Jr. of Industrial Pollution Control 28(1)(2012) pp 51-56

WASTEWATER TREATMENT OF ALCOHOL DISTILLERY PLANT BY CATALYTIC THERMOLYSIS

ANKIT KADAM*[1] AND KANJAN UPADHYAY[2]

[1, 2] Department of Chemical Engineering, Ujjain Engineering College, Ujjain 456 010, (M.P.) India

Key words : Thermal pretreatment, Catalytic thermolysis, Distillery spentwash(DSW), Biodigester effluent (BDE)

(Received 1 December 2011; accepted 10 January 2011)

ABSTRACT

This paper presents the treatment of water effluent of alcohol distillery plant (Som Distillery Pvt. Ltd., Raisen Road, Bhopal, M.P.) by catalytic thermolysis.The effluents were thermally preheated at atmospheric pressure and 80-100°C in a vertical condenser equipped atmospheric glass reactor (AGR). The effluent charge along with the catalyst was heated to the desired temperature with constant magnetic stirring and the liquid samples were withdrawn at definite time intervals for analysis. The liquid sample was filtered and the filtrate was centrifuged and analyzed for COD by standard dichromate reflux method. The effect of initial pH and the duration of treatment with each catalyst (at a concentration of 3 kg m^{-3}) were investigated. Both homogeneous CuSO4 and FeCl3and heterogeneous (CuO, ZnO, MnO) composite oxides were used for the assessment of effectiveness of catalytic thermolysis in enhancing the removal of COD from both the DSW and BDE.

INTRODUCTION

One of the most important environmental problems faced by the world is management of wastes. Industrial processes create a variety of wastewater pollutants; which are difficult and expensive to treat. Wastewater characteristics and levels of pollutants vary significantly from industry to industry. Now-a-days emphasis is laid on waste minimization and revenue generation through byproduct recovery. Pollution prevention focuses on preventing the generation of wastes, while waste minimization refers to reducing the volume or toxicity of hazardous wastes by water recycling and reuse and process modifications and the byproduct recovery as a fall out of manufacturing process creates ample scope for revenue generation thereby offsetting the costs substantially.

Production of ethyl alcohol in distilleries based on cane sugar molasses constitutes a major industry in Asia and South America. The world's total production of alcohol from cane molasses is more than13 million m3/annum. The aqueous distillery effluent stream known as spent wash is a dark brown highly organic effluent and is approximately 12-15 times by volume of the product alcohol. It is one of the most complex, troublesome and strongest organic industrial effluents, having extremely high COD and BOD

***Address for correspondence -** Ankit Kadam, **Email :** ankitkadam7@gmail.com

values. Because of the high concentration of organic load, distillery spent wash is a potential source of renewable energy.

The catalytic thermolysis is a new and novel approach to reduce the pollution load of the high strength wastewaters of the pulp and paper mills and alcohol distilleries. It may be economical and a good supplement to the anaerobic digestion and oxidation processes. In this process, a considerable amount of moderate organic substrate is obtained in the form of solid precipitates by heating the DSW at higher temperatures (160-250 ^{o}C) and corresponding autogenous pressures. The charred solid residue formed also has a high heating value (17-24 MJ kg-1) and could be easily separated by filtration and then dried. Studies in our laboratory at Ujjain Engineering College Ujjain revealed that the pollution load (BOD and COD) of many high organic strength wastewaters like effluent from large integrated and/orsmall paper mills, the distillery spent wash and the effluent of bio methanation plant treating distillery spent wash, could be drastically reduced if the thermal pretreatment is carried out at moderate temperatures and moderate pressures in the presence of some metal salts (Chaudhari *et al*., 2005, 2008; Garg *et al*., 2005; Raju 2003; Garg 2005). In the present study different catalysts, both homogeneous and heterogeneous, have been used for the thermal pretreatment of DSW and BDE at atmospheric pressure and different temperatures (80-100 ^{o}C).

EXPERIMENTALS AND MATERIALS

Distillery Spent Wash (DSW) was obtained from the SOM Distillery Pvt. Ltd., Raisen Road, Bhopal (M.P.). Typical analysis of the effluent is presented in Table 1

Table 1. Parameter ranges of Distillery Spent Wash.

