Journal of Chemical Technology and Biotechnology *J Chem Technol Biotechnol* (in press)
DOI: 10.1002/jctb.1280

Catalytic wet oxidation of phenol with homogeneous iron salts

Jesús Vicente,[1] Roberto Rosal[2] and Mario Díaz[1]*

[1]*Departamento de Ingeniería Química y Tecnología del Medio Ambiente, Universidad de Oviedo, E-33071, Oviedo, Spain*
[2]*Departamento de Química Analítica e Ingeniería Química, Universidad de Alcalá, E-28771 Alcalá de Henares, Spain*

Abstract: The catalytic wet oxidation of phenol has been investigated in a 1 L semi-batch reactor in the presence of both ferrous and ferric salts. Oxidation reactions follow first-order kinetics with respect to phenol and half-order kinetics with respect to dissolved oxygen. The activation energy for the reaction was 44.5 and 48.3 kJ mol^{-1} for runs employing Fe^{3+} and Fe^{2+}, respectively. Rate constants and induction periods were also similar for both catalysts. This result could be explained by analysing the evolution of iron during the oxidation process. For pH > 2, Fe^{2+} was rapidly oxidized under reaction conditions to Fe^{3+}, resulting in a unique catalytic redox system Fe^{2+}/Fe^{3+}. It was also shown that if pH < 2 the dissolved oxygen was unable to oxidize ferrous ion, resulting in a much slower oxidation rate of phenol. The absence of a redox pair resulted in a complete lack of catalytic activity of the dissolved iron salt.

Keywords: wet oxidation; phenol; catalyst; iron

NOMENCLATURE

D_{O_2}	diffusivity of oxygen in the liquid phase (m^2 s^{-1})
E_a	activation energy (kJ mol^{-1})
k	kinetic constant (units depend on reaction order)
k_r	pseudo first-order kinetic constants (s^{-1})
k_L	mass transfer coefficient for oxygen in the liquid phase (m s^{-1} and s^{-1})
n	order of reaction
C_{Ph}	phenol concentration (ppm)
C_{O_2}	oxygen concentration (mol L^{-1})
Ha	Hatta number $= \sqrt{bk_r D_{O_2} k_L^{-1}}$

INTRODUCTION

Wet oxidation is an alternative technique for treating organic waste streams that are toxic or refractory to conventional biological treatments.[1] The process is carried out in liquid phase at relatively elevated temperatures and pressures using a gaseous source of oxygen. The high cost of this technique when applied to the complete oxidation of all organics in a waste stream is mainly due to the formation of low molecular mass carboxylic acids that are difficult to convert into CO_2 and H_2O.[2] In such cases, it has been suggested that a partial oxidation of organics may be followed by biological methods of abatement.[3] A catalyst is used in many situations to allow operation under milder conditions.[4–8] However, the development of catalytic processes requires more effort in reactor engineering and in the search for more efficient catalysts. Both homogeneous and heterogeneous catalysts have been reported for wet oxidation of organic compounds.[4] The use of heterogeneous catalysts has received much more attention in recent years, even though these have some disadvantages. The enhanced mass transfer resistance inside catalyst pores reduces reaction rates, requiring larger reactors, and the development of heterogeneous catalysts thus involves high investment cost. Another hurdle is that three-phase reactors operate under conditions that are difficult to model and control.[3] On the other hand, homogeneous catalytic processes can operate in smaller reactors but they require a downstream auxiliary demetallation unit for the recovery of catalyst.

Several wet oxidation processes have been reported that use homogeneous catalysts. The LOPROX process, patented by Bayer AG, uses Fe^{2+} as a homogeneous catalyst with the main objective of improving the biodegradability of wastewaters. It is a pure oxygen process operating at a temperature below 230 °C and a pressure not higher than 3.5 MPa with the purpose of leaving the bulk of the degradation work to a downstream biological treatment unit.[9] The chemical oxidation of organic compounds in the presence of hydrogen peroxide and iron salts (Fenton reagent) has been proposed as a wastewater treatment technology.[10] Litvintsev *et al*[11,12] studied

---

* Correspondence to: Mario Díaz, Departamento de Ingeniería Química y Tecnología del Medio Ambiente, Universidad de Oviedo, E-33071, Oviedo, Spain
E-mail: mariodiaz@uniovi.es

