

Insight into heterogeneous catalytic wet oxidation of phenol over a Ru/TiO₂ catalyst

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Abstract

The kinetics of wet oxidation of phenol over a Ru/TiO₂ catalyst was studied in the temperature range of 175–200 °C, oxygen partial pressure range of 0.34–1.38 MPa and a catalyst loading range of 0.5–1 kg m⁻³ at near neutral conditions (pH ~ 6.5). Also studied was the effectiveness of this catalyst in a strongly alkaline medium (pH > 12). The catalyst used for the purpose was powdered 5% Ru/TiO₂. This heterogeneous catalyst was found to be very effective for oxidation of phenol and the acetic acid formed, at near neutral conditions. However, the amount of acetic acid formed in its presence in a strongly alkaline medium was very high. The effects of the addition of hydroquinone as a free radical initiator and *t*-butanol as a free radical scavenger on wet oxidation of phenol were studied in presence of this catalyst at near neutral conditions and also in a strongly alkaline medium. The rate of reaction was enhanced in the presence of the Pyrex liner which reduces the destruction of free radicals by the reactor wall. Addition of hydroquinone enhanced wet oxidation of phenol which is expected because hydroquinone is known to be a free radical initiator. On the other hand, the presence of *t*-butanol, a free radical scavenger, reduced the rate of degradation of phenol.

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1. Introduction

Chemical, petrochemical, pharmaceutical and coal processing industries often discharge phenolics, viz. phenol, substituted phenols, cresols and naphthols, which are classified as priority pollutants, in a fairly large quantity. These aqueous waste streams containing phenol and its derivatives need to be treated before discharge. However, such toxic and refractory organic pollutants are resistant to conventional biological treatment, especially when present in the wastewater in high concentrations. The water conservation program undertaken in chemical process industries (CPI) is expected to result waste streams exhibiting very high concentration of pollutants resulting in very high chemical oxygen demand (COD) and bio-chemical oxygen demand (BOD). The very high levels of BOD may make bio-treatment unviable.

An effective alternative to biological treatment is wet oxidation. Wet oxidation is a very promising technology in advanced wastewater treatment. Wet oxidation, also known as wet air oxidation, involves sub-critical oxidation of organics and some oxidizable inorganics in the aqueous phase at high temperatures and pressures, typically around

150–325 °C and 0.5–20 MPa, respectively. It also provides a feasible option to incineration, particularly when the waste stream contains phenolics, substituted phenolics and chloro-aromatics [1].

Since wet oxidation is prohibitively expensive, catalytic wet oxidation is often practiced to reduce the severity of the operating conditions required. Various homogeneous and heterogeneous catalysts have been reported for wet oxidation [1–3]. Catalytic wet oxidation using a homogeneous catalyst leads to the presence of metal ions in the effluent from the reactor so that an additional step is necessary to recover these toxic ions. This might have some adverse impact on economics of the wet oxidation process. There is always a trade off between capital and operating cost impact due to reduction in severity of operation and the recovery and recycle cost associated with a homogeneous catalyst. So, at times it is desirable to use a solid catalyst, which is easily recoverable, and eventually reusable and which reduces the severity of the conditions required for oxidation. It was, therefore, decided to find such a heterogeneous catalyst suitable for the treatment of phenol-contaminated wastewater streams. In the present work, phenol was selected as a model refractory pollutant. Maugans and Akgerman [4] have studied wet oxidation of phenol over a Pt/TiO₂ catalyst. The wet oxidation of phenol often results in the formation of low molecular weight

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Nomenclature

A	phenol
B	oxygen
C_A	concentration of phenol in the aqueous phase (kmol m^{-3})
C_B	concentration of oxygen in the bulk liquid phase (kmol m^{-3})
k_1	forward reaction rate constant in Eq. (3) ($(\text{kmol m}^{-3})^{1/2} \text{min}^{-1}$)
k_{-1}	backward reaction rate constant in Eq. (3) ($\text{kmol m}^{-3} \text{min}^{-1}$)
k_2	reaction rate constant in Eq. (4) (min^{-1})
k_3	reaction rate constant in Eq. (5) ($\text{kmol m}^{-3} \text{min}^{-1}$)
k_4	reaction rate constant in Eq. (6)
k_s	surface reaction rate constant in Eq. (1)
K_A	adsorption equilibrium constant for A in Eq. (1)
K_B	adsorption equilibrium constant for B in Eq. (1)
n	stoichiometric coefficient in expression (6)
r	overall rate of reaction ($\text{kmol kg cat}^{-1} \text{min}^{-1}$)
X	active site

carboxylic acids. Acetic acid is very difficult to oxidize to CO_2 and H_2O . As a result, the destruction of phenol by wet oxidation results in a stream exhibiting finite COD due to the presence of low molecular weight acids. In contrast to platinum, ruthenium is an active metal for oxidation of acetic acid in an aqueous medium, particularly when it is supported on carbon or graphite [5]. Moreover, ruthenium is cheaper than platinum. Wet oxidation of phenol has also been studied in the presence of Ru/CeO₂ [6]. Previous studies carried out by Beziat et al. [7] indicate a high stability of the titania supported ruthenium catalyst, when used in an acidic and oxidizing medium for oxidation of aqueous solutions of carboxylic acids. Bearing this in mind, a ruthenium catalyst supported on titania was selected for the present studies.

Since wet oxidation is a free radical assisted process, it is expected that the addition of a free radical initiator will increase the overall rate of reaction. Likewise, the presence of a free radical scavenger will inevitably have an adverse effect on the rate of oxidation. The waste, at times, may have free radical generators or scavengers depending upon its origin. There is scanty information available in the published literature on this aspect. Recently, Vaidya and Mahajani [8] have studied how the free radical generator and scavenger affect wet oxidation of phenol in the presence and absence of homogeneous catalyst. So, it would be worth investigating the effects of the presence of a free radical initiator and a scavenger on the course of wet oxidation, especially in presence of a heterogeneous catalyst. These studies would enable a thorough insight into heterogeneous catalytic wet oxidation.

In the present investigation, catalytic wet oxidation of phenol was studied over a 5% Ru/TiO₂ catalyst at near neutral conditions (pH ~ 6.5). Also studied was the influence

that the initial pH has on the performance of this catalyst. Attempts were made to develop kinetic rate expressions for the destruction of phenol. The effects of the addition of hydroquinone as a free radical initiator and *t*-butanol as a free radical scavenger on wet oxidation of phenol were studied in presence of this catalyst at near neutral conditions and also in a strongly alkaline medium.

2. Experimental

2.1. Materials and catalyst preparation

Phenol and all other reagents used for COD analysis were of analytical reagent grade and were purchased from s.d. Fine Chemicals, Mumbai, India. Ruthenium trichloride trihydrate (pure) was obtained from SISCO Research Laboratories, Mumbai. High surface area titania (Degussa, Germany) was used as a support. Oxygen from a cylinder with a minimum stated purity of 99.5% was obtained from Industrial Oxygen Company Ltd., India, and was used for oxidation. All water used in experimentation and cleaning was distilled.

In order to prepare the 5% Ru/TiO₂ catalyst, an aqueous solution containing an appropriate amount of ruthenium trichloride trihydrate ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$) in deionized water was rapidly contacted with the finely divided titania support and the slurry was stirred for an hour at room temperature. This provided the degree of intimate contact between species that was desired. The slurry was then contacted with an aqueous solution of sodium hydroxide to precipitate ruthenium as a hydroxide. It was then stirred again and heated at 60 °C for 1 h. After settling, the top aqueous layer was separated from the precipitate below. Deionized water was then added to the precipitate and this solution was then allowed to digest at 80 °C for an hour to provide homogeneity to the catalyst. After about an hour, excess of formaldehyde and an additional amount of sodium hydroxide were added to the mixture to ensure the completion of reduction and heating at 80 °C was continued for another hour. This was followed by cooling, filtration, washing and drying. A silver nitrate solution was used to ascertain the absence of Cl^- ions. The main characteristics of this catalyst are listed in Table 1. The characterization was conducted in a BET apparatus (Micromeritics Model ASAP 2010). The particle size range was determined by using a particle size analyzer (Coulter LS 230).

