

CATALYTIC WET AIR OXIDATION OF DYE INDUSTRY WASTEWATER USING METALIC CATALYST

Romil R. Modi¹, Dr. Dipak S. Vyas², Mrs. Sejal M. Patel³

¹ ME Student, Environmental Engineering, BVM Engineering College, Vallabh vidhyanagar, Gujarat, India

² Professor, Civil Engineering Department, BVM Engineering College, Vallabh Vidyanagar, Gujarat, India

³ Head Chemical engineering department, Unistar Research and labs Pvt. Ltd, Vapi, Gujarat, India

ABSTRACT

Phenol and COD is a major pollutant found in wastewater streams generating from dye industries. The presence of excess phenol makes the wastewater unsuitable for conventional biological treatment. The treatment of dye industry wastewater by catalytic wet air oxidation (CWAO) at low operating conditions (80-90°C temperature and 2-4 bar total air pressures) was studied in a batch reactor. For the study there were different four types of catalyst used. In study the efficiency of the all four catalyst for phenol removal and COD removal were examined and compared by CWAO process. Among the all catalyst Cu-Fe-AC (20% wt.) catalyst exhibited the best performance with approx. 81% phenol removal at 80°C temperature, 2 bar total air pressures and 90 minutes run time. ZnO catalyst supported on activated carbon showed good capability of removing COD up to 54% at same condition and 90 minutes run time.

Keyword: - Catalytic Wet Air Oxidation, CWAO, Dye industry, Catalysts, Phenol removal, COD removal,

1. INTRODUCTION

The Indian dyestuff industry is only about 40 years old though a few MNCs set up dyestuff units in the pre independence era. Like the rest of the chemical industry, the dyestuff industry is also highly fragmented. A remarkable feature of the Indian dyestuff industry is the co-existence of units in the small, medium and large sectors, actively involved in the manufacture of dyestuffs and their intermediates.

Table 1: Dye Production data

Sector		Production						
		2006-07	2007-08	2008-09	2009-10	2010-11	2011-12	2012-13 (Up to Sept, 12)
Dyes and Dye Intermediate	Production	90	117	110	149	164	171	86
	Growth rate(%)	29.5	30.5	-6.5	35.8	10.5	4	

Note: Figures in Thousand Metric Ton, production is aggregated based on monthly production return from manufacturers under large and medium scale.

1.1 Dye Industry Waste

The dyes and dye intermediate industries sector are one of the most polluting industrial sectors. The waste generated from this sector is highly toxic/hazardous, difficult to treat and very large in quantum. The effluent discharged from this industrial sector is highly acidic and contains toxic compounds; many of them are carcinogenic and highly hazardous to human health and the environment. This is due to the presence of benzene, naphthalene and other nitro-aromatic based compounds in the wastewater, which are used as raw materials during the production of dye intermediates. Due to the excess use of acid and alkali quantity, the wastewater contains high concentration of inorganic salts that results in the high concentration of TDS. Due to this, treatment of effluent is very difficult and highly expensive.

2. NEED FOR STUDY

Effluents from the dyeing and textile industry are considered one of the most problematic wastewaters and its disposal has become a major environmental problem. Catalytic Wet Air Oxidation (CWAO) is advanced oxidation processes used to treat wastewater with a high organic content and in particular wastewater containing toxic components that cannot be treated using biological processes. Catalytic wet air oxidation (CWAO) of aqueous solutions containing refractory organic compounds, such as phenol and dyes, is emerging as an economically and technologically viable technique for reducing toxicity.

3. CATALYTIC WET AIR OXIDATION

Wet Air Oxidation (WAO) and Catalytic Wet Air Oxidation (CWAO) are processes used to remove pollutants from wastewaters with high organic content. In the WAO process pollutants are oxidized at high temperature (up to 320 °C) and high pressure (up to 20 MPa) using molecular oxygen. Carbon dioxide and water are the final products if complete oxidation is achieved.

WAO is a clean process that has been used to treat various wastewaters including pulp and paper mills effluent, pharmaceutical wastewater, dye manufacturing industries, petrochemical wastewater, alumina refinery wastewater, oil refinery wastewater, distillery wastewater, food industries wastewater, and municipal wastewater. Despite being an efficient and clean process WAO has a limitation of very expensive infrastructure due to the high temperature, high pressure and corrosive reaction environment.⁸ Also, WAO process suffers from unexpected high maintenance costs.