Contract/grant sponsor: European Union; contract/grant number: 7220-EB/004
(*Received 27 May 2004; revised version received 13 September 2004; accepted 20 January 2005*)

the Fenton oxidation in the presence of catechol (1,2-dihydroxybenzene) as co-catalyst and in the presence of a combined Fe(II)–Ce(IV) catalytic system.[13] Other homogeneous iron-based systems, such as photocatalytic H_2O_2/Fe/UV or Photo-Fenton reagent, have been proposed for the removal of phenol and substituted phenols from wastewaters.[14] Shende and Mahajani[15] and Imamura[16] reported higher activity of Cu^{2+} homogeneous catalyst than Fe^{3+} salts for the oxidation of carboxylic acids.

The commercial significance of phenol and substituted phenols, their high toxicity and the limitations for the biotreatment of streams containing over 200 ppm of such compounds[17] justifies the large experimental effort devoted to developing wet oxidation processes for wastewaters containing phenol and its derivatives. However, experimental results show a large dispersion resulting from a lack of fundamental information. The aim of this work was the study of the kinetics of the homogeneous oxidation of phenol in the presence of Fe^{3+}, Fe^{2+} and their mixture. Special attention was paid to ensure that mass transfer effects could be neglected throughout.

EXPERIMENTAL

Apparatus and procedure

Runs were carried out in a 1 L stainless steel Parr T316SS reactor (100 mm diameter) equipped with two six-bladed magnetically driven turbine agitators. The reactor was preceded by a 2 L stainless steel water reservoir filled with deionized water up to about 70% of its total capacity. Oxygen, supplied from a compressed cylinder, was bubbled through the water reservoir in order to saturate it before it reached the reactor. The flow of oxygen was measured and controlled by a Brooks mass flow electronic device. Once the equipment was pressurized and preheated up to the desired conditions, a predetermined amount of a concentrated solution of phenol (90% in deionized water) was injected into the reactor by means of pressure from the bottled compressed oxygen. A valve and a coil fitted to the top of the vessel allowed the withdrawal of samples during the reaction. The pressure was kept constant by means of a back-pressure controller located at the end of the gas line and the stirring speed was adjusted to 500 rpm. Further details can be found elsewhere.[18,19]

Analysis

The concentration of phenol was monitored by the 4-aminoantipyrine method, a colorimetric procedure developed by Ettinger *et al*[20] and based on the formation of a red complex between 4-aminoantipyrine and phenol in the presence of an oxidant such as potassium hexacyanoferrate III, $K_3Fe(CN)_6$. The absorbance of the complex was monitored with a Perkin-Elmer spectrophotometer and was a maximum at 510 nm.

The concentration of Fe^{2+} in solution was determined by titration with potassium dichromate following the standard ASTM 310A procedure. Total iron was measured by atomic absorption spectrophotometry according to ASTM 301A-II.

RESULTS AND DISCUSSION

The oxidation of phenol takes place in two periods with different kinetic behaviour. An induction stage where the oxidation proceeds slowly is followed by a steady-state reaction that is first-order with respect to the organic compound.[4,18] It has been stated that the length of the induction period is determined by the time required for the free-radical reacting species to reach a critical concentration. The rapid step begins when the concentration of radicals reaches the critical value required for a stationary state.[21] Another relevant characteristic of free-radical reactions is the dependence of reaction rates on the total amount of organic load. It has been determined elsewhere that the kinetic constant during the first-order period depends linearly on the initial reactant concentration.[18] In order to avoid this source of variability, all runs performed in this work used the same initial amount of phenol ($C_{Ph_0} = 1000\,\text{ppm} = 1.06 \times 10^{-2}\,\text{mol}\,\text{L}^{-1}$).

The overall oxidation process requires the transfer of oxygen from the gas phase to the liquid phase, which depends on the convective mass transfer coefficient in the liquid phase, k_L. Once the stationary state is reached, the rate of oxygen transfer must equal the rate of consumption due to the chemical reaction with phenol.