Table 1
Characteristics of the heterogeneous catalyst Ru/TiO₂

BET surface area ($\text{m}^2 \text{g}^{-1}$)	58.3
External surface area ($\text{m}^2 \text{g}^{-1}$)	59.9
Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	0.001
Average pore diameter (Å)	333.2
Particle size range (μm)	7–60
Mean diameter (μm)	30.2

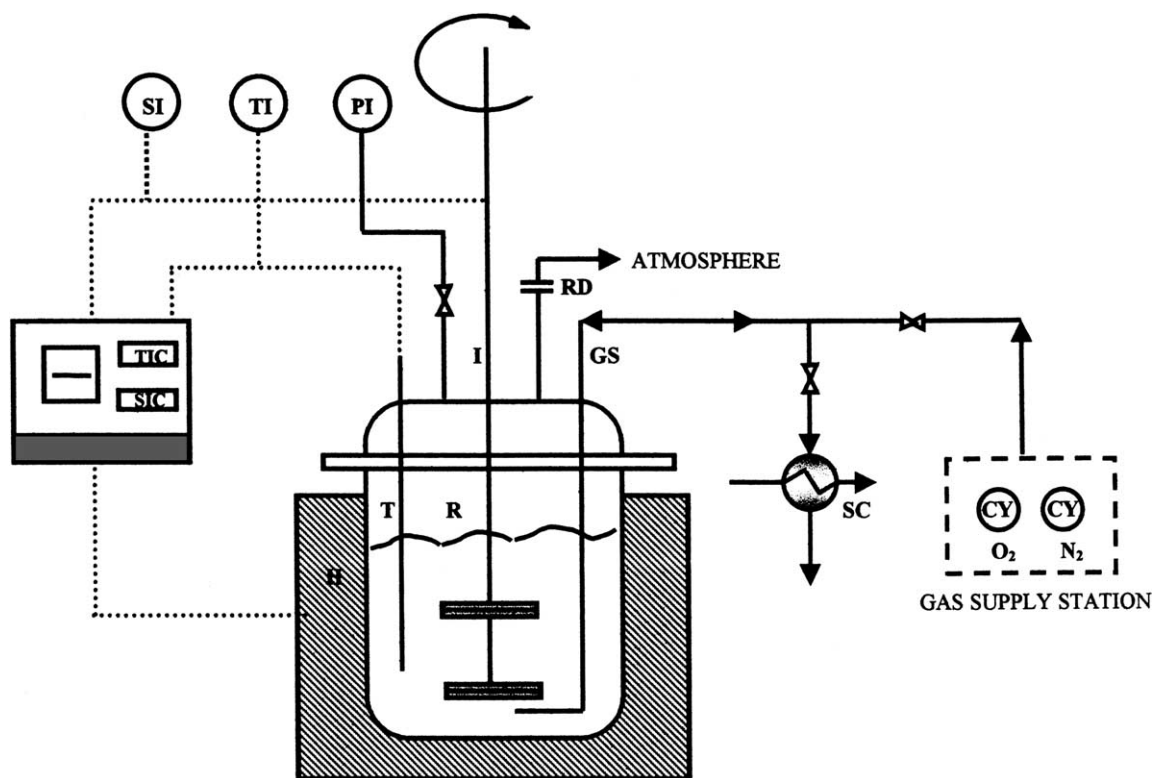


Fig. 1. Schematic diagram of experimental set-up for wet oxidation: PI, pressure indicator; TI, temperature indicator; SI, speed indicator; R, reaction vessel/autoclave; T, thermocouple; H, electric heater; RD, rupture disk; I, impeller; GS, gas sparger; SC, sample condenser; CY, gas cylinder.

2.2. Experimental set-up

Phenol was oxidized in an SS-316 Parr high pressure reactor of capacity 0.3 dm^3 . The reactor was equipped with an electrically heated jacket, a turbine agitator and a variable speed magnetic drive. The temperature and the speed of agitation were controlled by means of a Parr 4842 controller. The gas inlet, gas release valve, cooling water feed line, pressure gauge and rupture disk were situated on top of the reaction vessel. The liquid sample line and the thermocouple well were immersed in the reaction mixture. A chilled water condenser was fitted on the sample valve exit line to avoid flashing of the sample. The reactor was also provided with a cooling coil. A schematic diagram of the experimental set-up is shown in Fig. 1.

2.3. Experimental procedure

The reactor was first charged with 0.15 dm^3 of an aqueous solution of phenol and a predetermined amount of the catalyst. The catalyst concentration was maintained at 0.5 kg m^{-3} , unless stated otherwise. The reactor was then purged with nitrogen, prior to the start of the experiment to ensure an inert atmosphere inside the reactor. All the lines were closed. The speed of agitation was adjusted to a pre-determined value. The reaction temperature was set. The reactor contents were heated to the desired temperature and a

sample was withdrawn. This was considered 'zero' time for the reaction. Oxygen from the cylinder was then sparged into the liquid phase directly beneath the impeller to attain the desired partial pressure of oxygen. The wet oxidation reaction being exothermic, the temperature increased and it was maintained constant by means of cooling water. The amount of oxygen was far in excess than that theoretically required. Samples were withdrawn periodically after sufficient flushing of the sample line. The consumption of oxygen due to reaction as well as due to small sampling led to decrease in the total pressure as indicated on the pressure gauge. So more oxygen was charged intermittently from the cylinder through manually operated control valve to make up for that consumed during the reaction, thus maintaining a constant total pressure. The entire system was in batch mode. In some typical experiments, sodium hydroxide was added to the feed solution to adjust its pH. Some experiments were conducted in a vessel wherein a glass liner was placed inside the reactor to eliminate the destruction of free radicals by the reactor wall.

3. Product analysis

The standard dichromate reflux method was used for COD analysis [9].

In order to detect acetic acid formed as an intermediate, if at all, during wet oxidation of phenol over Ru/TiO₂,

samples of the reaction mixture withdrawn at preset reaction times were analyzed by gas chromatography (GC instrument used: Chemito 3865, Toshniwal Instruments India). A glass column (Carbopack BD-A 4% and Carbowax 20 M, length 2 m, diameter 0.63 cm) was used for the purpose in the flame ionization detector (FID) mode of operation.

High performance liquid chromatography (HPLC, TOSOH Instruments) using a UV-8010 detector set at a wavelength of 230 nm determined the residual phenol concentration with the help of an RP 18 (Merck) HPLC column. A mixture of methanol (50%) and deionized water (50%) was used as the mobile phase at a flow rate of 1 ml min^{-1} . The use of HPLC technique also facilitated the identification of a number of reaction intermediates. Hydroquinone, maleic acid, oxalic acid and propionic acid were among the various intermediates identified.

The error in all experimental measurements was less than 3%.

4. Results and discussion

Heterogeneously catalyzed wet oxidation of phenol is a complex reaction involving gas–liquid–solid phase operation. The following steps are involved in series when a gas–liquid reaction occurs in the presence of solid particles as a catalyst:

- Transfer of the solute gas oxygen from the bulk of the gas phase to the gas–liquid interface (gas phase mass transfer).
- Instantaneous saturation of the interface with oxygen.
- Diffusion of the solute gas through the gas–liquid interface to the bulk of the liquid (liquid-phase mass transfer).
- Transfer of the solute gas to the external surface of the catalyst particle (liquid–solid mass transfer).
- Transfer of the reactant in the liquid phase to the external surface of the catalyst particle.
- Intra-particle diffusion followed by chemical reaction at the active centers.
- Diffusion of the products like CO_2 and H_2O back into the bulk of the liquid and finally desorption of CO_2 from the bulk of the liquid to the gas phase.

Doraiswamy and Sharma [10] have presented an excellent account of insight into such gas–liquid–solid operation known as slurry reactor (if solid catalyst is suspended) or trickle bed reactor (solid catalyst is confined to a bed). Owing to the high diffusivity of oxygen in the gas phase and its low solubility in water, the gas phase mass transfer resistance was estimated to be negligible. The intensity of turbulence in the liquid phase would then decide the extent of resistance offered to the liquid-phase mass transfer and the transfer of phenol and dissolved oxygen in the liquid phase to the external surface of the catalyst particle.

The following assumptions were made while studying heterogeneous catalytic wet oxidation of phenol:

1. The mechanical agitation was sufficient to maintain the solid particles in the suspension. No settling of the solid particles occurred and the entire surface area was available for chemical reaction. This was observed at room temperature in a glass reactor having a similar intensity of turbulence in the bulk liquid phase.
2. Desorption of the products offered no resistance.

The kinetics of wet oxidation of phenol was studied in the presence of the heterogeneous catalyst Ru/TiO_2 . Experiments were performed over a range of temperature, pressure and catalyst loading. Samples were analyzed for phenol as well as for COD content in order to determine and hence present a model for the phenol degradation rate. This is expected to aid design of a commercial contactor.