To reduce the severe temperature and pressure requirements of WAO a catalyst is required. Over the last four decades, research scholars around the world have been researching WAO/CWAO. There have been a large number of commercial WAO reactors implemented compared to CWAO.

3.1 Homogeneous CWAO

Early studies on CWAO are mainly focused on the homogeneous catalyst, and homogeneous CWAO has been studied more in Europe (Luck, 1999). Homogeneous catalyst represented by Cu, Fe, Ni, Co and Mn is better. According to the literature (Wang et al., 1993; Lin and Ho, 1996; Bi, 1999; Liu and Zhou, 1998), usually ammonia is added as a stabilizer when Cu²⁺ is used as a homogeneous catalyst, then alkali is added and ammonia is evaporated out after CWAO treatment, So this can precipitate out of copper and residual copper is made a resin treatment for recovery. Although homogeneous catalyst has high activity, strong selectivity and is easy to obtain, the homogeneous catalyst is difficult to recovery and easy to drain, which will cause secondary pollution easily.

3.2 Heterogeneous catalytic wet air oxidation

Heterogeneous catalyst has the advantages of high activity, easy separation and has no secondary pollution, so studies on heterogeneous catalysts have been widely concerned since late 70s in the 20th century. Heterogeneous

catalyst can be divided into two categories namely non-noble metal catalysts and noble metal catalysts. In recent years, carbon materials catalysts have also been reported.

Non-noble metal catalyst

Non-noble metal catalysts are mainly one or several of Cu, Mn, Co, Ni, Bi and other metals. The advantage of non-noble metal catalysts is inexpensiveness, but catalytic activity is relatively low, the active component of non-noble metal catalyst is largely leaching, therefore, non-noble metal catalysts mainly are focused on improving their stability.

Noble metal catalyst

Noble metal catalyst is typically made for one or more of Ru, Rh, Pt, Ir, Au, Ag and other precious metal loaded on the carrier. Although noble metal is high cost, the catalytic activity is better. Components of noble metals are more stable in the CWAQ process, so the stability of noble metal catalyst primarily depends on the stability of the carrier. Al₂O₃ is the most common carrier.

4. EXPERIMENTAL

4.1 Wastewater and Other Chemicals

The related wastewater was collected from the inlet of Effluent treatment plant (ETP) of a Dye manufacturing industry located near Vapi, Gujarat. The related wastewater was neutralized after collected from the inlet line. All the chemicals used in the experimental study of treated as well as untreated wastewater were of analytical grade (AR).

4.2 Catalyst Preparation

For the study mainly five different catalysts were used, (i) Activated carbon (ii) Titanium dioxide (TiO₂) supported on Alumina balls (iii) Zinc oxide (ZnO) supported on Activated carbon (iv) Cu-Fe-AC etc.

To prepare Titanium dioxide catalysts fine powdered TiO₂ is mixed with activated charcoal of mesh size of 2mm-5mm. manually mixed to make uniform distribution of TiO₂ in charcoal pores. To prepare ZnO catalysts extra pure Zinc oxide (ZnO- 99.9% purity) was mixed with 8mm size alumina balls.

To prepare Cu-Fe (AC) catalysts consecutive impregnation method was used. There were two different types of Cu-Fe-AC prepared based on different concentration of catalyst loading. First, separately 10% CuSO₄ and 10% FeSO₄ each of 250ml solution prepared by 1hr magnetic stirrer process. Then the solution was mixed with 1kg of activated carbon (Size 2mm-5mm). The mixture was dried in atmospheric condition for 24 hr. After that dried sample was put into furnace at 180° for 3hrs for catalyst activation.

Another Catalyst was made by the same process only the concentration of solution was changed by 20% FeSO₄ and 20% CuSO₄ used. The rest of the procedure (like oven drying and calcinations) was the same as that used above.

4.3 Untreated wastewater analysis

Characteristics of raw dye industry waste water are carried out to know the nature of the wastewater. To select the proper treatment process the characterization of sample are useful. 40 Lit sample was collected from a dye industry from the discharge point of untreated effluent and the appearance of sample was Dark Brown. All characterization tests were carried out using standard methods.

