10%, and (□) 0%.

All the catalysts presented activity, under identical operational conditions, regarding the conversion of phenol. The catalyst impregnated with 1% potassium allowed for the highest efficiency, reaching 90% of conversion of TOC in 60 min of reaction. Another interesting fact considered herein is the high initial rate of reaction for the catalysts containing 1% and 4% of potassium, which demonstrates the fast phenol consumption in the initial instants of reaction (up to 10 min). The results obtained with the catalyst in the absence of potassium show that its efficiency is equivalent to the catalysts with potassium contents of 7% and 10%. The conversion profile curves corroborate the results obtained in the characterization of the catalyst (Table 1), whereby an increase in the content of impregnated potassium retards phenol degradation and causes loss of catalyst activity. According to Hussain et al. [1], the involvement of metals, regarded as modifiers or chemical promoters, in the wet oxidation affects the activity of the catalyst, conferring stability to it and increasing its performance. The main function of potassium is to directly or indirectly interact with the catalyst, producing active radicals in the first step of the reaction. Potassium possesses electron-donor's ability, capturing oxygen atoms from the reaction medium and forming K_2O, which subsequently changes to peroxide, O_2^{2-}, generating an electron-rich environment that is favorable to the activation of oxygen. This in turn contributes to the production of more peroxide by the catalyst. Such mechanism favors a better performance of the oxidation reaction, which means that, in a very short period of time, there occurs less formation of carbonated deposits and intermediary compounds that may poison the catalyst surface.

3.3. Influence of catalyst concentration

The effect of the catalyst concentration (1% K–MnO_2/CeO_2) was studied with an initial pH value equal to 7.5. The results are presented in Fig. 3.

It is observed that the speed of phenol degradation considerably increases as the catalyst concentration increases, with consequently larger conversion rates. That is explained by the fact that an increase in the concentration of the catalyst promotes an increase in the number of active sites involved in the phenol degradation. This behaviour has also been described by Larachi et al. [4], based on interpretations of the results presented by Sadana and Katzer [6]. These authors comment that if the reaction only happened on the surface of the catalyst, through a
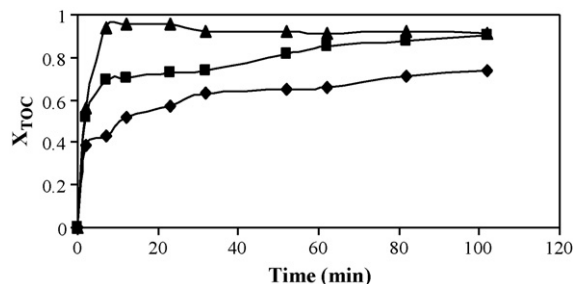
Fig. 3. Effect of the catalyst concentration on the conversion of total organic carbon: (♦) 1.5 g/L, (■) 3.0 g/L, and (▲) 5.0 g/L.

mechanism involving free radical or not, the observed reaction rate per unit of catalyst mass would consequently be independent of the catalyst concentration. On the other hand, if the reaction involved a mechanism composed of a heterogeneous stage with formation of free radicals and a homogeneous stage where the free radicals would react forming and generating new radicals, the consumption rate per unit of catalyst mass would be a function of the catalyst concentration.

3.4. Effect of initial pH

The processes of wet oxidation of industrial waste are characterized by the formation of organic acids that reduce the pH of the medium as the reaction is proceeded. This behaviour was observed in the catalytic oxidation of phenol [7] and lignine [8]. In general, acetic acid is the most common substance found in the processes of wet oxidation of organic pollutants. The difficulty to transform these pollutants in CO_2 is one of the most important characteristics of this type of oxidation. The experimental study on the influence of initial pH value applied to catalytic oxidation of phenol was accomplished in the presence of the catalyst 1% K–MnO_2/CeO_2. Fig. 4 presents the experimental results for three different initial pH values, namely, 6.8, 7.5 and 8.5. The results show that, as the initial pH value is increased, a significant effect on the activity of the catalyst as well as on the rate of phenol degradation occurs.