4.1. Mass transfer considerations

The effect of speed of agitation on the rate of reaction was studied in the range of 5–20 rps at 200°C , 0.69 MPa oxygen partial pressure and a catalyst loading of 1 kg m^{-3} . The initial phenol concentration, viz. $8.9 \times 10^{-3} \text{ kmol m}^{-3}$ and the reaction time were the same in all experiments. It was observed that the rate of destruction of COD (and phenol) was independent of the speed of agitation above an impeller speed of 15 rps, thus indicating the absence of resistance to mass transfer of oxygen in the liquid phase and from the liquid to the solid surface. In order to ascertain the absence of pore diffusion, the catalyst was sieved carefully and experiments were performed with two particle sizes in the range 25–60 and 150–210 μm at 200°C , 0.69 MPa oxygen partial pressure and a catalyst loading of 1 kg m^{-3} . The reduction in COD and phenol was monitored with respect to time. It was observed that there was no effect of the size of the catalyst particles on the rate of reaction, thereby indicating the effectiveness factor to be unity. From the foregoing, it was concluded that it was possible to ascertain true kinetics from experimental data. All further experiments were carried out at an impeller speed of 20 rps.

4.2. Effect of temperature

Experiments were conducted at 175, 185 and 200°C at 0.69 MPa oxygen partial pressure with a catalyst loading of 0.5 kg m^{-3} to study the effect of temperature with results presented in Fig. 2. In all these experiments, the initial COD was 2 kg m^{-3} . The reaction proceeded rather slowly at 175°C . However, at 200°C , phenol degradation was complete and COD removal was around 94% at the end of an hour. Thus, an increase in temperature significantly increased the rate of reaction.

4.3. Effect of oxygen partial pressure

The effect of oxygen partial pressure on the catalyst performance was studied over the range of oxygen partial

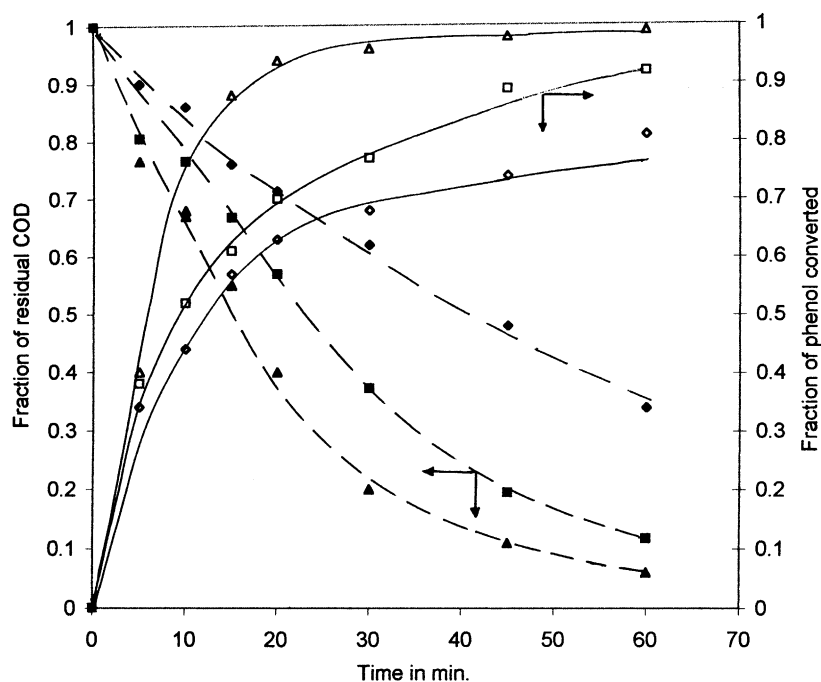


Fig. 2. Effect of temperature (O_2 pressure 0.69 MPa, initial COD 2 kg m^{-3} , initial pH 6.5, catalyst loading 0.5 kg m^{-3}): (◆) fraction of residual COD at 175°C ; (■) fraction of residual COD at 185°C ; (▲) fraction of residual COD 200°C ; (◇) fraction of phenol converted at 175°C ; (□) fraction of phenol converted at 185°C ; (△) fraction of phenol converted at 200°C .

pressures 0.34–1.38 MPa at 185°C using a catalyst loading of 0.5 kg m^{-3} . The results are shown in Fig. 3. These results indicated that the rate of reaction increased with an increase in the oxygen partial pressure.

4.4. Effect of catalyst loading

It was expected that the catalyst loading would have a positive effect on the rate of reaction. Experiments were

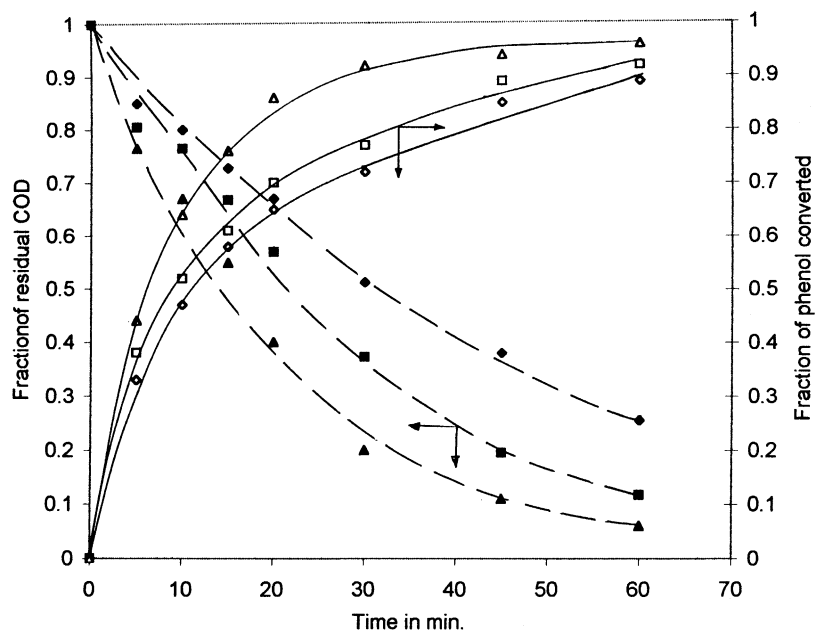


Fig. 3. Effect of O_2 pressure (185°C , initial COD 2 kg m^{-3} , initial pH 6.5, catalyst loading 0.5 kg m^{-3}): (■) fraction of residual COD at 0.69 MPa; (▲) fraction of residual COD at 1.38 MPa; (◇) fraction of phenol converted at 0.34 MPa; (□) fraction of phenol converted at 0.69 MPa; (◆) fraction of residual COD at 0.34 MPa; (△) fraction of phenol converted at 1.38 MPa.

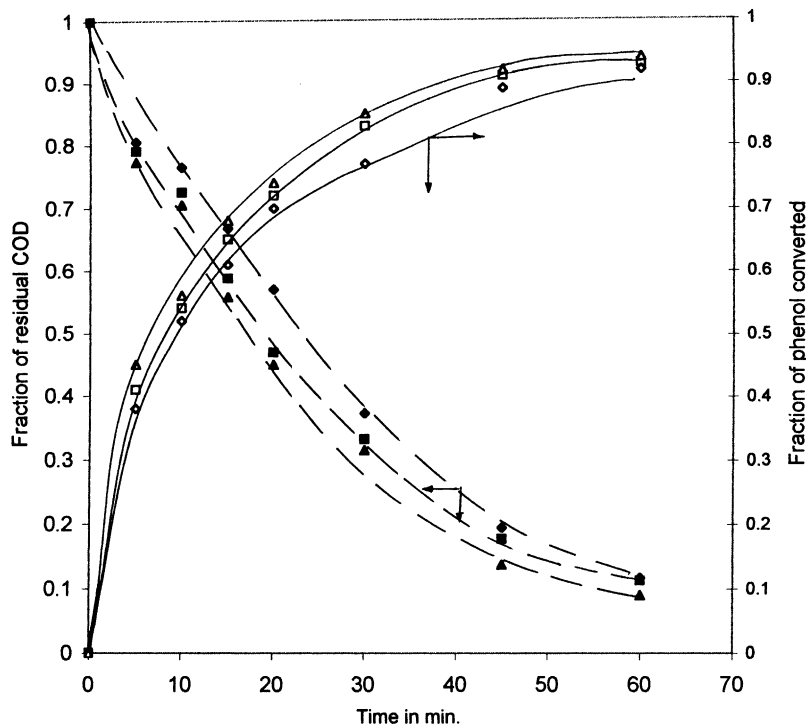


Fig. 4. Effect of catalyst loading (185 °C, system pressure 1.79 MPa, O₂ pressure 0.69 MPa, initial COD 2 kg m⁻³, initial pH 6.5): (◆) fraction of residual COD at 0.5 g/l; (■) fraction of residual COD at 0.75 g/l; (▲) fraction of residual COD at 1 g/l; (◇) fraction of phenol converted at 0.5 g/l; (□) fraction of phenol converted at 0.75 g/l; (△) fraction of phenol converted at 1 g/l.

performed with no catalyst as well as with 0.5, 0.75 and 1 kg m⁻³ of catalyst concentration, at 185 °C and 0.69 MPa oxygen pressure with results for both COD and phenol degradation shown in Fig. 4. Catalyst loading results indicated that the presence of the catalyst significantly increased the rate of reaction. As expected, the rate increased with the amount of catalyst achieving complete phenol degradation rapidly. The enhancement in the rate of COD reduction in presence of this catalyst was even more pronounced at a temperature of 200 °C as shown in Fig. 5.

