



Influence of operation conditions on the copper-catalysed homogeneous wet oxidation of phenol: Development of a kinetic model



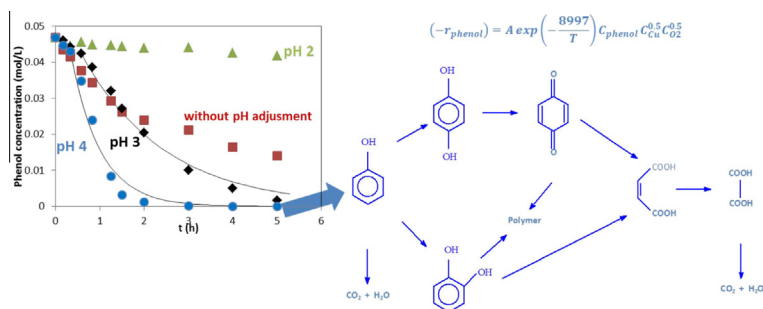
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HIGHLIGHTS

- Deep oxidation of phenol catalysed by Cu(II) homogeneous catalysts.
- The effect of phenol, oxygen, pH, and catalyst concentration is studied.
- pH plays a major role on the reaction performance.
- A generalised kinetic model is proposed and experimentally validated.

GRAPHICAL ABSTRACT



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ABSTRACT

This article presents a comprehensive study about the influence of pH, temperature and concentrations on the homogeneous catalytic oxidation of aqueous phenol at high concentrations (0.0467 mol/L), using copper (II) as homogeneous catalyst in a stirred batch reactor.

The oxidation of phenol exhibits an induction period with very low phenol conversion. This induction period increases as the temperature decreases and it is inversely proportional to oxygen pressure. The reaction proceeds through different intermediate products; the following were identified: hydroquinone, p-benzoquinone, catechol, maleic and oxalic acid.

COD analysis suggests that phenol oxidation takes place involving a free radical mechanism via two routes: (1) directly to carbon dioxide, and (2) through organic intermediates. A reaction pathway is proposed and supported by the good fitting to experimental results of a kinetic model derived from the reaction pathway.

The influence of pH (2–4), Cu(II) concentration ($0\text{--}2.4 \cdot 10^{-3}$ mol/L), oxygen pressure (0.5–1.25 MPa) and temperature (373–413 K) on the reaction kinetics in the constant catalytic activity regime was studied. It was found that reaction rate increases on increasing pH, and reaction orders were 1 on phenol concentration and 0.5 on Cu(II) and oxygen. The activation energy of the reaction was 75 ± 15 kJ/mol.

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1. Introduction

Phenol is a common organic pollutant in industrial wastewaters, such as those from oil refineries (6–500 mg/L), coke ovens

(28–3900 mg/L), coal processing (9–6800 mg/L), and petrochemical industries (2.8–1220 mg/L) [1]. These wastewaters must be treated before being released to the environment, since phenol is considered a priority pollutant, as it is very harmful to organisms even at low concentrations. As a consequence, great attention has been paid to processes for reducing its concentration in aqueous effluents, mainly in the last decades when regulations became tighter. Thus, the European Community Directive 80/778/EEC

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states that the maximum admissible concentration of phenolic compounds in drinking water should be $0.5 \mu\text{g L}^{-1}$ for the total content and $0.1 \mu\text{g L}^{-1}$ for individual contents.

Several methods have been proposed for the abatement of this pollutant: solvent extraction, adsorption, filtration, precipitation, ion exchange, biological treatment and destructive techniques such as ozonation, oxidation and incineration [1]. The economics of these processes, however, limits their use to treating refractory micropollutants, rather than treating highly concentrated waste water streams. Due to this reason, most of the phenol abatement processes that are currently used in the industry are based on chemical oxidation processes, such as the LOPROX process patented by Bayer.

Among the chemical oxidation processes, advanced oxidation processes (AOPs), wet air oxidation (WAO) and supercritical water oxidation (SCWO) are nowadays considered as the most promising ones.

In recent years, the use of hydrogen peroxide as the oxidising agent in the presence of a catalyst has attracted great interest in AOPs. A variety of catalysts containing iron, copper, ruthenium, gold, cerium and manganese un-supported and supported on different materials have been tested [2–11]. However, this technique is commonly used for treating relatively low concentrations of pollutants in water ($\text{COD} < 5 \text{ mg/L}$) because of the high cost of the reactant hydrogen peroxide.

Therefore, WAO and SCWO are nowadays considered as the most attractive alternatives to treat both diluted and concentrated streams (COD between 20 and 200 g/L) [12,13], although both work at high temperature and pressure (398–573 K and 0.5–20 MPa for WAO, and above 647 K and 22.1 MPa for SCWO). WAO seems to be more accepted than SWAO, and the use of catalysts in WAO has arisen as an interesting alternative, since it allows considerable reduction of temperature and pressure.

