Catalytic wet air oxidation of toxic nitrogen containing compounds (pyridine) from wastewater

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Cu-Co/C (heterogeneous) and CuSO₄ (homogeneous) were used as catalysts for wet air oxidation to remove nitrogen containing toxic organic compounds from wastewater. For this purpose, a model compound, pyridine, was treated in a high-pressure batch autoclave at mild conditions of temperature and pressure. Copper and cobalt are relatively inexpensive catalytic material and have shown higher conversion efficiencies. Both CuSO₄ and Cu-Co/C have optimum activity at an initial pH 4 of the pyridine solution. After 2 h of reaction time, % conversion with CuSO₄ (75.1 %) was more in comparison to Cu-Co/C (71.8 %) using 5 mg/l catalyst concentration at 160°C and 9 bar total pressure.

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Introduction

Wet air oxidation (WAO), a well-established technique for treating wastewater particularly the toxics and highly organic wastes1-5, involves the liquid phase oxidation of organic or oxidizable inorganic components at elevated temperatures (140-320°C) and at high pressure (5-20 bar) using gaseous source of oxygen. Enhanced solubility of oxygen in aqueous solutions at elevated temperatures and pressures provides a strong driving force for oxidation. Elevated pressures are required to keep water in liquid state. Water also acts as a moderant by providing a medium for heat transfer and removing excess heat by evaporation. WAO has been demonstrated to oxidize organic compounds to CO₂ and other innocuous end products. WAO of nitrogen containing organic compounds in water using noble/non-noble metal catalysts seems to be a promising and an environment friendly method to improve water quality. The process uses air/oxygen as the oxidant, which is contacted with the organic compound over a catalyst at elevated temperatures and pressures. Catalytic WAO (CWAO) process is capable of converting nitrogen containing organic contaminants ultimately to CO₂ and water and other compounds of nitrogen into its inert forms. However, one of the major drawbacks of noble metal catalysts, such as platinum etc, is deactivation during liquid phase oxidation. Furthermore, CWAO technology with the use of noble metals is, at present, one of the costliest processes of pollution control.

In this paper, non-noble metals based catalysts, copper and cobalt, which are cheaper and easily available as compared to other traditional and costlier catalysts such as platinum and gold, were used. The model reactions were carried on pyridine oxidation. The compound represent typical nitrogen based organic pollutant present in the aqueous environment.

Materials and Methods

Experimental Apparatus and Methods

Experiments were conducted in a batch reactor at 140-160°C and at total pressure of 9 bars. Reactor (500 ml), a stainless steel (S.S. 316) vessel, has one inlet for oxygen, one outlet for product along with a temperature indicator-cum-controller (PID), digital pressure indicator and a magnetic stirrer (Fig. 1). During reaction, reactor temperature was controlled within ± 2°C. Liquid outlet of reactor is connected to a condenser. Liquid samples are drawn periodically and analysed by an UV spectrophotometer for residual pyridine concentration in the product.

Catalyst Preparation

Laboratory grade CuSO₄ is used directly in the reaction while Cu-Co/C (Cu 5 wt%, Co 5 wt% supported on carbon) was prepared in the laboratory...
using nitrate salt of copper and cobalt in appropriate amounts and mixing with activated carbon (8 g) in cleanly rinsed beaker. The mixture was dissolved in distilled water (100 ml). Beaker was kept stirring for 30 min, then it was allowed to precipitate by adding ammonium hydroxide solution drop by drop in the beaker. The precipitate was separated and washed 3-4 times with distilled water. Catalyst was dried overnight at 110°C in an oven and calcined in a silica crucible. Stepwise calcination was started from 200°C with rise in temperature (50°C) in constant steps of 30 min reaching up to 600°C, when catalyst was kept for 2 h. Stepwise calcinations helped in getting a uniform structure of the catalyst.

Results and Discussion

Effect of pH, catalyst concentration and comparative activity of different catalysts for percentage removal of pyridine was observed.