4.5. Kinetic model for phenol oxidation

An attempt was made to develop a kinetic rate expression for heterogeneous catalytic wet oxidation of phenol. The disappearance of phenol was monitored which was of interest from environmental engineering point of view as phenol is considered to be one of the priority pollutants. Non-catalytic wet oxidation of phenol might have been significant under the conditions employed for this study. So, strictly speaking, the rates of reaction for non-catalytic wet oxidation need to be subtracted from those observed in the presence of the catalyst in order to highlight the true effect of the catalyst on the rate of reaction. However, TiO₂ crystal lattice when excited might donate its oxygen for reaction with adsorbed phenol and itself get re-oxidized by molecular oxygen from solution. Maugans and Akgerman [4] in their studies on wet oxidation of phenol over a Pt/TiO₂ catalyst have explored such

a mechanism. Alternatively, a mechanism which involves surface reaction between adsorbed phenol and adsorbed oxygen as the rate controlling step might be prevailing. So, in the presence of this catalyst, it is difficult to compute a

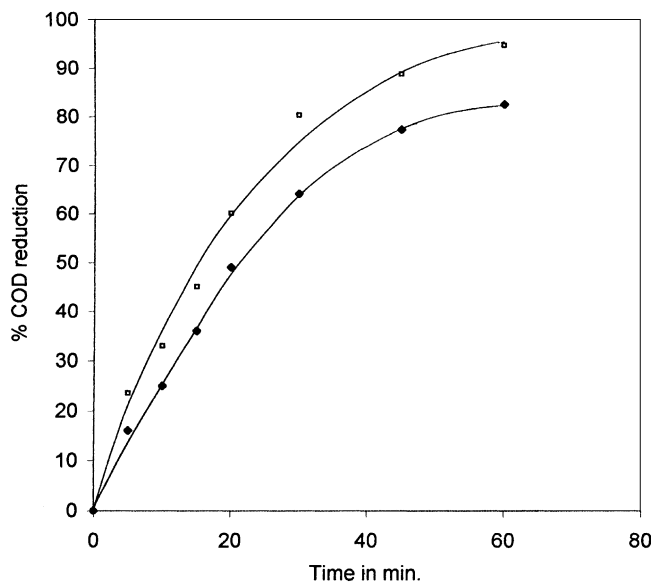


Fig. 5. Effect of the presence of catalyst Ru/TiO₂ on percentage of COD reduction (200 °C, system pressure 2.27 MPa, O₂ pressure 0.69 MPa, initial COD 2 kg m⁻³, initial pH 6.5, catalyst concentration 0.5 kg m⁻³): (◆) without catalyst; (□) with catalyst.

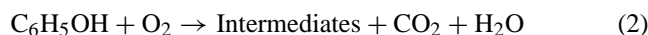
true measure of the role of oxygen from solution in the completion of reaction. We do not know which possibility prevails and hence we have refrained ourselves from separating the effects of catalytic and non-catalytic wet oxidation.

When a simple power law model was fitted, the order with respect to oxygen was observed to be 0.5 indicating adsorption of oxygen by dissociative way. As mentioned earlier, assuming that both phenol and oxygen are adsorbed on the same type of active sites and that surface reaction between adsorbed phenol and adsorbed oxygen is the rate controlling step, the following rate expression is obtained:

$$r = \frac{K_A K_B^{1/2} k_s C_A C_B^{1/2}}{(1 + K_A C_A + K_B^{1/2} C_B^{1/2})^2} \quad (1)$$

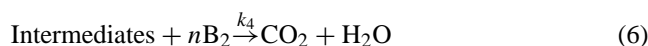
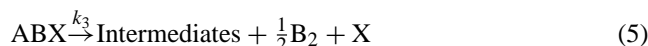
Pintar and Levec [11] have studied wet oxidation of phenol in the presence of a catalyst comprising of supported copper, zinc and cobalt oxides and have proposed a model where the rate determining step was the surface reaction between adsorbed phenol and adsorbed oxygen. Maugans and Akgerman [4] also have studied a similar model for the degradation of phenol in presence of the heterogeneous catalyst Pt/TiO₂.

However, statistical analysis of the experimental data generated using Eq. (1) proved to be unsatisfactory. So an alternative mechanism was suggested in which phenol in the liquid phase reacts with dissociatively adsorbed oxygen to form a complex. This complex is decomposed further to form intermediates which react with oxygen to form CO₂ and H₂O. As per this mechanism, the following series of steps was proposed for the overall reaction and the mechanistic treatment presented here follows that by Smith [12]:



- Reversible adsorption of oxygen by a dissociative mechanism forming an oxidized site on the surface of the catalyst.
- Reaction of this oxidized site with phenol in the liquid phase to form a complex.
- Decomposition of this complex into intermediate products, according to a rate constant k_3 .
- Further reaction with more oxygen to give CO₂ and H₂O.

If A and B denote phenol and oxygen, respectively, the individual reactions according to this mechanism are:



The decomposition of the complex ABX formed into intermediates was considered to be the rate determining step

(expression (5)). Applying stationary state hypothesis to the complexes BX and ABX, the overall rate of the reaction could be expressed as

$$r = \frac{k_1 k_2 C_A C_B^{1/2}}{k_{-1} + k_2 C_A + k_1 C_B^{1/2} + k_1 k_2 C_A C_B^{1/2} / k_3} \quad (7)$$

Evaluation of this model resulted in a better fit of the experimental data when compared to the model discussed earlier. Moreover, plots of $C_B^{1/2}/r$ vs. $1/C_A$ at various temperatures and constant oxygen concentration were linear as shown in Fig. 6. These were of the form

$$\frac{C_B^{1/2}}{r} = a \left(\frac{1}{C_A} \right) + b \quad (8)$$

where a and b denote the slopes and intercepts at various temperatures, respectively. Eq. (8) can be rearranged as

$$r = \frac{(1/a)C_A C_B^{1/2}}{1 + (b/a)C_A} \quad (9)$$

Since oxygen was in excess (about three times) and pressure was constant, C_B was constant. The value of C_B can be determined from a knowledge of oxygen solubility at these conditions. Moreover, at any given temperature, the individual rate constants in Eq. (7) are constant. So, Eq. (7) can be simplified to a type similar to Eq. (9). Since Eq. (9) correctly correlates with the experimental data, the model represented by Eq. (7) stands validated. The values of various rate constants in Eq. (7) obtained at 185 °C by using non-linear regression analysis [13] and the 95% confidence intervals are as reported in Table 2. A comparison of the phenol concentrations predicted by this model and those observed is as in Fig. 7.

4.6. Insight into heterogeneous catalytic wet oxidation of phenol

4.6.1. Effect of Pyrex liner

The role of the metal walls of the reactor in the termination of free radicals, which promote oxidation was studied in the presence of heterogeneous catalyst Ru/TiO₂. For this purpose, an experiment was conducted at 175 °C in a glass-lined vessel placed inside the reactor. The rate of reaction was enhanced in the presence of the Pyrex liner. It is well known that hydrogen peroxide is formed during wet oxidation of phenol. The increase in the rate of reaction could be possibly due to the fact that in the presence of the liner, the metal walls of the reactor (SS 316) did not destroy the free radicals. These free radicals, in turn, participated in the reaction, thereby increasing its rate. Kolaczowski et al. [14] have studied non-catalytic wet oxidation of phenol in a glass-lined vessel placed inside the reactor and have observed similar results. The conclusion here is that the material of construction of the reactor influences the overall rate of reaction even in heterogeneously catalyzed reaction (may