The pH of the waste water was measured by a digital pH meter. The standard spectrophotometer method was used for measuring the phenol compounds concentration in the wastewater. To determine the COD of treated as well as untreated wastewater, the standard closed reflux method was used.

4.4 Setup and procedure for CWAO

4.4.1 Setup for CWAO

CWAO experiments were conducted in a stainless steel (SS 316) high pressure batch reactor with capacity of 10 liter having size 90cm (height) and diameter of 15cm.

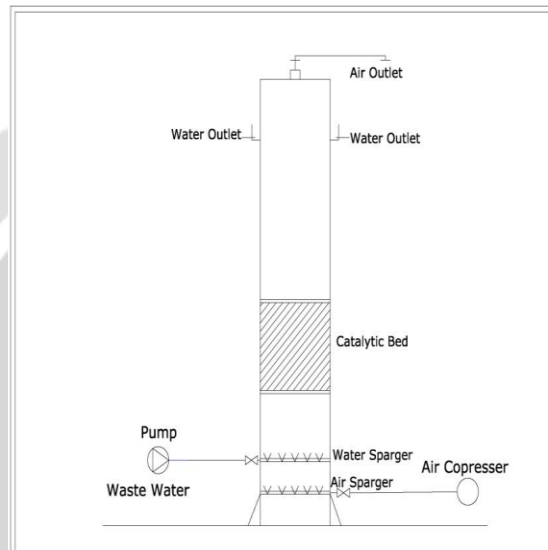


Fig-1: Schematic diagram of CWAO system



Fig-2: Reactor for CWAO process



Fig-3: Catalyst and catalytic bed in reactor for CWAO process

CWAO experiments were conducted in a stainless steel (SS 316) high-pressure batch reactor. The reactor was equipped with a heating device, air introduction port, sampling port, and pressure release valve. For a typical duration run, the reactor was charged with wastewater and the predetermined amount of the catalyst filled into catalytic bed. The reactor was preheated for raising the temperature to the desired level. Upon achieving the set temperature, a sample was withdrawn and compressed air was introduced in the reactor to enhance total pressure MPa and start the oxidation process. During the reaction, the samples were withdrawn periodically and filtered before analyzing for various parameters. All the measurements for phenol and COD removal were completed in duplicate and the average values were calculated.

5. RESULTS

5.1 Raw wastewater characterization

Full Characterization of wastewater collected from the ETP plant inlet before treatment done as shown in table below:

Table 2: Characterization of untreated wastewater

Sr. No	Parameter		Values
1.	pH	Standard Method by APHA Ed.22nd .2012,4500 - H+B	3.46
2.	TDS	Standard Method by APHA Ed.22nd .2012,2540 - C	49,532 mg/L
3.	TSS	Standard Method by APHA Ed.22nd .2012,4500 - D	52 mg/L
4.	NH ₄ -N	Standard Method by APHA Ed.22nd .2012,4500 NH ₃ -B & C	162.5 mg/L
5.	COD	Standard Method by APHA Ed.22nd .2012,5220 - B	4488.84 mg/L
6.	BOD		1170 mg/L
10.	Phenolic Compounds	IS 3025(Part 43)1992,A md. 2	78.3 mg/L

5.2 CWAO using Activated Carbon as catalyst [Temp.-80° Pressure – 2 bar]

Table 3: CWAO using Activated Carbon as catalyst

Sr. No.	Time (min)	COD (mg/l)	% Reduction in COD	Phenol (mg/l)	% Reduction in Phenol
1	0	3319.7	0%	78.3	0%

2	30	2620.8	21%	74.38	5%
3	60	2213	33%	72.03	8%
4	90	1931.9	41%	69.68	11%

5.3 CWAO using ZnO-AC as catalysts [Temp.-80° Pressure – 2 bar]

Table 4: CWAO using ZnO-AC as catalysts

Sr. No.	Time (min)	COD (mg/l)	% Reduction in COD	Phenol (mg/l)	% Reduction in Phenol
1	0	4488.84	0%	78.3	0%
2	30	3073.44	31%	65.77	16%
3	60	2730.8	39%	55.59	29%
4	90	2083.7	54%	49.3	37%