All the reactions described in this work were performed under kinetic control. Verification was done by using the Hatta number, *Ha*, developed from the film theory of mass transfer:

$$Ha = \sqrt{\frac{b k_r D_{O_2}}{k_L}}$$

During all runs, $Ha < 0.02$, thus ensuring the absence of mass transfer limitations. For the case of chemical control, the overall kinetics may be expressed as follows:

$$-\frac{dC_{Ph}}{dt} = k C_{Ph} C_{O_2}^n$$

In the conditions studied in this work, the catalyst loading had no significant effect on the kinetic constant k. Consequently, the amount of catalyst was not included in any kinetic expression. Rate expressions showing other than first-order behaviour with respect to catalyst concentration have been reported in other studies and reflect the role of radical generation played by catalysts in wet oxidation processes.[22] No deviation was detected in this work from first-order kinetics with respect to phenol, which is in agreement with most results found in the literature.[4] The data from the evolution of phenol were fitted to a kinetic expression n-order in oxygen, yielding a value whose deviation from $n = 1/2$ was not statistically significant. This value agrees with those provided by other investigators

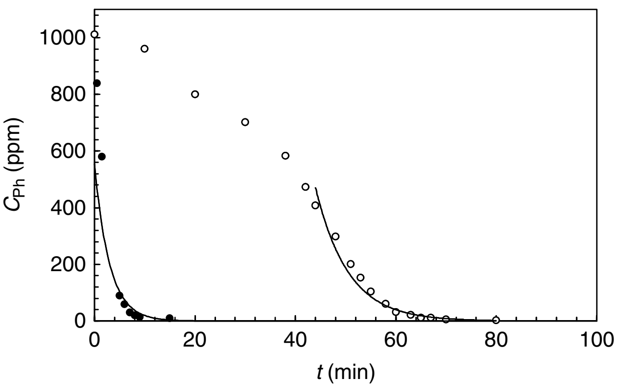

Figure 1. Evolution of phenol during oxidation in the absence of catalyst (○) and using 5.00×10^{-3} mol L^{-1} of Fe^{3+} (●); $P = 5.1$ MPa of oxygen and $T = 200$ °C.

for the rapid degradation step in the catalytic wet oxidation of phenol.[21–23] On the other hand, first-order kinetics have been reported for the induction period[21] and for the non-catalytic process,[18,24] even in the presence of hydrogen peroxide.[25]

Oxidation catalysed by ferric ion (Fe^{3+})

Figure 1 compares the non-catalytic oxidation of a 1000 ppm solution of phenol with the reaction carried out in the presence of 5.00×10^{-3} mol L^{-1} of Fe^{3+}. The reaction was performed under 5.1 MPa of oxygen at 200 °C. The solid lines represent the first-order fitting of data excluding those corresponding to the induction period in the non-catalysed reaction. The data show that the induction period completely disappears in the catalysed reaction in agreement with the expected role of the catalyst in the generation of free radicals. For lower temperatures, an induction period still existed, but always much shorter than that corresponding to a non-catalytic reaction. For example, at 170 °C and 10.2 MPa, the induction period in a non-catalysed reaction was 155 min, whereas at 150 °C and 5.1 MPa in the presence of 5.00×10^{-3} mol L^{-1} of Fe^{3+}, the observed induction time was 20 min.

The disappearance of phenol and the evolution of pH for runs performed at 150 °C and 5.1 MPa are represented in Fig 2 for various loads of Fe^{3+}. For all runs, the initial value of pH rapidly dropped to an almost constant value slightly below 3.0 and was practically independent of process conditions. This pattern has been attributed to the early formation of carboxylic acids from phenol. It has been noted in previous work[18] that carboxylic acids react slowly under wet oxidation conditions and tend to accumulate, resulting in a residual chemical oxygen demand of about 500 ppm.

In order to evaluate the activation energy of the process, several runs were performed at 5.1 MPa and temperatures of between 150 and 200 °C, starting with 1000 ppm of phenol and 5.00 10^{-3} mol L^{-1} of catalyst. The kinetic constants for the steady-state reaction following the induction period were fitted to an Arrhenius-type expression, which yielded an activation energy of 44.5 kJ mol^{-1}. This value is in good agreement with other reported activation energies for the oxidation of phenol, a selection of which is summarized in Table 1. It has to be remarked, however, that the literature data show a certain dispersion also encountered in the non-catalytic oxidation of phenol. In general, conditions that induce the formation of tar have been associated with higher activation energies.