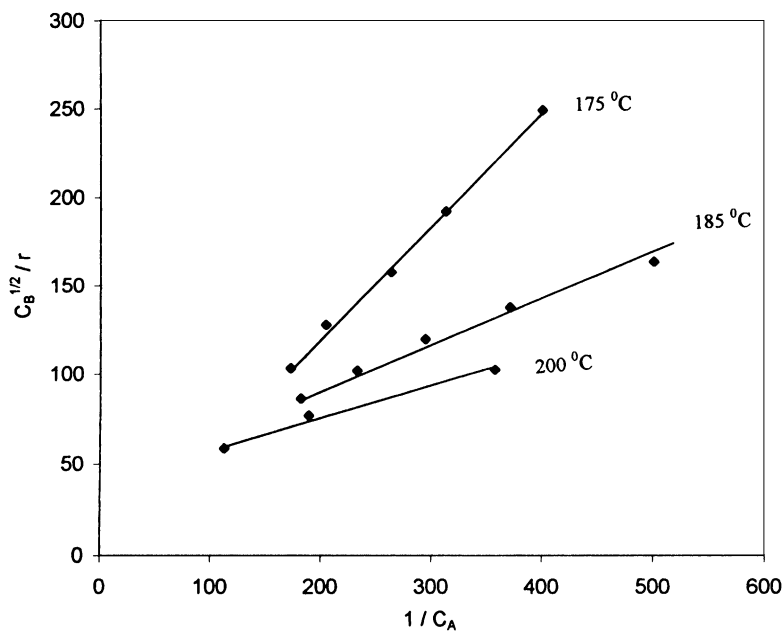


Fig. 6. Plots of $C_B^{1/2}/r$ vs. $1/C_A$ at various temperatures (O_2 pressure 0.69 MPa, initial COD 2 kg m^{-3} , initial pH 6.5, catalyst loading 0.5 kg m^{-3}).

Table 2

Parameters in expression (7) at 185°C with 95% confidence intervals (O_2 pressure 0.69 MPa, initial phenol concentration $8.9 \times 10^{-3} \text{ kmol m}^{-3}$, initial COD 2 kg m^{-3} , initial pH ~ 6.5 , catalyst loading 0.5 kg m^{-3})

k_1 ($\text{kmol m}^{-3})^{1/2} \text{ min}^{-1}$)	k_2 (min^{-1})	k_3 ($\text{kmol m}^{-3} \text{ min}^{-1}$)	k_{-1} ($\text{kmol m}^{-3} \text{ min}^{-1}$)
10 ± 23.35	$2.08 \times 10^{-1} \pm 7.17 \times 10^{-2}$	$7.58 \times 10^{-3} \pm 2.18 \times 10^{-3}$	$2 \times 10^{-2} \pm 3 \times 10^{-3}$

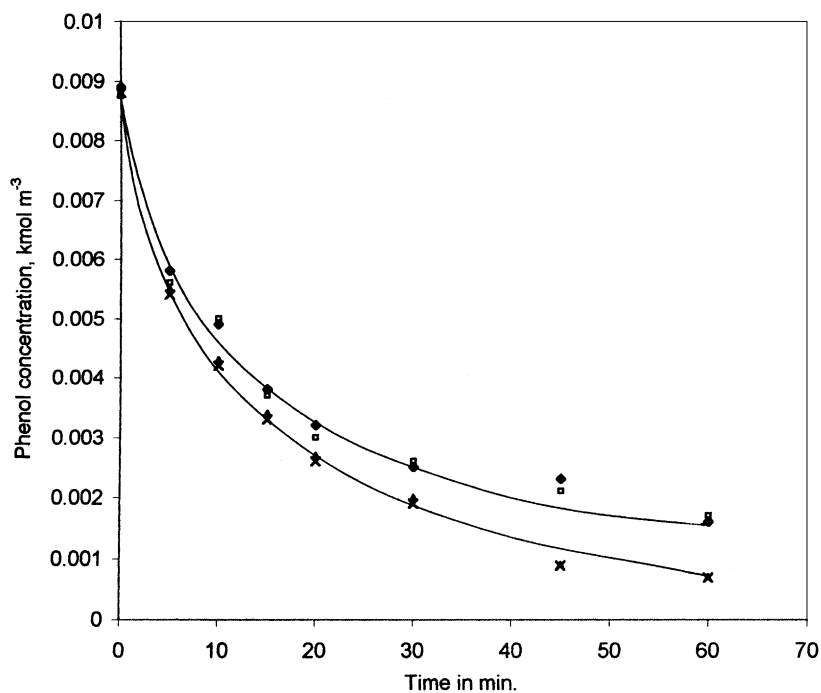


Fig. 7. Phenol concentration vs. time at various temperatures: experimental vs. predicted values (expression (7)) (O_2 pressure 0.69 MPa, initial COD 2 kg m^{-3} , initial pH 6.5, catalyst loading 0.5 kg m^{-3}): (◆) 175°C , experimental; (□) 175°C , predicted; (▲) 185°C , experimental; (×) 185°C , predicted.

be homogeneous and heterogeneous reactions operating in parallel).

4.6.2. Effect of the free radical initiator, hydroquinone

Heterogeneous catalytic wet oxidation of phenol was studied in the presence of the free radical initiator hydroquinone at a concentration of $3.63 \times 10^{-4} \text{ kmol m}^{-3}$ at 175°C . Addition of hydroquinone even in such trace amounts enhanced the rate of reaction.

4.6.3. Effect of the radical scavenger, *t*-butanol

In order to study the influence of the free radical scavenger *t*-butanol on catalytic wet oxidation of phenol, an experiment was performed in the presence of $5.4 \times 10^{-3} \text{ kmol m}^{-3}$ of *t*-butanol at 175°C . Even in the presence of heterogeneous catalyst, the presence of *t*-butanol reduced the rate of degradation of phenol. Stoffler and Luft [15] in their studies on wet oxidation of *p*-toluenesulfonic acid in the presence of *t*-butanol obtained similar results.

All these results are presented in Fig. 8.

4.6.4. Influence of pH

The influence of pH on heterogeneous catalytic liquid-phase oxidation of aqueous phenol was determined in a series of runs performed at an initial pH greater than 12.

Variation in pH value was achieved by adding sodium hydroxide to the feed solution. The effectiveness of this catalyst in a strongly alkaline medium was evident from the enhanced rates of reaction in its presence at 200°C . The results are as shown in Fig. 9.

Catalytic wet oxidation of phenol using heterogeneous Ru/TiO₂ was studied in the temperature range of $175\text{--}200^\circ\text{C}$, oxygen partial pressure range of $0.41\text{--}0.96 \text{ MPa}$ and a catalyst loading $0.25\text{--}0.75 \text{ kg m}^{-3}$ in a strongly alkaline medium. The effects of temperature, oxygen partial pressure and catalyst loading on COD reduction are shown in Figs. 10–12, respectively. It was observed that as temperature, oxygen partial pressure and catalyst loading increased, reduction in COD also increased. For a catalyst loading of 0.5 kg m^{-3} , a maximum COD reduction of 90% was achieved at 200°C in 1 h. In all these experiments, the degradation of phenol was rapid.

Experiments were performed at 175°C at 0.69 MPa oxygen partial pressure with a catalyst loading of 0.5 kg m^{-3} at a pH greater than 12 to study the effects of a Pyrex liner, the free radical initiator hydroquinone and the radical scavenger *t*-butanol on the rates of oxidation. As seen earlier, the rate of reaction was enhanced in presence of the glass-lined vessel and hydroquinone. However, the reaction proceeded rather slowly in the presence of *t*-butanol. About 62% COD

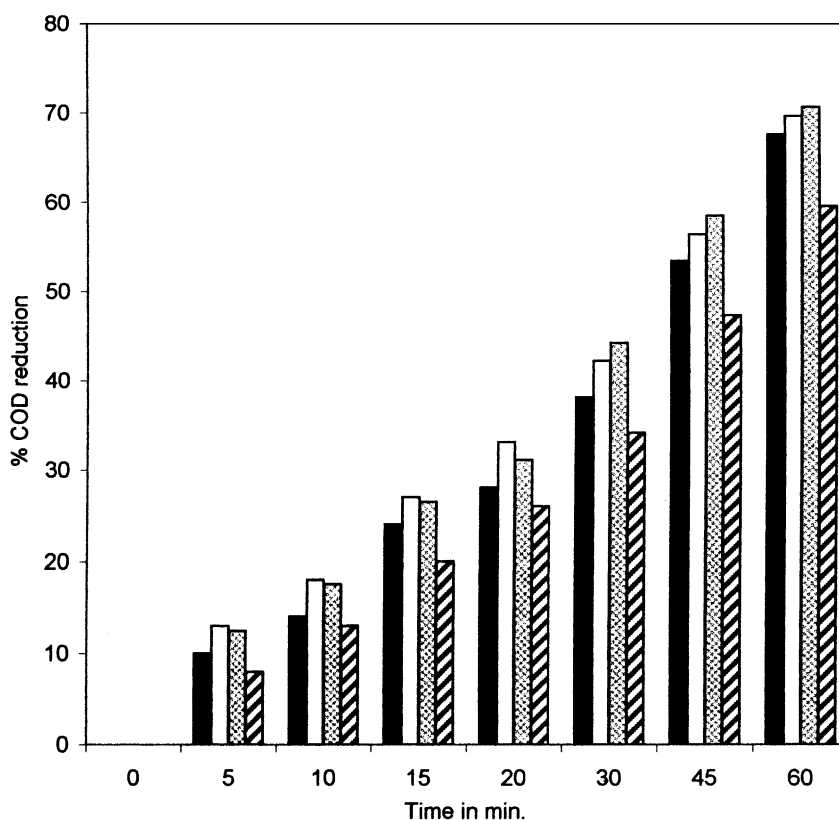


Fig. 8. Effect of Pyrex liner, hydroquinone and *t*-butanol on percentage of COD reduction in the presence of Ru/TiO₂ catalyst (175°C , system pressure 1.58 MPa , O₂ pressure 0.69 MPa , initial COD 2 kg m^{-3} , initial pH 6.5, catalyst loading 0.5 kg m^{-3}): (■) 175°C ; (□) Pyrex liner; (▨) hydroquinone; (▩) *t*-butanol.