5.4 CWAO using TiO₂-Al₂O₃ as catalyst [Temp. - 80° Pressure – 2 bar]

Table 5: CWAO using TiO₂-Al₂O₃ as catalyst

Sr. No.	Time (min)	COD (mg/l)	% Reduction in COD	Phenol (mg/l)	% Reduction in Phenol
1	0	4488.84	0%	78.3	0%
2	30	4367.53	3%	50.89	35%
3	60	3801.36	16%	41.49	47%
4	90	3073.44	31%	35.23	55%

5.5 CWAO using Cu-Fe-AC (10%) as catalyst [Temp. - 80° Pressure – 2 bar]

Table 6: CWAO using Cu-Fe-AC (10%) as catalyst

Sr. No.	Time (min)	COD (mg/l)	% Reduction in COD	Phenol (mg/l)	% Reduction in Phenol
1	0	4488.8	0%	78.3	0%
2	30	3380.2	25%	34.5	55%
3	60	3138.7	31%	26.5	66%
4	90	2716.8	40%	18.5	75%

5.6 CWAO using Cu-Fe-AC (20%) as catalyst [Temp. - 80° Pressure – 2 bar]

Table 7: CWAO using Cu-Fe-AC (20%) as catalyst

Sr. No.	Time (min)	COD (mg/l)	% Reduction in COD	Phenol (mg/l)	% Reduction in Phenol
1	0	4488.8	0%	78.3	0%
2	30	3010.8	33%	42.8	45%
3	60	2702	40%	23.1	70%
4	90	2161.6	52%	14.5	81%

5.7 Phenol Reduction

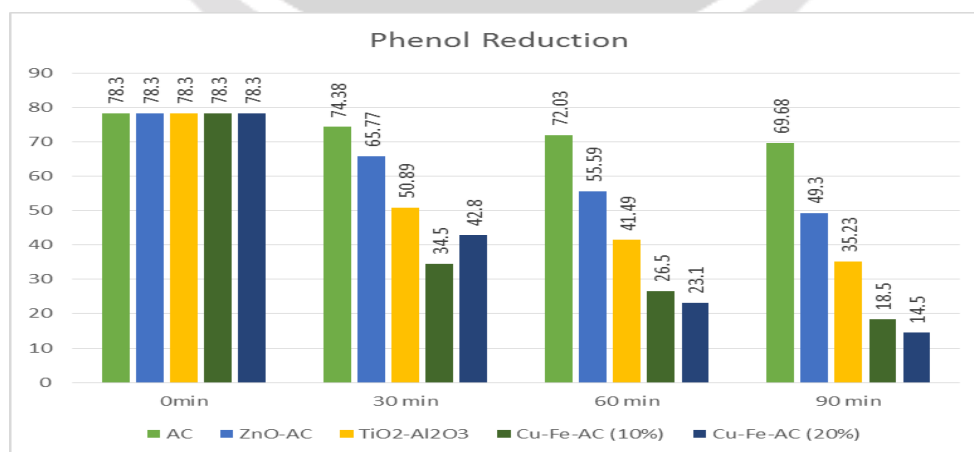


Chart 1: Reduction of phenolic compounds by using different catalysts and at different time interval