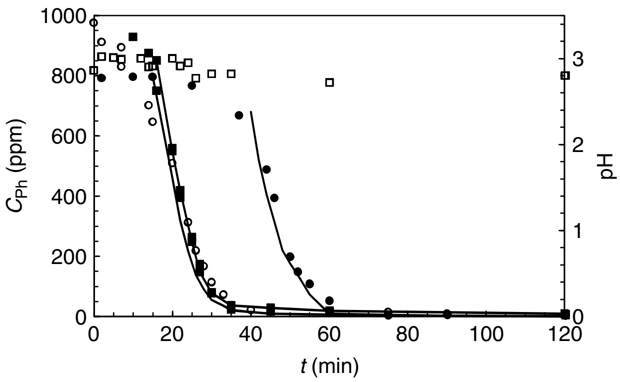

Figure 2. Oxidation of phenol at 150 °C and 5.1 MPa with 5.00×10^{-4} mol L^{-1} Fe^{3+} (●), 2.50×10^{-3} mol L^{-1} Fe^{3+} (■) and 5.00×10^{-3} mol L^{-1} Fe^{3+} (○); the evolution of pH is also represented (□).

Table 1. Reported activation energies for catalytic and non-catalytic oxidation of phenol

Catalyst	Temperature (°C)	Activation energy (kJ mol^{-1})	Reference
Cu^{2+} ($CuSO_4$)	80–110	57.5	Kulkarni and Dixit[26]
Cu/Zn/Co oxides (EX1144.8 Süd-Chemie)	130–160	61	Pintar *et al*[27]
CuO/Al_2O_3	114–200	57.4	Katzer *et al*[5]
CuO/Al_2O_3	120–160	76–85	Fortuny *et al*[28]
CuO/Al_2O_3	120–230	85.7	Otha *et al*[29]
—	170–220	67.4	Vicente *et al*[18]
—	180–210	107	Shibaeva *et al*[30]
—	130–200	112	Willms *et al*[21]
—	145–180	56.6	Jaulin and Chornet[31]
—	150–180	50	Jogeklar *et al*[32]
—	160–220	46.9	Rivas *et al*[33]

Oxidation catalysed by ferrous ion (Fe^{2+})

The results obtained during the oxidation of phenol in the presence of Fe^{2+} from $FeSO_4$ are shown in Fig 3. The runs performed at 150 °C and 5.1 MPa followed a similar pattern to those in the presence of Fe^{3+} described before. The evolution of pH also dropped to 2.4–2.6 from a higher initial value (around 6.5) corresponding to phenol aqueous solution. The activation energy obtained for the oxidation catalysed by Fe^{2+} was 48.3 kJ mol^{-1}, similar to the result reported above for Fe^{3+} catalyst. Rate constants for runs employing Fe^{2+} were in all cases slightly lower

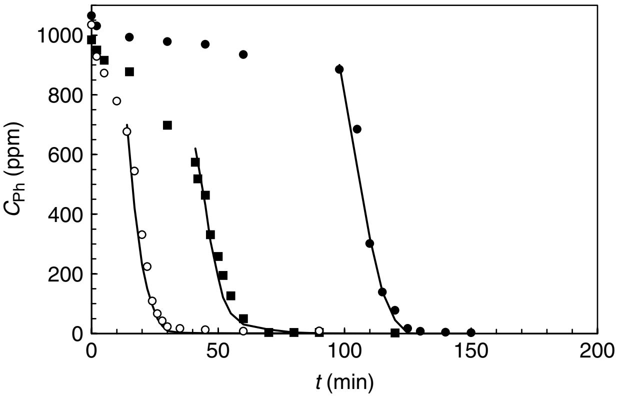

Figure 3. Oxidation of phenol at 150 °C and 5.1 MPa with 3.29×10^{-4} mol L^{-1} Fe^{2+} (●), 6.58×10^{-3} mol L^{-1} Fe^{2+} (■) and 3.29×10^{-3} mol L^{-1} Fe^{2+} (○).