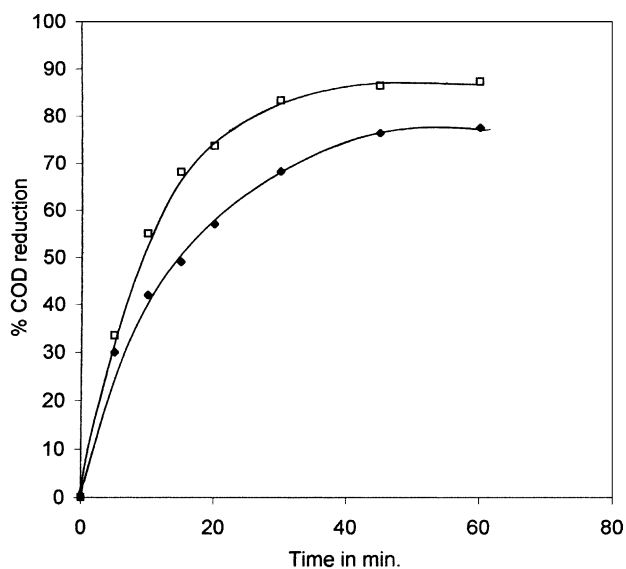


Fig. 9. Effect of the presence of the catalyst Ru/TiO₂ on the percentage of COD reduction in a strongly alkaline medium (200 °C, system pressure 2.27 MPa, O₂ pressure 0.69 MPa, initial COD 2 kg m⁻³, initial pH > 12, catalyst loading 0.5 kg m⁻³): (◆) without catalyst; (□) with catalyst.

reduction was achieved in 1 h in its presence. The results are as shown in Fig. 13.

To summarize, the results indicate that phenol conversion is markedly affected by pH in the presence of the catalyst Ru/TiO₂.

4.6.5. Reaction intermediates

GC analysis indicated that trace amounts of acetic acid were formed in the presence of heterogeneous catalyst Ru/TiO₂. The phenol concentration was determined by HPLC. The various other products identified by HPLC included hydroquinone, maleic acid, propionic acid and oxalic acid. For an experiment completed at 185 °C with a catalyst concentration of 1 kg m⁻³ at near neutral conditions, a maleic acid concentration of 1.3×10^{-4} kmol m⁻³ was observed at the end of 15 min. However, other acids were detected only in trace amounts.

In a strongly alkaline medium, a different distribution of reaction intermediates was observed. In this case, the concentration of maleic acid was much lower in comparison to that observed at near neutral conditions. However, oxalic acid (oxalate) was formed in large amounts. Moreover, at this pH, the yield of acetic acid (acetate) was substantially higher. A comparison of the amounts of acetic acid formed in the absence and presence of this catalyst at 200 °C in a strongly alkaline medium and at near neutral conditions is presented in Fig. 14. The presence of alkali is known to stabilize acids formed as sodium salts thereby increasing byproduct acids. It is interesting to note that uncatalyzed wet oxidation of organic substrates proceeds slowly under strongly alkaline conditions due to less stability of hydroxyl radicals. However, while using Ru/TiO₂ catalyst, the rates of destruction have been enhanced under alkaline conditions. For alkaline conditions, the support TiO₂ is obviously preferred to other supports such as Al₂O₃ and SiO₂ due to their

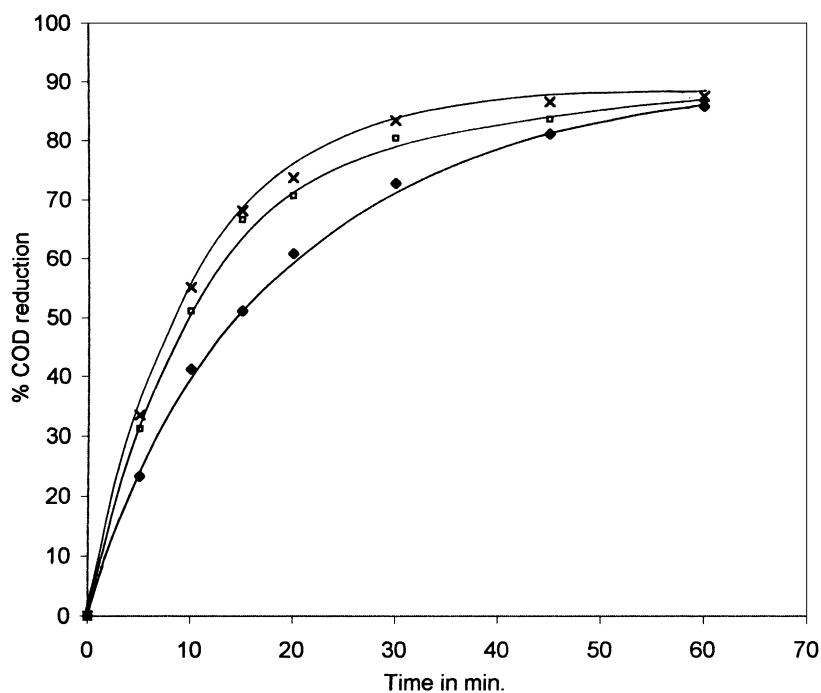


Fig. 10. Effect of temperature on COD reduction (O₂ pressure 0.69 MPa, initial COD 2 kg m⁻³, initial pH > 12, catalyst loading 0.5 kg m⁻³): (◆) 175 °C; (□) 185 °C; (×) 200 °C.

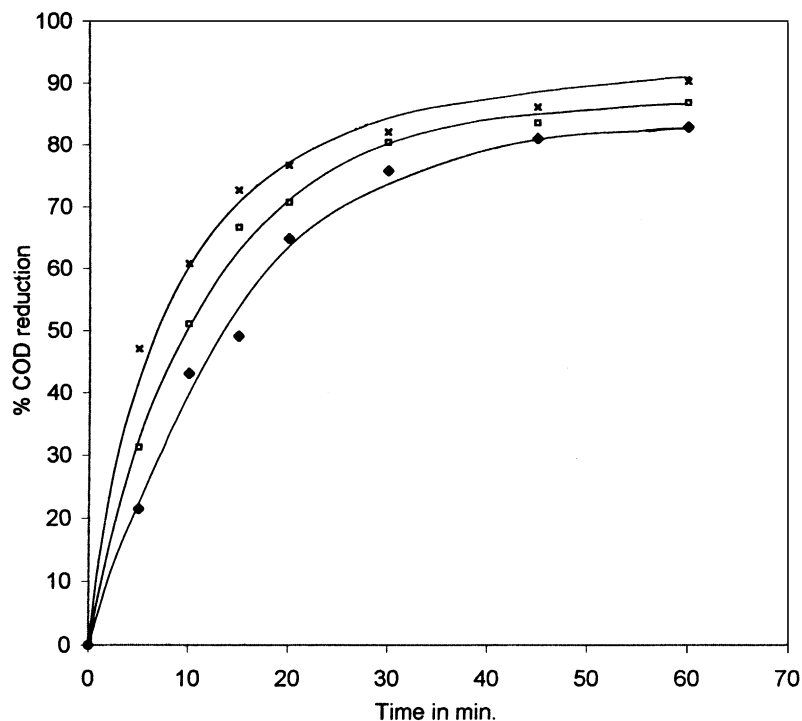


Fig. 11. Effect of O_2 pressure on COD reduction ($185^\circ C$, initial COD 2 kg m^{-3} , initial pH > 12 , catalyst loading 0.5 kg m^{-3}): (\blacklozenge) 0.41 MPa ; (\square) 0.69 MPa ; (\times) 0.96 MPa .

possible interaction with alkali under elevated temperature conditions.