Effect of pH

(a) CuSO₄ Catalyst

Using synthetic samples containing pyridine (10 mg/l) and CuSO₄ (2 mg/l) as catalyst at 150°C and 9 bar for 1.5 h, maximum removal of pyridine (56%) was at pH 4 (Fig. 2). Pyridine removal was higher at 160°C (64.3%) than at 150°C (56%).

(b) Cu-Co/C Catalyst

Using similar reaction conditions as with CuSO₄, catalyst Cu-Co on carbon has optimum reactivity at pH 4 (Fig. 2). Removal of pyridine at 160°C (53%) was higher than at 150°C (51%).

Effect of Catalyst Concentration

(a) CuSO₄ Catalyst

Using CuSO₄ catalyst (2-5 mg/l) and pyridine (10 mg/l) at optimum pH 4 at 160°C and 9 bar for 2 h, pyridine removal was maximum at catalyst concentration of 5 mg/l (Fig. 3).

(b) Cu-Co/C Catalyst

Using Cu-Co/C catalyst under same conditions as with CuSO₄, removal of pyridine increased rapidly with increase in catalyst concentration from 2 mg/l onwards (Fig. 3); the rate of increase of pyridine removal was rather slower after 4 mg/l concentration. However no optimum value was observed within the range of studies conducted.

Comparative Activity of Different Catalysts

Pyridine removal at different concentrations of catalysts increased with increase in catalyst concentration (Fig. 4). Pyridine removal at 160°C and 9 bar total pressure was more for CuSO₄ (69%) than Cu-Co/C (64%) in 1.5 h reaction time. Removal of pyridine increases with time; CuSO₄ (74%) has higher conversion in comparison to Cu-Co/C (71%) after 2 h of reaction time (Fig. 4).
Kinetic Parameter Studies

Rate constant for pyridine removal was assumed to be the function of substrate concentration as well as the oxygen partial pressure. Since in all the runs, total pressure is kept constant, rate constant of the reaction would invariably be a function of substrate concentration. The global equation rate was also mentioned in Eq. (1) as

\[
\text{Rate} = k_0 \exp(-E_a/RT).[C]^\alpha.[\text{dissolved O}_2]^\beta \quad \ldots (1)
\]

where, \(k_0\) = pre-exponential factor \((g \text{ litre}^{-1})(1-\alpha-\beta) \text{ min}^{-1}\), \(E_a\) = activation energy \((J/mol)\), \(R\) = ideal gas constant \((8.314 \text{ J/mol-K})\), \(T\) = temperature \((K)\), \([C]\) = concentration of the organic reactant \((g/l)\), \([\text{dissolved O}_2]\) = concentration of the oxidant \((g/l)\), \(\alpha\) = partial order of the reaction with respect to the organic reactant; and \(\beta\) = partial order of the reaction with respect to the oxidant.

In most cases, a first-order reaction with respect to the organic substrate was observed\(^6\). In present experiment, the rate was considered to follow a first order kinetics and tried to show its applicability through the experimental data. For a first order reaction,

\[
-r_A = \frac{dC_A}{dt} = kC_A \quad \ldots (2)
\]

or, \(k t = - \ln(1-X_A)\) \ldots (3)

For determining rate constant of the reaction of a 1st order equation a plot between \(- \ln(1-X_A)\) vs reaction time is plotted (Fig. 5). Rate constant for each catalyst was found at 160°C. The catalysts concentration was varied (2-5 mg/l). Partial pressure of the air, reactor pressure (9 bars) at pH 4.0, was kept constant in all the cases. Rate constant value with respect to pyridine concentration using CuSO\(_4\) and Cu-Co/C catalysts fits a straight line, showing the validity of first order rate expression.

Conclusions

Homogenous catalyst CuSO\(_4\) and the heterogeneous catalyst Cu-Co/C had optimum activity of pyridine at pH 4, catalyst concentration of 5 mg/l at 160°C for 2 h of reaction time. Rate constant value with respect to pyridine concentration using CuSO\(_4\) and Cu-Co/C catalysts fit a straight line, showing the validity of first order rate expression.

References