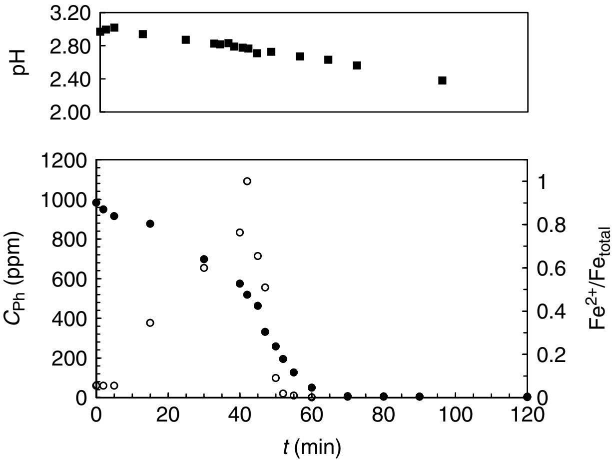

Figure 4. Oxidation of phenol at 150 °C and 5.1 MPa with 6.58×10^{-4} mol L^{-1} Fe^{2+} (●); the ratio Fe^{2+}/Fe$_{total}$ is represented on the right-hand axis (○); the upper part of the figure shows the evolution of pH (■).

than the corresponding reactions catalysed by Fe^{3+}. For example, at 150 °C and 5.1 MPa, the kinetic constant was 6.0×10^{-2} L$^{0.5}$ s^{-1} mol$^{-0.5}$ for Fe^{2+} and 6.9×10^{-2} L$^{0.5}$ s^{-1} mol$^{-0.5}$ for Fe^{3+} with a catalyst load of 3.29×10^{-4} mol L^{-1} of cation. At 200 °C and 84.6 MPa, rate constants were 0.18 L$^{0.5}$ s^{-1} mol$^{-0.5}$ and 0.15 L$^{0.5}$ s^{-1} mol$^{-0.5}$ with a catalyst load of 6.58×10^{-4} mol L^{-1} of Fe^{3+} and Fe$^{2+,}$ respectively. In most cases, however, confidence intervals for both parameters overlap, indicating that the difference is not statistically significant. The comparison between Figs 2 and 3 also reveals that the length of the induction period is similar for runs using Fe^{2+} and Fe^{3+} as catalyst.

The analysis of the samples withdrawn during the reaction revealed that the oxidation state of dissolved iron changes as the reaction proceeds. Figure 4 shows the evolution of the ratio Fe^{2+}/Fe$_{total}$ during the oxidation of a 1000 ppm solution of phenol at 150 °C and 5.1 MPa in the presence of 6.58×10^{-4} mol L^{-1} of Fe^{2+}. The figure also shows pH values evolving towards 2.4 as a consequence of the accumulation of reaction products. After the injection of catalyst into the reaction bulk, Fe^{2+} was rapidly converted into Fe^{3+}, which was steadily reduced back to Fe^{2+} during the induction period. At the beginning of the first-order period, the concentration of Fe^{2+} reached a maximum after which the iron was oxidized again to Fe^{3+}.

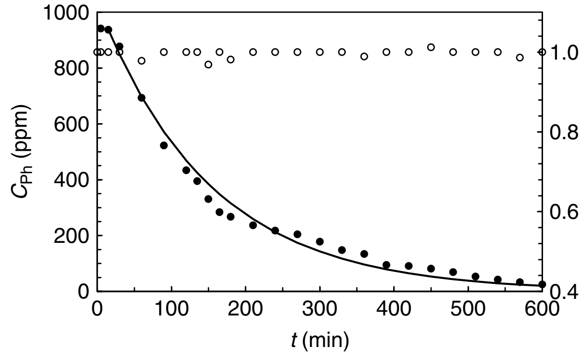

Figure 5. Oxidation of phenol at 150 °C and 5.1 MPa at pH < 2 with 6.58×10^{-4} mol L^{-1} Fe^{2+} (●); the ratio Fe^{2+}/Fe$_{total}$ is also represented (○).

Figure 5 represents the evolution of phenol and Fe^{2+}/Fe$_{total}$ in the same conditions but keeping $\text{pH} < 2$ by adding sulfuric acid to the reaction mixture. In this case, rate constant was 6.60×10^{-3} min^{-1}, much lower than those obtained in the same conditions with Fe^{3+} and Fe^{2+}/Fe^{3+} systems. The redox potential of the Fe^{2+}/Fe^{3+} system rapidly decays at a pH value slightly above 2, but is relatively high for $\text{pH} < 2$ ($E_h = 0.77$ V). The catalytically less active form, Fe^{2+}, is therefore stable only at highly acidic conditions, being rapidly converted into Fe^{3+} when pH is allowed to freely evolve as phenol is oxidized to refractory carboxylic acids. The results also showed that phenol is able to reduce Fe^{3+} for a short period at the beginning of the rapid degradation step, when the reaction rate and oxygen consumption are higher. The interconversion between Fe^{2+} and Fe^{3+} explained the similarity of the rate constants obtained in runs where the pH was above 2.