When pH of the reaction medium was greater than 12, the presence of hydroquinone significantly increased the forma-

tion of acetic acid. Hydroquinone, being a free radical initiator, the reaction mechanism might be altered in its presence. We postulate that adsorption of hydroquinone on active sites might be responsible for more acetic acid formation. The

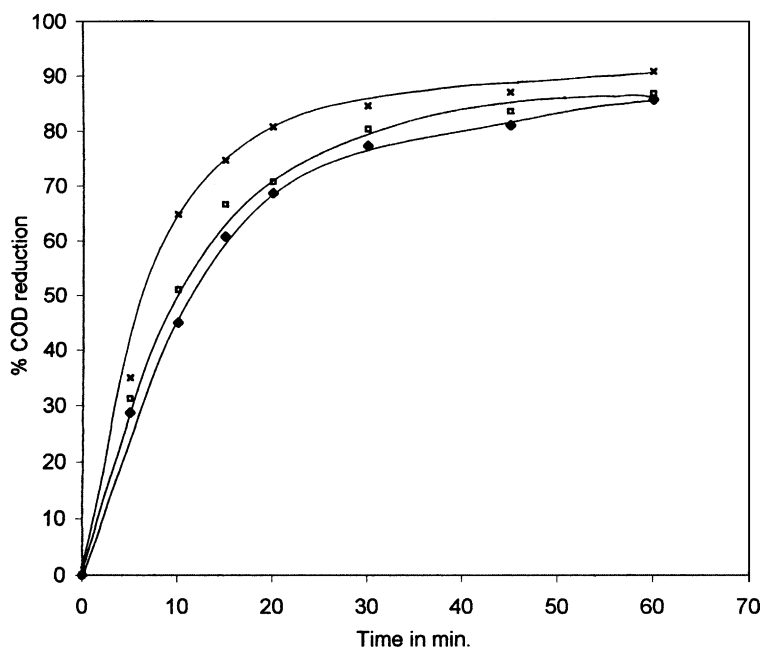


Fig. 12. Effect of catalyst loading on COD reduction ($185^\circ C$, system pressure 1.79 MPa , O_2 pressure 0.69 MPa , initial COD 2 kg m^{-3} , initial pH > 12): (\blacklozenge) 0.25 g/l ; (\square) 0.5 g/l ; (\times) 0.75 g/l .

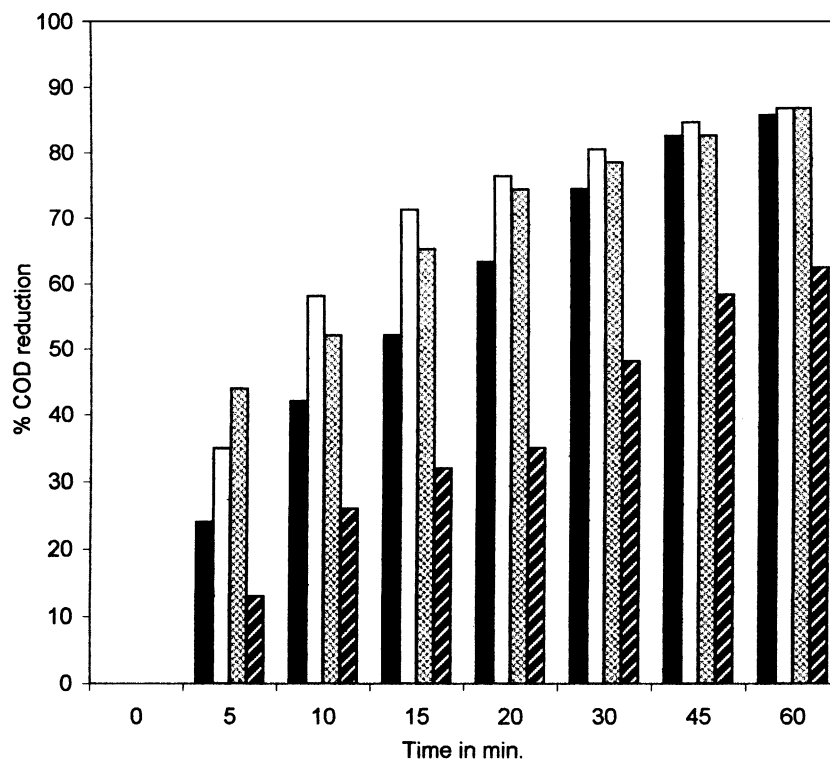


Fig. 13. Effect of Pyrex liner, hydroquinone and *t*-butanol on the percentage of COD reduction in a strongly alkaline medium (175 °C, system pressure 1.58 MPa, O₂ pressure 0.69 MPa, initial COD 2 kg m⁻³, initial pH > 12, catalyst loading 0.5 kg m⁻³): (■) 175 °C; (□) Pyrex liner; (▨) hydroquinone; (▩) *t*-butanol.

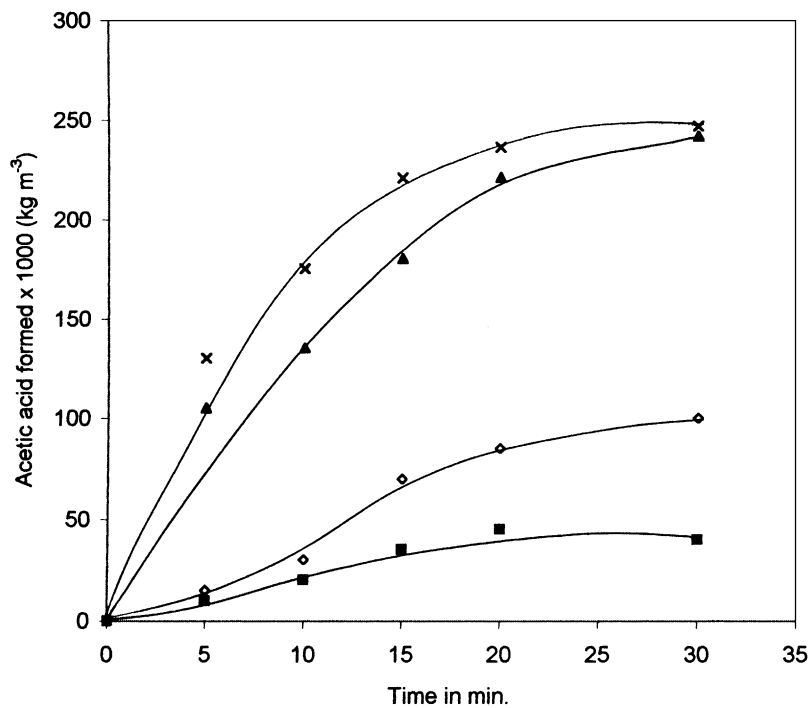


Fig. 14. Effect of pH on acetic acid formation (200 °C, system pressure 2.27 MPa, O₂ pressure 0.69 MPa, initial COD 2 kg m⁻³, catalyst loading 0.5 kg m⁻³): (◇) without catalyst at pH 6.5; (■) with catalyst at pH 6.5; (▲) without catalyst at pH > 12; (×) with catalyst at pH > 12.

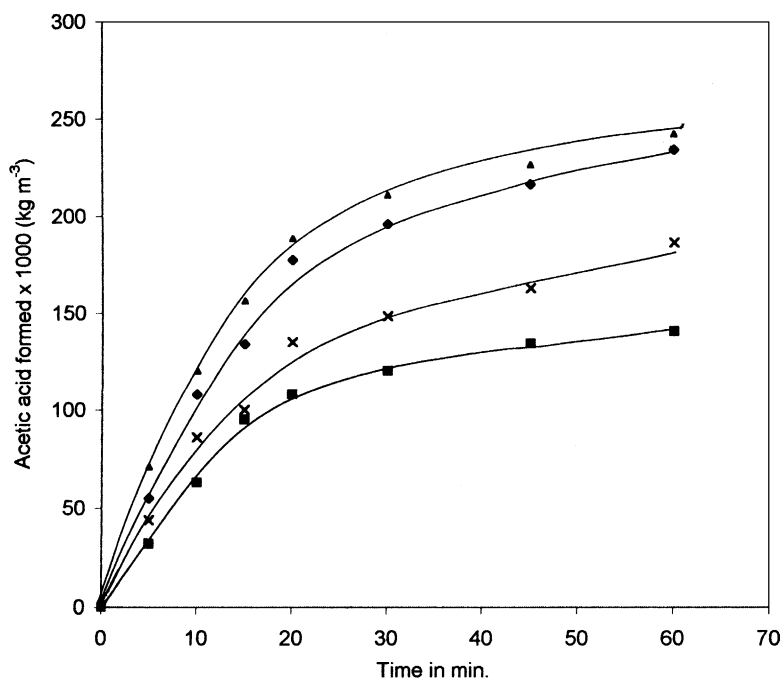


Fig. 15. Effect of Pyrex liner, hydroquinone and *t*-butanol on the formation of acetic acid in a strongly alkaline medium (175°C , system pressure 1.58 MPa, O_2 pressure 0.69 MPa, initial COD 2 kg m^{-3} , initial pH > 12 , catalyst loading 0.5 kg m^{-3}): (◆) 175°C ; (■) Pyrex liner; (▲) hydroquinone; (×) *t*-butanol.