Several catalysts have been employed for the wet oxidation of phenol. Transition-metal oxides such as CuO [14–17], MnO_2 [18,19], or CoO [20,21], noble metals as Pt and Ru [22–26], and metallic salts as copper nitrate, copper sulphate and manganese sulphate [27,28] have been proposed as homogeneous or heterogeneous catalysts.

Copper oxide was found to be the most active among transition metals oxides. Several authors investigated the influence of temperature on the wet oxidation of phenol, reporting activation energies of 50–77 kJ/mol for the non-catalytic reaction, 57.5–101 kJ/mol for the homogeneously catalysed reaction, and 85 and 85.7 kJ/mol for the heterogeneous catalytic reaction (Table 1).

The studies of WAO using noble metals heterogeneous catalysts reveal a certain tendency to deactivation by poisoning with carbonaceous deposits formed during the oxidation [29–31], while Cybulski and Trawczynski [32] reported that platinum and ruthenium, both supported on mixed silica–titania, exhibit small catalytic activity in WAO of phenol. The discovery of low-cost active, selective and stable catalysts still remains the main drawback for the heterogeneous process.

As a consequence, WAO using non-precious homogeneous catalysts is an attractive alternative to carry out the oxidation of phenol, since most active catalysts are cheap and non-toxic metals. For example, platinum, on a per mole basis, is approximately 4000 times more expensive than nickel and 10,000 times more expensive than iron. Similarly, palladium is 3000 times more expensive than copper, while ruthenium is 2000 times more expensive than iron [33].

To the best of our knowledge, there are no published comprehensive studies on the effect of pH on the homogeneous catalytic oxidation of phenol using copper as catalyst. For example Kolaczowski et al. [12] studied the influence of pH at 2, 4, 8, 10 and >12 on the non-catalytic wet oxidation of phenol and they found that the initial pH has a significant effect on reaction rate. However there was no explanation for this effect, especially under acidic conditions. Wu et al. [28] studied the catalytic wet air oxidation of 1000 mg/L phenol using copper nitrate as homogeneous catalyst at various temperatures (313–333 K), oxygen partial pressures (0.6–1.9 MPa), and copper concentrations (0–13 mg/L). The effect of pH was not studied.

Besides, most works in the literature have been based on global kinetic expressions, rather than on expressions that allow determining the intrinsic kinetic constant and the influence of the operating conditions, which are very useful for the process design and optimization.

The goal of this work is to determine the influence of operating conditions (pH, temperature and concentrations) in the kinetics of phenol oxidation in acidic conditions, working in a batch stirred tank reactor and using copper nitrate as homogeneous catalyst. The importance of the catalysed reaction has been determined and quantified by means of a kinetic model.

2. Experimental

2.1. Materials

Phenol solutions (0.011–0.0467 mol/L) were prepared by mixing phenol (99%, Sigma–Aldrich) and distilled water in adequate proportions. The homogeneous Cu(II) catalyst was obtained by dissolving $\text{Cu(NO}_3)_2 \cdot 5\text{H}_2\text{O}$ (98–103%, Panreac) in distilled water ($0\text{--}2.4 \cdot 10^{-3} \text{ mol/L}$). Several experiments were replicated using Cu chlorides and sulphates, obtaining the same results, and suggesting that counter-anion has not any significant effect on the catalytic performance. pH was kept constant during the reaction using buffer solutions (pH 3, 4) prepared by mixing the following compounds in the required amounts according to the desired pH: Na_2HPO_4 (99%, Panreac), NaH_2PO_4 (99–105%, Panreac) and H_3PO_4 (98%, Panreac).

2.2. Experimental set-up

The experimental equipment consists of a stirred 1 L batch stainless steel autoclave reactor (Autoclave Engineers), connected to a feed vessel, from which phenol is fed to the reactor at the beginning of each experiment. The reactor is surrounded by a temperature-controlled oven; and temperature is measured inside the reactor in the liquid phase. Agitation is accomplished by a propeller consisting of three blades with 20 mm length, set at 650 rpm in all runs, enough for considering perfect mixing. Oxygen is supplied from gas cylinders (99.9%, Praxair) and introduced in the reactor at constant flow rate of 60 mL/min (s.t.p.) using a mass flow controller (Bronkhorst). The gas is dispersed as rising bubbles using a stainless steel mesh as diffuser. The turbulence inside the reactor ensures oxygen concentrations in the aqueous phase close to saturation. Pressure inside the reactor is maintained constant

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

Catalyst	Temperature (K)	Activation energy (kJ/mol)	Reference
None	443–493	67.4	[54]
None	423–453	50	[55]
None	423–573	77	[56]
Cu^{2+}	313–333	101	[28]
Cu^{2+}	353–383	57.5	[57]
$\text{CuO/Al}_2\text{O}_3$	393–433	85	[50]
$\text{CuO/Al}_2\text{O}_3$	393–503	85.7	[16]

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