Characteristics	Average value
Color	Dark brown
pH	3.5-3.65
COD (mg/L)	1540
BOD (5 days 20^{o}c), mg/L	840
Solids mg/L	
(i) Total	9900
(ii) Suspended	350
(iii) Dissolved	985
(iv) Volatile	6250
Nitrogen mg/L	
(i) Total	1135
(ii) Ammonia	28
Chloride, mg/L	5500
Sulphates, mg/L	4200
Volatile acid as acetic acid, mg/L	6000
Total acidity (as CaCOa), mg/L	1685
Minaral acidity (as $CaCo_3$) mg/L	200
Potassium (K), mg/L	507
Sodium (Na), mg/L	1100
Calcium(Ca), mg/L	2700
Magnesium (Mg), mg/L	240
Iron (Fe), mg/L	60

Experimental Procedure

Thermal pretreatment runs were carried out at atmospheric pressure and 80-100^{o}C in a vertical condenser equipped atmospheric glass reactor (AGR). The effluent charge along with the catalyst was heated to the desired temperature with constant magnetic stirring and the liquid samples were withdrawn at definite time intervals for analysis. The liquid sample was filtered and the filtrate was centrifuged and analyzed for COD by standard dichromate reflux method (Clesceri *et al*., 1989). The effect of initial pH and the duration of treatment with each catalyst (at a concentration of 3 kg m^{-3}) were investigated. Bothhomoge-neous CuSO4 and FeCl3 heterogeneous (CuO, ZnO, MnO) composite oxides were used for the assessment of effectiveness of catalytic thermolysis in enhancing the removal of COD from both the DSW and BDE

Analytical Procedure

COD was determined by the standard dichromate reflux method. BOD was determined by incubating the seed sample for 3 days at 27 °C. The chloride content was determined by a standard titrimetric Volhard method. The elemental (C, H, N, and S) analysis was done using an elemental analyzer (model Vario EL III; Elementar, Hanau, Germany). The ash content was evaluated by combustion in a muffle furnace at 925 °C for 7 min. The specific energy of the residue was determined by using the standard bomb calorimeter.16 The amounts of metal ions leached out in the solution and those fixed in thesolid residue were determined by using an atomic absorption spectrometer (model Awanta; GBC, Dandenong, Victoria, Australia).

Reaction Kinetics

During catalytic thermolysis, the organic molecules, both smaller and larger, present in the effluent undergo chemical and thermal breakdown and complexation with metals forming insoluble precipitates.

At the same time, larger molecules also undergo breakdown into smaller molecules which are soluble. Due to these, the COD of the supernatant gets reduced. The formation of the solid residue depends on reaction pH, temperature and autogenous pressure. A significant amount of organic solid residue formation and simultaneous reduction in COD, BOD and organics like proteins, reduced carbohydrates, lignin, etc. was observed when the effluents were thermally treated at moderate temperature (100- 140 ^{o}C) and moderate pressure (0.2-0.9 MPa) (Chaudhari *et al*. 2005, 2008). Thus, the reduction in COD can be attributed to the reduction in the amount of organic molecules like proteins, reduced carbohydrates, lignin, etc. The presence of catalysts accelerates the thermolysis process, resulting in the enhancement of COD reduction.

$$\text{Complex organic matter} \xrightarrow[+\text{heat}]{+H_2O} \text{solid residue + lower molecular weight organics}$$

The thermolysis process of the DSW and BDE can be represented as

$$\text{Organics} \xrightarrow[+H_2O+\text{heat}]{+\text{catalyst}} \text{solid residue + lower molecular weight organics}$$

In the presence of catalyst, the solid residue formation gets hastened and its yield increased. The reaction equation can be written as

$$A \xrightarrow[+H_2O+heat]{+catalyst\ (W)} \text{B (insoluble solid) +}$$
$$\text{C (a host of soluble organics)}$$

$$-\frac{dC_A}{dt} = k_c C_A^n C_w^m$$

Or

The global rate expression for the thermolysis can thus be written as

$$-\frac{dC_A}{dt} = kC_A^n$$
$$\text{where k} = k_c C_w^m$$

For constant catalyst loading (Cw = constant) equation 4 gets reduced to

DWW and BDE contain various organics represented by COD. Thus CA may be taken as the COD, and above equation may be written as

$$\frac{d[COD]}{dt} = k[COD]^n$$

$$-ln(1 - X_A) = kt$$

For first order kinetics, equation 7 can be presented in the form of COD conversion (X) as

whereas, for zero order kinetics

COD = k t (9)

The plot of our experimental data did not follow zero order kinetics. However, the data fitted well with first order kinetics. Equation 8 has been plotted in Figure 6 (a-d) for BDE and DSW. It is seen that the thermolysis is a two step series process.