CONCLUSIONS

The catalytic oxidation of phenol takes place in two steps in series: an induction period and a steady-state decay. In all cases, the induction period is shorter than that corresponding to non-catalytic oxidation. Concerning the steady-state decay, the experimental results show that the oxidation of phenol in the presence of ferrous and ferric salts obeys first-order kinetics with respect to the organic compound and half-order kinetics with respect to dissolved oxygen. The values of the activation energy were similar for Fe^{2+} and for Fe^{3+} catalysts (44.5 and 48.3 kJ mol^{-1}, respectively). Rate constants were somewhat lower for Fe^{2+}, but the uncertainty in their determination supports the assumption that they are not significantly different from those obtained with Fe^{3+}. When pH was allowed to evolve freely, it decreased during every run reflecting the accumulation of refractory carboxylic acids in the reaction mixture. At all times the pH remained higher than 2. The spectrophotometric analysis of iron in samples withdrawn during the runs revealed that there exists an interconversion between Fe^{2+} and Fe^{3+} irrespective of the form in which iron is introduced in the reaction bulk. Oxygen in solution oxidizes Fe^{2+} to Fe^{3+}, that was the dominant oxidation form except at the end of the induction period, when first-order oxidation of phenol started. In another set of runs, sulfuric acid was added to keep $pH < 2$ throughout the reaction period. In this case, the oxidation rate of phenol became very small and the analysis proved that Fe^{2+} was not converted into Fe^{3+}. Under those conditions, the establishment of a Fe^{2+}/Fe^{3+} redox system is required for the oxidation to take place at high rates.

ACKNOWLEDGEMENT

The financial support of this study by means of European Union contract 7220-EB/004 is acknowledged.

REFERENCES

1 Copa WM and Gitchell WB, Wet oxidation, in *Standard Handbook of Hazardous Waste Treatment and Disposal*, ed by Freeman HM. McGraw-Hill, New York, pp 77–90 (1989).

2 Shende RV and Levec J, Wet oxidation kinetics of refractory low molecular mass carboxylic acids. *Ind Eng Chem Res* **28**:3830–3837 (1999).

3 Matatov YI and Steintuch M, Catalytic abatement of water pollutants. *Ind Eng Chem Res* **37**:309–326 (1998).

4 Mishra VS, Vijaykumar VM and Joshi JB, Wet air oxidation. *Ind Eng Chem Res* **34**:2–48 (1995).

5 Katzer JR, Ficke HH and Sadana A, An evaluation of aqueous phase catalytic oxidation. *J WPCF* **48**:920–933 (1976).

6 Pintar A and Levec J, Catalytic liquid-phase oxidation of phenol aqueous solutions: a kinetic investigation. *Ind Eng Chem Res* **33**:3070–3077 (1994).

7 Pintar A, Bercic G and Levec J, Catalytic liquid-phase oxidation of aqueous phenol solutions in a trickle-bed reactor. *Chem Eng Sci* **52**:4143–4153 (1997).

8 Santos A, Yustos P, Durbán B and García F, Oxidation of phenol in aqueous solution with copper catalysts. *Catal Today*, **66**:511–517 (2001).

9 Kolaczkowski ST, Plucinski P, Beltrán FJ, Rivas FJ and McLurgh DB, Wet air oxidation: a review of process technologies and aspects in reactor design. *Chem Eng J* **13**:143–160 (1999).

10 Grigoropoulou H and Ohilippopoulos C, Homogeneous oxidation of phenols in aqueous solution with hydrogen peroxide and ferric ions. *Water Sci Technol* **36**:151–154 (1997).

11 Litvintsev IY, Mitnik YV and Mikhailyuk AI, Kinetics and mechanism of catalytic hydroxylation of phenol by hydrogen peroxide. I. General relationships of process variables. *Kinet Catal* **34**:71–75 (1993).

12 Litvintsev IY, Mitnik YV and Mikhailyuk AI, Kinetics and mechanism of catalytic hydroxylation of phenol by hydrogen peroxide. II. Modelling of the initial stage in the presence of catalytic system Fe(II)/pyrocathecol. Influence of concentration of initial reactants. *Kinet Catal* **34**:76–82 (1993).