This trend of the concentration profile has been described by Miroâ et al. [9], who defined that such behaviour can be explained by the different dissolution rates in the aqueous solution and the increase in solubility of the carbonaceous deposits. High pH values prevent the leaching of potassium, which will remain on the surface of the catalyst for a longer period of time,
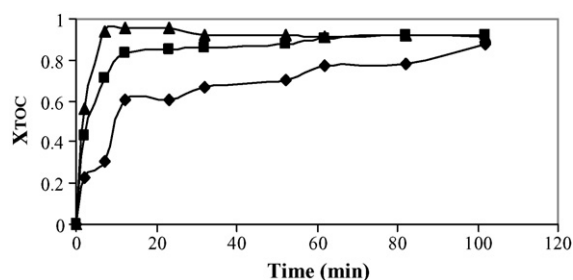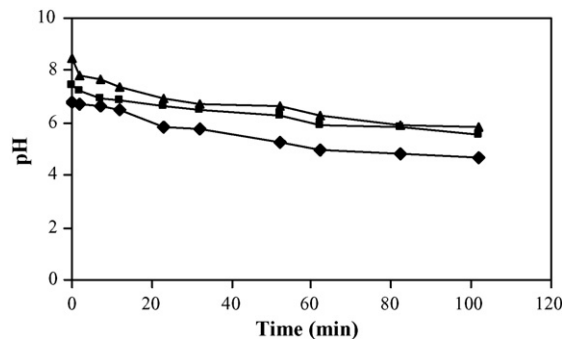

Fig. 5. Variation of pH as a function of reaction time: (♦) 6.8, (■) 7.5, and (▲) 8.5.

thus increasing catalytic activity and reducing the catalyst deactivation speed.

The nature of the medium was examined during the catalytic degradation of phenol. The experimental results indicate probable formation of intermediate acidic products during the degradation of phenol, which reduces the pH as a function of time (see Fig. 5). This shows that, at higher pH values, the deactivation of the catalyst 1% K–MnO_2/CeO_2 seems to happen in a slower way.

3.5. Catalyst deactivation

The results were obtained with a concentration of catalyst equal to 3.0 g/L and at pH 7.5. By analyzing of the curves of phenol conversion as a function of time (Fig. 6), it can be concluded that catalyst deactivation (probably by means of poisoning provoked by composites formed during the reaction, such as acetic acid) is significantly effected with successive catalyst recycles. It is important to provide proper conditions so that acetic acid is quickly decomposed during the reaction. Leitenburg et al. [10] showed that the oxidation of acetic acid is complete when ternary catalysts with zirconium oxide (CeO_2–ZrO_2–MnO_2) are used.

4. Macroscopic kinetic modelling

The kinetic study with the experimental results was carried out starting from the time zero of reaction. The reaction was performed under a total pressure of 20.4 atm, a temperature of 130 °C, initial phenol concentration equal to 0.5 g/L and with optimal conditions, that is, pH equal to 8.5, catalyst of the type 1% K–MnO_2/CeO_2 and load of catalyst

Fig. 4. Effect of the initial pH on the conversion of total organic carbon: (♦) 6.8, (■) 7.5, and (▲) 8.5.
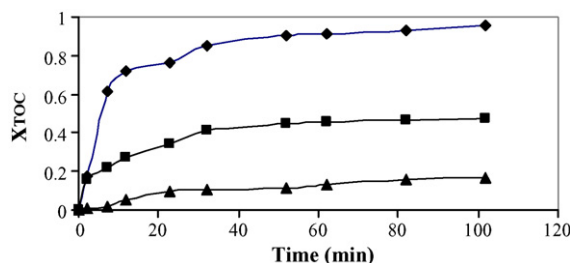

Fig. 6. Total organic carbon conversion as a function of reaction time: (♦) fresh catalyst, (■) second use, and (▲) third use.

equal to 5.0 g/L. The analyses of the residual total organic carbon were made in consecutive intervals of time during the reaction.

The mechanism proposed to develop the kinetics of the catalytic reaction of phenol degradation is based on a pseudo first-order model. The respective kinetic model was based on that proposed by Zhang and Chuang [8] and Luna [3], and contemplates two parallel stages:

$$A \xrightarrow{k_1} CO_2$$
$$A \xrightarrow{k_2} B$$
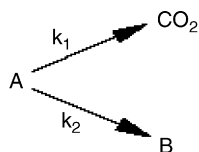
where A represents the residual phenol concentration + non-refractory intermediates (organic carbon degraded during the reaction, possibly catechol or hydroquinone, etc.) and B is the refractory intermediate concentration (non-degraded carbon) formed during the reaction. The kinetic constants for formation of the constituents CO_2 and B are represented by k_1 and k_2, respectively. One may define C_A and C_B as the concentrations of non-refractory and refractory residual carbon relative to initial TOC at $t = 0$, respectively, that is

$$C_A = \frac{\text{concentration of carbon of the intermediate phenol not refractorys}}{TOC_0} \quad (1)$$

$$C_B = \frac{\text{concentration of carbon refractory intermediate}}{TOC_0} \quad (2)$$