The two rate constants, k1 and k2 for the first (fast) step and the second (slow) step, respectively, can thus be determined. From the data it can be seen that the rate constant increases with an increase in temperature for both the steps. An increase in value of rate constant for the first step with an increase in temperature is smaller than that of the second step. Thus, the ratio k1/k2 was found to decrease from its value of 2.5 at 80 ^{o}C to 1.67 at 100 0C for DSW and 3.5 at 80 ^{o}C to 1.85 at 100 ^{o}C for BDE. The values of k1 and k2 at different temperatures are shown in Table 2. It may also be seen from the Table that the ratio of k1/k2 is higher for BDE than that for DSW. This shows greater degradation of BDE during the first step of the treatment. The rate constants in both the steps are also found to be higher for BDE than that for DSW. The activation energy and frequency factor are determined by the Arrhenius equation.

k = k0 exp (-E/RT)

RESULT AND DISCUSSION

Effect of ph in presence of various catalyst

Effect of pH on COD Reduction at 10 min

The COD reduction of DSW as the function of the initial pH for various catalyst is presented in Fig. 1

Effect of pH on COD Reduction at 30 min and 60 min

The COD reduction of DSW as the function of the initial pH for various catalyst is presented in Fig. 2 & 3.

Effect of pH on %COD Reduction

The % COD reduction of DSW as the function of initial pH for various catalysts is presented in Fig. 4.

