Treatment of pulp and paper mill effluent

Anurag Garg, V V V S Narayana, Parmesh Chaudhary and Shri Chand*
Department of Chemical Engineering, Indian Institute of Technology, Roorkee 247 667

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Pulp and paper mill effluent (COD= 0.7 kg/m$^3$) was treated for the removal of non-biodegradable and toxic compounds by wet air oxidation (WAO) using heterogeneous catalysts. The catalysts include (CuO-ZnO) supported on alumina and ceria as well as lanthanum based perovskites. The activity tests were carried out at 95°C under atmospheric pressure conditions. A maximum COD reduction of 83 per cent for (CuO-ZnO)/CeO$_2$ catalyst was obtained in 2 h reaction time at a catalyst conc. of 5 kg/m$^3$ and the initial pH of wastewater sample at 3.0. LaCoO$_3$ catalyst showed the maximum COD reduction in the basic medium (pH 9.0), whereas the two other catalysts were active in acidic region.

**Keywords**: Pulp, Paper, Effluent, Wet air oxidation, Catalyst

**IPC Code**: Int. Cl.$^7$: C 02 F 1/100

**Introduction**

In pulp and paper mills the processing and subsequent bleaching is done using large quantity of water. The kraft process consists of the chemical removal of lignin from the polysaccharides fibres by cooking the chipped wood in a sodium hydroxide and sodium sulphide liquor at 170°C. The residual lignin present in paper pulp can be eliminated in bleaching process. It consists sequential chemical operations of treatment with chlorine dioxide and washing, thus generating acidic effluents, which is followed by alkaline extraction and washing, generating alkaline effluents.

Industrial effluent from paper and pulp mill contains several toxic and non-biodegradable organic materials, which include, sulphur compounds, pulping chemicals, organic acids, chlorinated lignins, resin acids, phenolics, unsaturated fatty acids and terpenes$^1$. Wood consists of polysaccharides (a mixture of cellulose and hemicellulose) and lignin. Lignin is a complex, highly cross-linked hydroxylated and methoxylated phenylpropane polymer. About 300m$^3$ of wastewater is generated per tonne of pulp manufacture. Thus, chemicals and energy can be recovered from the black liquor. It is a necessity for the manufacturing units to meet local discharge standards. Pollution prevention techniques have resulted in improved recovery of NaOH and Na$_2$S and reduced water usage. However the bleaching process yields recalcitrant organic compounds in the effluent, which are not easily degraded by biological wastewater treatment. Therefore, development of efficient wastewater treatment technologies has become a major concern worldover prior to biological treatment.

Wet air oxidation (WAO) has proved to be an effective method for the treatment of effluents containing high organic matter content and toxic chemicals. To carry out the oxidation process at lower temperatures and pressures than in the uncatalysed WAO, different catalysts can be used. Several homogeneous and heterogeneous catalysts have been used for the WAO reaction. Homogeneous catalysts require a post treatment to be separated and recycled, while heterogeneous catalysts can be separated easily after the reaction from the resulting effluent. Though, noble metals show better activity than the mixture of transition metals, but due to high cost, WAO reaction becomes expensive. In the past, mixtures of metal oxides of Cu, Zn, Co, Mn, and Bi are reported to exhibit good activity, but leaching of these catalysts was detected, which can be reduced by using stable supports.

In the present work, an effort has been made to treat paper mill effluent at atmospheric pressure conditions in the presence of base metal based catalysts using Al$_2$O$_3$ and CeO$_2$ as supports.

**Materials and Methods**

**Catalyst Selection and Preparation**

Based on the literature survey the catalysts chosen to
be tested for wet air oxidation of pulp and paper mill effluent at atmospheric pressure and moderate temperatures are CuO-ZnO/Al₂O₃, CuO-ZnO/CeO₂ and perovskites.

The selection of the CuO-ZnO was based on the findings of earlier investigators who found excellent activities of CuO-ZnO/Al₂O₃ catalyst for the liquid phase oxidation of phenol, p-chlorophenol and p-nitrophenol\(^2,3\). A catalyst having 42 per cent CuO, 47 per cent ZnO and 10 per cent Al₂O₃ were used and an activity of 100 per cent phenol removal was obtained at 130°C, 5.6 kg/cm² O₂ partial pressure, 5 kg/m³ catalyst conc. within 1 h of reaction time. The activity test CuO-ZnO based catalyst have not been used for the treatment of complex organic pollutant mixture such as, pulp and paper mill effluent.