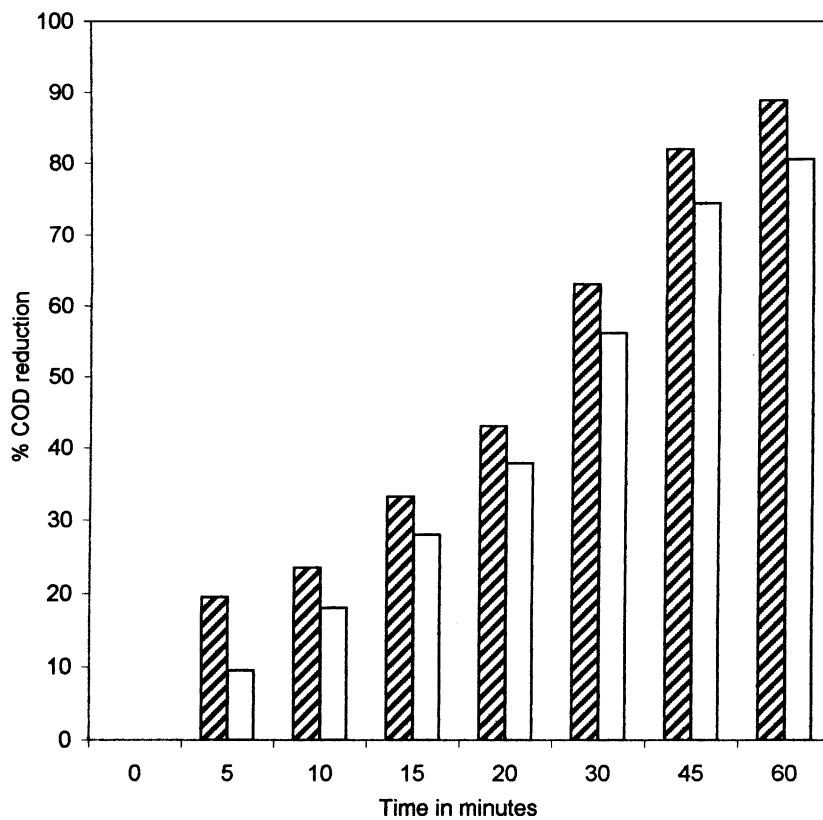


Fig. 16. Reusability of the heterogeneous catalyst Ru/TiO₂ (185°C , system pressure 1.79 MPa, O_2 pressure 0.69 MPa, initial COD 2 kg m^{-3} , initial pH 6.5, catalyst loading 0.5 kg m^{-3}): (▨) fresh catalyst; (□) reused catalyst.

large number of free radicals formed rapidly tend to destroy these intermediates further to acetic acid. However, during the course of the reaction, these free radicals are destroyed and are no more available for oxidation of the large amounts of acetic acid formed. Hence acetic acid tends to accumulate in the system. This is of significance in actual treatment of industrial wastes where high rates can be obtained by the presence of a solid catalyst along with an initiator, thus reducing severity of the conditions required for oxidation. Acetic acid, formed in large amounts, can then be recovered as a valuable product.

As expected, acetic acid formed in the presence of the glass liner at pH greater than 12 was much lower than that formed in its absence. Wet oxidation of phenol proceeds through a free radical reaction mechanism in which different intermediates are formed in varying amounts depending on the reaction pathways. The presence of Pyrex liner prevents destruction of free radicals by the metal walls of the reactor. These radicals, in turn, may attack intermediates including acetic acid formed during oxidation, thereby reducing the amount of acids. It was observed that the formation of acetic acid was reduced in the presence of *t*-butanol. *t*-Butanol, being a free radical scavenger, scavenges free radicals. So, these are no more available for destruction of various intermediates formed into acetic acid. Hence amount of acetic acid formed during the reaction in the presence of *t*-butanol itself may be very less, thus indicating a different reaction pathway. These observations have been exhibited in Fig. 15.

4.6.6. Reusability of the heterogeneous catalyst Ru/TiO₂

Starting with the fresh 5% Ru/TiO₂ catalyst, two experiments were conducted on fresh aqueous solutions of phenol with the same catalyst reused after separation from the oxidized solution by filtration. The results are shown in Fig. 16. The marginal reduction in the activity of the catalyst after the first experiment warrants further in-depth experimental investigation to determine the reasons for this loss in activity and if it can be arrested and further possibly reversed. In other words, regeneration studies need to be undertaken.

5. Conclusions

- The kinetics of heterogeneous catalytic wet oxidation of phenol over a Ru/TiO₂ catalyst was studied.
- The heterogeneous catalyst Ru/TiO₂ was found to be very effective for oxidation of phenol. The enhancement in the rates of reaction in the presence of this catalyst was even more pronounced in a strongly alkaline medium. More-

over, when the pH was greater than 12, the amount of acetic acid formed in its presence was very high. Therefore, this catalyst can be very promising in the treatment of spent caustic containing phenolics where high rates of COD reduction can be achieved and the large amounts of acetic acid formed can be recovered, thus obtaining *wealth from waste*.

- The free radical initiator hydroquinone exhibited a marked increase in the rate of destruction of COD (phenol) under alkaline conditions on Ru/TiO₂ catalyst.

Acknowledgements

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References

- [1] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Wet air oxidation, *Ind. Eng. Chem. Res.* 34 (1995) 2–48.
- [2] Y.I. Matatov-Meytal, M. Sheintuch, Catalytic abatement of water pollutants, *Ind. Eng. Chem. Res.* 37 (1998) 309–326.
- [3] S. Imamura, Catalytic and non-catalytic wet oxidation, *Ind. Eng. Chem. Res.* 38 (1999) 1743–1753.
- [4] C.B. Maugans, A. Akgerman, Catalytic wet oxidation of phenol over a Pt/TiO₂ catalyst, *Wat. Res.* 31 (1997) 3116–3124.
- [5] J. Barbier Jr., F. Delanoë, F. Jabouille, D. Duprez, G. Blanchard, P. Isnard, Total oxidation of acetic acid in aqueous solutions over noble metal catalysts, *J. Catal.* 177 (1998) 378–388.
- [6] S. Imamura, I. Fukuda, S. Ishida, Wet oxidation catalyzed by ruthenium supported on cerium(IV) oxides, *Ind. Eng. Chem. Res.* 27 (1988) 718–721.
- [7] J.C. Beziat, M. Besson, P. Gallezot, S. Durecu, Catalytic wet air oxidation on Ru/TiO₂ catalyst in trickle-bed reactor, *Ind. Eng. Chem. Res.* 38 (1999) 1310–1315.
- [8] P.D. Vaidya, V.V. Mahajani, Insight into sub-critical wet oxidation of phenol, *Adv. Environ. Res.*, in press.
- [9] F.D. Snell, L.S. Ettre, *Encyclopedia of Industrial Chemical Analysis*, Vol. 17, Wiley, New York, 1967.
- [10] L.K. Doraiswamy, M.M. Sharma, *Heterogeneous Reactions: Analysis, Examples and Reactor Design*, Vol. 2, Wiley, New York, 1984.
- [11] A. Pintar, J. Levec, Catalytic liquid phase oxidation of phenol aqueous solutions. A kinetic investigation, *Ind. Eng. Chem. Res.* 33 (1994) 3070–3077.
- [12] J.M. Smith, *Chemical Engineering Kinetics*, 3rd Edition, McGraw-Hill, Singapore, 1981.
- [13] S.C. Chapra, R.P. Canale, *Numerical Methods for Engineers*, 2nd Edition, McGraw-Hill, Singapore, 1990.
- [14] S.T. Kolaczowski, F.J. Beltran, D.B. McLurgh, F.J. Rivas, Wet air oxidation of phenol: factors that may influence global kinetics, *Trans. IChemE B* 75 (1997) 257–265.
- [15] B. Stoffer, G. Luft, Influence of the radical scavenger *t*-butanol on the wet air oxidation of *p*-toluenesulfonic acid, *Chem. Eng. Technol.* 21 (1999) 409–412.