13 Litvintsev IY, Mitnik YV and Saponuk VN, Kinetics and mechanism of catalytic hydroxylation of phenol by hydrogen peroxide. III. The effect of the nature of a bimetallic catalytic system. Simulation of the initial reaction stage in the presence of the Fe(II)-cathecol-Ce(IV) catalytic system, *Kinet Catal* **36**:482–487 (1995).

14 Zepp RG and Faust BC, Hydroxyl radical formation in aqueous reaction of iron (II) with hydrogen peroxide: The photo Fenton reaction. *Environ Sci Technol* **26**:313–319 (1992).

15 Shende RV and Mahajani VV, Kinetics of wet oxidation of formic acid and acetic acid. *Ind Eng Chem Res* **36**:4809–4814 (1997).

16 Imamura S, Catalytic and noncatalytic wet oxidation. *Ind Eng Chem Res* **38**:1743–1753 (1999).

17 Pruden BB and Le H, Wet air oxidation of soluble components in wastewater. *Can J Chem Eng* **54**:319–325 (1976).

18 Vicente J, Rosal R and Díaz M, Noncatalytic oxidation of phenol in aqueous solutions. *Ind Eng Chem Res* **41**:46–51 (2002).

19 Vicente J and Díaz M, Thiocyanate wet oxidation. *Environ Sci Technol* **37**:1452–1456 (2003).

20 Ettinger MB, Ruckhoft CC and Lishka RJ, Sensitive 4-aminoantipyrine method for phenolic compounds. *Anal Chem* **23**:1783–1785 (1951).

21 Willms RS, Balinsky AM, Reible DD, Wetzel DM and Harrison DP, Aqueous phase oxidation: the intrinsic kinetics of single organic compounds. *Ind Eng Chem Res* **26**:148–154 (1987).

22 Sadana A and Katzer JR, Catalytic oxidation of phenol in aqueous solution over copper oxide. *Ind Eng Chem Fundam* **13**:127–134 (1974).

23 Sadana A, Catalytic oxidation of maleic acid in aqueous solution. *Ind Eng Chem Process Des Dev* **20**:576–577 (1981).

24 Vicente J and Díaz M, Thiocyanate/phenol wet oxidation interactions. *Environ Sci Technol* **37**:1457–1462 (2003).

25 Rivas FJ, Kolaczkowski ST, Beltrán FJ and McLurgh DB, Hydrogen peroxide promoted wet air oxidation of phenol: influence of operating conditions and homogeneous metal catalysts. *J Chem Tech Biotechnol* **74**:390–398 (1999).

26 Kulkarni US and Dixit SG, Destruction of phenol from wastewater by oxidation with SO3^{2-}-O$_2$. *Ind Eng Chem Res* **30**:1916–1920 (1991).

27 Pintar A, Bercic G and Levec J, Catalytic liquid-phase oxidation of aqueous phenol solutions in a trickle-bed reactor. *Chem Eng Sci* **52**:4143–4153 (1997).

28 Fortuny A, Ferrer C, Bengoa C, Font J and Fabregat A, Catalytic removal of phenol from aqueous phase using oxygen or air as oxidant. *Catal Today* **24**:79–83 (1995).

29 Otha H, Goto S and Teshima H, Liquid phase oxidation of phenol in a rotating catalytic basket reactor. *Ind Eng Chem Fundam* **19**:180–185 (1980).

30 Shibaeva L, Metelitsa DI and Denisov ET, The kinetics of the oxidation of phenol with oxygen from aqueous solution. *Kinet Catal* **10**:832–839 (1969).

31 Jaulin L and Chornet E, High shear jet mixers as two-phase reactors: an application to the oxidation of phenol in aqueous media. *Can J Chem Eng* **65**:64–70 (1987).

32 Joglekar HS, Samant SD and Joshi JB, Kinetics of wet oxidation of phenol and substituted phenols. *Water Res* **25**:135–145 (1991).

33 Rivas FJ, Kolaczkowski ST, Beltrán FJ and McLurgh DB, Development of a model for the wet air oxidation of phenol based on a free radical mechanisms. *Chem Eng Sci* **53**:2575–2586 (1998).