Therefore, the residual concentration of total organic carbon present in the liquid phase will be

$$C_r = C_A + C_B \quad (3)$$

Applying a mass balance for the liquid phase, Eqs. (4) and (5) are obtained

$$-\frac{dC_A}{dt} = (k_1 + k_2)C_A \quad (4)$$

$$\frac{dC_B}{dt} = k_2 C_A \quad (5)$$

When in integrated form, Eqs. (4) and (5) allow to describe the concentration profile of A and B as a function of reaction time:

$$C_A = C_{A0} \exp[-(k_1 + k_2)t] \quad (6)$$

$$C_B - C_{B0} = \frac{C_{A0}k_2}{k_1 + k_2}\{1 - \exp[-(k_1 + k_2)t]\} \quad (7)$$

Combining Eqs. (6) and (7) with Eq. (3) and considering that, $C_r/C_{A0} = (C_A + C_B)/C_{A0}$ and that, at $t = 0$, $C_A = C_{A0}$, with $C_A/C_{A0} = 1$ and $C_{B0} = 0$, gives

$$\frac{TOC}{TOC_0} = \frac{C_r}{C_{A0}} + \frac{k_2}{k_1 + k_2} + \frac{k_1}{k_1 + k_2} \exp[-(k_1 + k_2)t] \quad (8)$$

Eq. (8) represents the concentration profile of total organic carbon present in the liquid phase as a function of reaction time, represented in Fig. 7. The model was tested through MathCAD 2000 Professional considering a "genfit function" by using Newton's non-linear method. The data are adjusted to the integrated
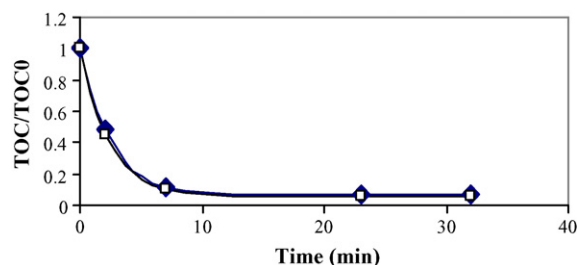

Fig. 7. Fitting of the kinetic model for phenol degradation: ($\square$) 1% K–MnO$_2$/CeO$_2$, ($\blacklozenge$) MnO$_2$/CeO$_2$, and (—) experimental model.

Table 2
Fitted kinetic constants ($T = 130\,°C$)

Catalyst	k_1 (min^{-1})	k_2 (min^{-1})
1% K–MnO$_2$/CeO$_2$	0.42	0.027
MnO$_2$/CeO$_2$	0.38	0.027

equation of the model where the kinetics constants are calculated (Table 2). The results obtained show good adjustment to the experimental data, with coefficients of correlation of 96%.

It is observed that the speed of phenol degradation is faster when it favors the formation of CO_2 (mainly in the presence of potassium), being governed by the second stage, which corresponds to the refractory constituent formation, regardless of the nature of the catalyst.

Luna [3] carried out the phenol degradation with the catalyst MnO$_2$/CeO$_2$ in identical conditions of temperature, pressure, initial phenol concentration and pH, finding, for the same kinetic model, the following values: $k_1 = 0.11$ min^{-1} and $k_2 = 0.13$ min^{-1}. Comparing these results with those of Table 2, a significant influence of the concentration of the catalyst on the kinetic constant is observed.

5. Conclusions

The main results obtained in this study, involving catalytic wet oxidation of organic substances, show that the compound K–MnO$_2$/CeO$_2$ possesses optimal activity as a catalyst in the process of wet oxidation of phenol, when compared with the non-promoted catalyst. The increase in the amount of impregnated potassium reduces phenol conversion. Potassium acts as a modifier or chemical promoter, improving the performance and stability of the catalyst. The load of the catalyst and the increase of pH favor phenol degradation. The results obtained experimentally show that the loss of activity of the catalyst is fast, requiring doping with other metals (Ag, Pt, Ru, in spite of the decrease in the degradation rate; Hamoudi et al. [11]) or even to test other catalysts, for example, CuO/ZnO/CoO [12], CuCeO$_x$ [13,14], Cu/MCM-41 [15], Fe/activated carbon [16] and activated carbon [17], in order to impair the deactivation process. The kinetic study of the catalytic wet phenol oxidation

revealed that the macroscopic model, composed by two parallel stages comprising total oxidation to CO_2 and partial oxidation to refractory constituents (stage-limiting), is well adjusted to the experimental data, accurately and satisfactorily describing the concentration profiles of the total organic carbon obtained at the temperature of 130 °C.

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