The selection of LaCoO₃ was based upon its excellent activity reported for the oxidation of unburnt hydrocarbon and CO present in the automotive exhaust. Nearly 100 per cent removal of these pollutants have been reported between 200-300°C (ref. 4).

Method of Preparation of CuO-ZnO Catalysts

Different compositions having CuO and ZnO in the range of 2-8 weight per cent (remaining Al₂O₃ or CeO₂) were prepared. Required amounts of Cu(NO₃)₂ and Zn(NO₃)₂ were dissolved in double distilled water the solution was mixed with required amount of Al₂O₃ or CeO₂ powder with the help of magnetic stirrer at 60°C or 2 h. The catalyst was left overnight at room temperature for further diffusion at molecular level. It was then dried at 110°C for 10 h and calcined at 450°C for 5 h.

Method of Preparation of Perovskite Based Oxides

LaCoO₃ was prepared by ceramic method. Stoichiometric amounts of lanthanum oxide (La₂O₃), cerium nitrate, and cobalt nitrate were mixed thoroughly after adding approximately 1cc acetone in a paste and mortar. The mixture was then calcined stepwise for 10-12 h at 800°C. The mixture was taken out and ground again in paste and mortar and calcined again as before at 800°C for 10 h. The catalyst was then used in powdered form in WAO experimentation.

The oxidative reaction on the pulp and paper effluent was carried out in a three-neck conical flask of 300 cm³ capacity, which consists of a magnetic stirrer. The flask was fitted with a vertical condenser at the centre and the remaining two necks with thermo-well and air inlet. Temperature in the reactor vessel was maintained constant at a desired level with an accuracy of ±1°C. The concentration of the catalyst used in the runs was varied from 1 – 5 kg/m³. The set up used for the experiments is shown in Figure 1.

Results and Discussion

Catalyst Characterization by X-ray Diffraction

The determination of structure of the perovskite catalyst was done by X-ray diffractometer in Institute Instrumentation Center (IIC), IIT, Roorkee. The intensity of peaks indicate values of 2θ, where Bragg’s Law \((nλ=2dsinθ)\) is fulfilled. Since \(λ\) value for Cu source is constant (1.5418) and 2d values are known from JCPDS files, the 2θ setting of each peak, which corresponds to certain wavelength was determined and matched with the 2θ values obtained from our sample. For LaCoO₃ the intensity peaks were found at \(2θ = 23.6\), 32, 33.4, 48, 59.4, respectively, as shown in the Figure 2. These values are in accordance with the standard LaCoO₃ peaks.

Results of Catalytic Wet Air Oxidation

The results for WAO of pulp and paper mill effluent are presented as the per cent COD reduction of the effluent as a function of various parameters such as, pH, catalyst concentration, temperature, and pressure. While varying the pH of the solution the other parameters were kept constant viz., initial COD 0.7 kg/m³; catalyst conc., 1 kg/m³; at 95°C.

The catalysts used in the present studies were CuO-ZnO/Al₂O₃, CuO-ZnO/CeO₂, and LaCoO₃.
Figures 3-5 present the comparative performance of the three catalysts for the variations in pH, catalyst concentration, and temperature, respectively.

**Effect of Initial pH**

The effects of initial pH on per cent COD reduction for these catalysts together have been shown in Figure 3. It is observed that the per cent COD reduction with CuO-ZnO/Al$_2$O$_3$ increased with pH initially giving a highest value of COD reduction of around 40 per cent at pH 4 which there after decreases as the pH is progressively increased up to a pH of 10. With CuO-ZnO/CeO$_2$ catalyst the pH 7 was found to be least active (around 13 per cent COD reduction), whereas this catalyst has shown higher COD reduction in acidic as well as alkaline medium. At an initial pH of 3, the per cent COD reduction obtained was around 40 per cent, whereas, at pH 9, it gave a reduction of around 34 per cent.

The activity of LaCoO$_3$ was different. It started with a COD reduction of around 2 per cent at pH 3 which continuously increased up to pH 9 getting a conversion of around 34 per cent with a marginal decline there after at pH of 10.