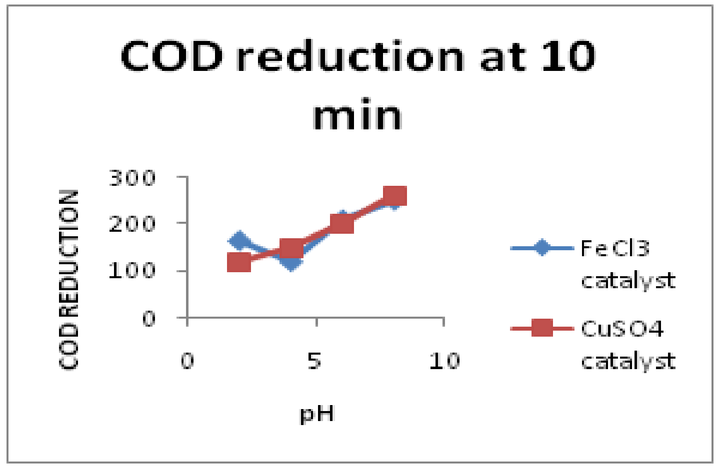

Fig. 1 Effect of pH on COD reduction of DSW during catalytic thermolysis

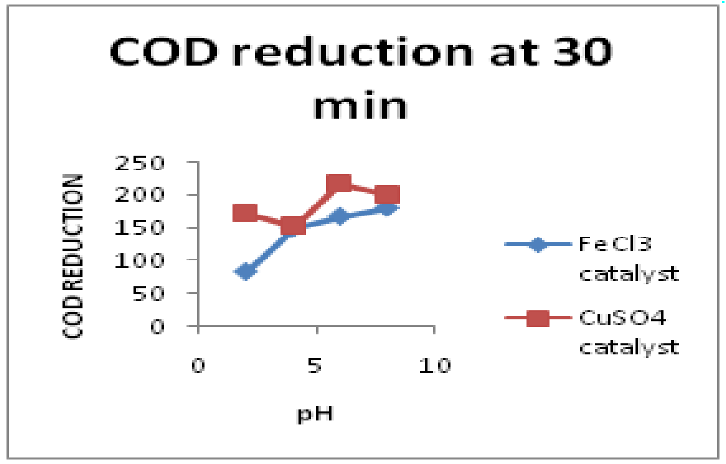

Fig. 2 Effect of pH on COD reduction of DSW during catalytic thermolysis

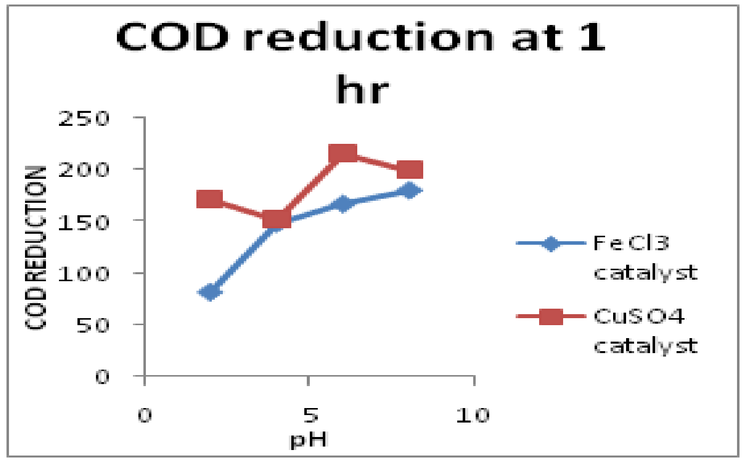

Fig. 3 Effect of pH on COD reduction of DSW during catalytic thermolysis

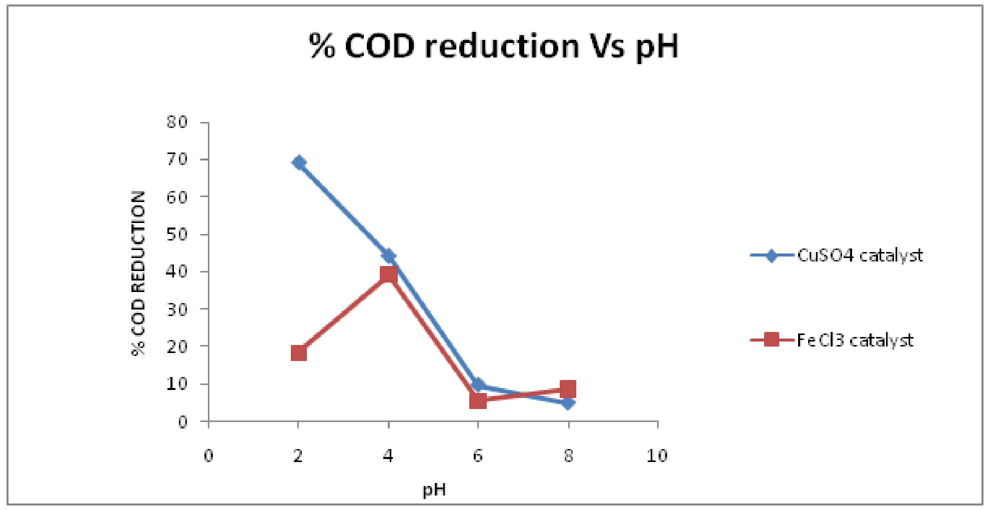

Fig. 4 Effect of pH on %COD reduction of DSW during catalytic thermolysis

DISCUSSION

A doze of 60 mm $FeCl_3$,Cu SO_4 gives COD reduction at different pH. The catalyst doses kept constant of 60mm.The COD reduction was found to be within the range increase from pH=6 and pH =8 for $FeCl_3$, $CuSO_4$ then increase with the further increase in pH value. The iron based compound ($FeCl_3$)have given much COD as compared to $CuSo_4$. This may be attributed to Fe_3+. has more coordination then Cu3+due to the presence of unfilled d-orbital. The anionic component of the BDE act as a good reagent and electron donors to the Fe^{3+}. With the $CuSO_4$ catalyst, the COD reduction was found to be maximum at about pH=8.0. COD reduction was increased for pH 2 to pH 8.0. With the $FeCl_3$ COD reduction increased from pH=2 , pH=6 and pH=8 then decreased from pH=4 .

The carboxylic and phenolic groups present in BDE coordinate with metal cations at low pH as compared to hydroxyl and aliphatic hydroxyl groups. However catalyst for a particular functional groups taking part in the coordination and complexation with metal cations depends on amount and types of functional groups. The removal of dissolved organics during thrmolysis and precipitation with the metal salts at different pH value follows two distinct mechanisms at low pH; the effluent containing anionic organic molecules coordinate with metal cations and form insoluble complexes. At higher pH and elevated catalyst doses, the organics absorbed onto reforms flock of metal hydroxides and gets precipitated. The net result of two mechanisms is that the removal of dissolved organic compounds with different functional group can occur over a wide range of pH and that maximum COD and color removed may occur at pH where the combine effect of both mechanisms is maximum.