Figure 3, therefore, predicts a maximum conversion of around 40 per cent with CuO-ZnO/CeO$_2$ at pH...
of 3. If we consider the comparative activities of these catalysts in neutral solution, (pH = 7) the activity of LaCoO$_3$ has been the best. The relative activities at pH of 7 were:

LaCoO$_3$(25 per cent) > CuO-ZnO/CeO$_2$(13 per cent) > CuO-ZnO/Al$_2$O$_3$(12 per cent)

**Effect of Catalyst Concentration**

Figure 4 presents the effect of catalyst concentration on per cent COD reduction for the three catalysts. The catalyst concentration was varied from 1 to 4 kg/m$^3$. It is generally observed that per cent COD reduction increases gradually with increase in catalyst concentration.

The results show a per cent COD reduction as high as 83 per cent using CuO-ZnO/CeO$_2$ at 4 kg/m$^3$ catalyst conc., 95$^\circ$C and pH 3. The selection of pH 3 for this catalyst was based on the results in Figure 3, which shows the highest activity for this catalyst at this pH.

**Effect of Temperature**

Figure 5 presents the effect of variation of temperature on per cent COD reduction for three catalysts. The activity of these catalysts with increase in reaction temperature from 60 - 95$^\circ$C was found to enhance its performance. It may be noted from Figure 5 that the COD reduction which varied between 2-6 per cent at 60$^\circ$C for three catalysts went up to around 34-42 per cent at 95$^\circ$C, noticing around 8 times increase. The maximum activity of around 42 per cent COD reduction was obtained with CuO-ZnO/CeO$_2$ at pH 3 and 95$^\circ$C in 2h.

From the results it is evident that the activity of CuO-ZnO/CeO$_2$ at pH 3 using 4 kg/m$^3$ catalyst conc. at 95$^\circ$C, 1 atmos (1 kg/cm$^2$) has been as high as 82 per cent COD reduction for the pulp and paper mill effluent of initial COD 0.7 kg/m$^3$. The performance of a similar catalyst has shown the conversions of phenol 100 per cent and 40 per cent respectively with catalysts (42 per cent CuO + 47 per cent ZnO)/alumina and 10 per cent CuO/alumina in 60 min. reaction time$^3$. The other reaction conditions were $T = 130^\circ$C, pO$_2$ = 5.6 bar, and catalyst conc. 5 kg/m$^3$. If we compare these results with our results the catalyst (CuO-ZnO)/CeO$_2$ has shown very encouraging performance at far less severe reaction conditions.

It has been generally observed that pH of the solution after the reaction, increases to alkaline nature (Table 1). The reason for this may be explained on the basis of the following redox mechanism$^5,6$:

\[
\text{ROOH} + \text{Me}^{(n-1)+} \rightarrow \text{RO}^* + \text{Me}^{n+} + \text{OH}^- \\
\text{ROOH} + \text{Me}^{n+} \rightarrow \text{ROO}^* + \text{Me}^{(n-1)+} + \text{H}^+ 
\]

... (1)

The presence of catalyst enhances both propagation through the formation of alkoxy radicals (reaction1) and decomposition of oxygen molecules. It seems that the catalyst used in the present work follows much of reaction (1) in acidic medium generating more OH$^-$ ions, which results in increase in pH after the reaction.

**Conclusions**

CuO-ZnO/CeO$_2$ has proved to be an effective catalyst for removing the non-biodegradable fraction by WAO of the pulp and paper mill effluent. A maximum reduction in COD of 83 per cent was observed, using CuO-ZnO/CeO$_2$ catalyst at a catalyst concentration of 5 kg/m$^3$ and an initial pH of 3. When pH was varied for the three catalysts CuO-ZnO based catalysts gave maximum COD reduction in acidic medium and pervoskite based oxide gave maximum conversion in basic medium. pH values of the entire oxidation reaction product samples were found to increase to an alkaline range. The activities of catalysts when compared at a neutral pH value of 7 were in the order:

LaCoO$_3$ (25 per cent) > CuO-ZnO/CeO$_2$ (13 per cent) > CuO-ZnO/Al$_2$O$_3$ (12 per cent).

In acidic medium the trend was in the order:

CuO-ZnO/CeO$_2$ > CuO-ZnO/Al$_2$O$_3$ > LaCoO$_3$.

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*Corresponding author
E-mail: schanfch@iitr.ernet.in, Fax: 01332-276535, 273560