CONCLUSION

- The catalytic thermolysis was found to be effective process for treatment of biodigester effluent of distillery. A dose of 60 mm FeCl3 and $CuSO_4$ sulphate reduced to COD 80% and 92% respectively at their optimum pH of 5, 5, 6 and 5.
- COD reduction was found to be extremely dependent on pH. The total COD reduction was depending on coagulation pH and functional groups present in BDE.
- The pH of BDE was found to decrease with adding of catalysts. pH decreasing order was $CuSO_4$ > $FeCl_3$
- The settling rate of flocculated sludge was found in order of $CuSO_4$ > $FeCl_3$.

NOTATIONS

BDE = biodigester effluent
BOD = biochemical oxygen demand, kg m^{-3}
CA = (COD) = concentration of organic matter expressed as COD in kg m^{-3}
CA_o = initial concentration of organic matter in the effluent expressed as COD in kgm^{-3}

COD = chemical oxygen demand, kg m^{-3}
COD_0 = initial concentration of organic matter in the effluent expressed as COD in kg m^{-3}
C_w = catalyst mass loading, kg m^{-3}
DSW = distillery wastewater spent wash
E = apparent activation energy, kJ mol-1
k = specific first-order reaction rate constant, min-1
k_1 = first-order reaction rate constant for fast thermoly- sis step, min-1
k_2 = first-order reaction rate constant for slow thermolysis step, min-1
k_c = specific nth order reaction rate constant, (mol.m-3)1-n. (kgm-3)-m min -1
m = order with respect to catalyst mass loading
n = order with respect to organic matter concentration (COD)
pH_0 = initial pH
pH_f = final pH
R = universal gas constant, 8.314 J(mole K)-1
t = time, s
T = temperature, °C
t = R treatment time, h
X_A = conversion of organic matter or COD, ($1-COD/COD_0$)

RECOMMENDATIONS

- Some other coagulants and coagulation aid may be used
- Thermolysis process may be used for the treatment of BDE
- Electro-coagulation process may be also used for the treatment of BDE
- Reverse osmosis process can also be tried for the same

ACKNOWLEDGEMENT

I greatefully acknowledge the valuable suggestions of Dr. Kanjan Upadhyay, Chemical Engineering Department, Ujjain Engineering College, Ujjain during this study. I am also thankful to Dr. S. K. Shringi, Scientist, Pollution Control Board, Ujjain for providing the necessary laboratory facilities.

REFERENCES

Al-Malack, M.H., Abuzaid, N.S. and El-Mubarak, A.H. 1999. Coagulation of polymeric wastewater discharged by a chemical factory. *Water Res.* 33 (2) : 521-529.

APHA-AWWA-WPCF 1989. *Standard Methods for the Examination of Water and Waste Water*, 17th ed., Washington, DC.

Chaudhari, P.K., Mishra, I.M. and Chand, S. 2005. Catalytic thermal pretreatment (catalytic thermolysis) of biodigester effluent of an alcohol distillery plant. *Ind. Eng. Chem. Res.* 44 : 5518-5525.

Clesceri, L.A., Greenberg, A.E. and Trussel, R.R. 1989. *Standard Methods for the Examination of Water and Wastewater.* 17th edn, APHA-AWWAWPCF, Washington.

Kirk-Othmer, 1993. *Encyclopedia of Chemical Technology*, 4th ed., John Wiley : New York, Vol. 4.

Licsko, I. 1993. Dissolved organics removal by solid-liquid phase separation (adsorption and coagulation), *Water Sci. Technol.* 27 : 245-248.

Migo, V.P., Matsumura, M., Rosario, E.J.D. and Kataoka, H. 1993. Decolorization of molasses wastewater using an inorganic flocculant. *J. Ferment. and Bioeng.* 75 (6) : 438.

Pandey, G.N. and Carney, G.C. *Environmental Engineering*, McGraw-HILL International .

Peavey, S. and Rowe, R. *Environmental Engineering*, McGraw-HILL International.

Randatke, S.J. 1988. Organic contaminant removal by coagulation and related process combinations. *J. Am. Wat. Wks. Assoc.* 80 (5) : 40-56.

Srivastava, V.C., Mall, I.D. and Mishra I.M. 2005. Treatment of pulp and paper mill wastewaters with polyaluminium chloride and bagasse fly ash, Colloids and Surf. A : Physiochem. *Eng. Aspects*. 260 : 17-28.

Garg, A., Mishra, I.M., Chand, S. 2005. Thermochemical precipitation as a pretreatment step for the chemical oxygen demand and colour removal from pulp and paper mill effluent. *Ind. Eng. Chem. Res.* 44 : 2016.