5.8 COD Reduction

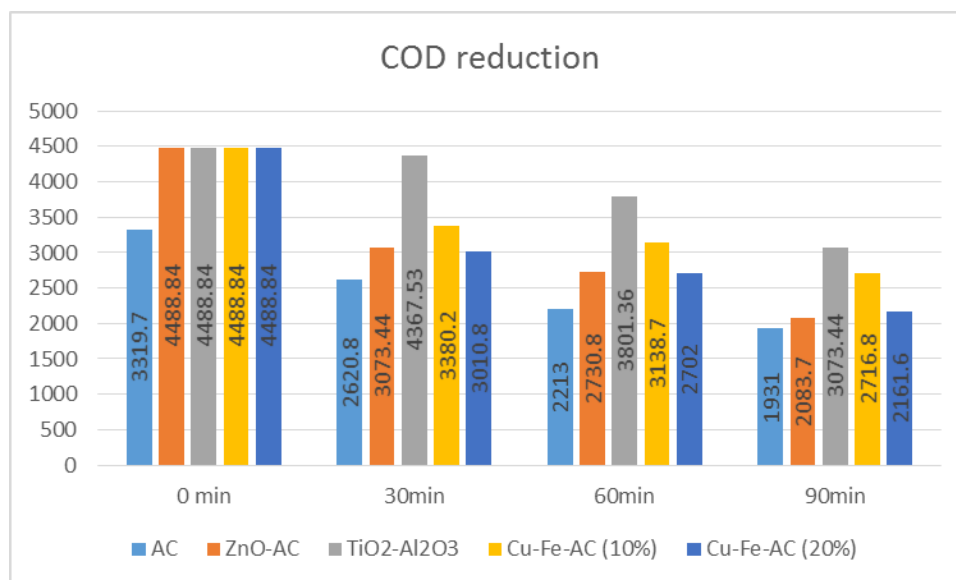


Chart 2: Reduction of COD by using different catalysts and at different time intervals

6. CANCLUSIONS

Several conclusions can be drawn from the present study. Among different catalysts used in the present study the Cu-Fe catalyst was found to be most effective for the phenol reduction from the wastewater. It showing approx. 81% phenol removal from the wastewater at 80°C temperature and 2 bar pressure. On other hands the ZnO (Zinc oxide) catalyst showing approx. 54% of COD reduction by using CWAO process at same condition. Hence, the CWAO process may be effective for the phenol removal from the wastewater from the dye industry. By using different catalyst high reduction may be obtain.

7. ACKNOWLEDGEMENT

I express sincere and heartfelt thanks to **Dr. F. S. UMRIGAR**, Principal, Birla Vishvakarma Mahavidyalaya Engineering College, Vallabh Vidhyanagar, **Dr. L. B. ZALA**, Professor & Head of Department, Civil Engineering Department, Birla Vishvakarma Mahavidyalaya Engineering College, Vallabh Vidhyanagar, **Dr. DIPAK S. VYAS**, Professor, Civil Engineering Department, Birla Vishvakarma Mahavidyalaya Engineering College, Vallabh Vidhyanagar and **Mrs. SEJAL PATEL**, Chemical engineering department head, Unistar research and environmental laboratories Pvt. Ltd., for giving me an opportunity to undertake this research subject for study.

I express a deep sense of gratitude to **Mr. HARISH JOSHI**, UNISTAR ENVIROMENTAL LABS AND RESEARCH PVT. LTD., VAPL **Mr. ANKUR KHANT** for their important guidance and response.

Finally, I am extremely thankful to my parents and my loving fiancé for their continuous moral and support. Their support and love always encouraged me significantly. All my gratitude to my friends, thank you for your love, support and encouraging me in my dissertation work.

8. REFRANCES

- [1]. Bhargava, S. K.; Tardio, J.; Prasad, J.; Foger, K.; Akolekar, D. B.; Grocott, S. C., "Wet oxidation and catalytic wet oxidation" *Industrial and Engineering Chemistry Research* **2006**, 45, (4), 1221-1258.
- [2]. Luck, F., 1999. *Catal. Today* 53, 8-9l.
- [3]. Wang, Y.Z., Li, Z., Yin, L., Hu, K.Y., 1993. *Environmental Chemistry* 12, 408- 413.
- [4]. Yang, S.X., Zhu, W.P., Jiang, Z.P., Chen, Z.X., Wang, J.B., 2006. *Applied Surface Science* 252, 8499-8505.
- [5]. Yang Zhang , Dongliu Li , Yang Chen , Xiaohong Wang, Shengtian Wang, " Catalytic wet air oxidation of dye pollutants by polyoxomolybdate nanotubes under room condition"
- [6]. Anurag Garg and Alok Mishra "Degradation of Organic Pollutants by Wet Air Oxidation Using Nonnoble Metal-Based Catalysts" ASCE
- [7]. Arun Kumar Kondru, Pradeep Kumar, Shri Chand "Catalytic wet peroxide oxidation of azo dye (Congo red) using modified Y zeolite as catalyst" *Journal of Hazardous Materials* 166 (2009) 342-347
- [8]. Andrzej Cybulski "Catalytic Wet Air Oxidation: Are Monolithic Catalysts and Reactors Feasible?" *Ind. Eng. Chem. Res.* 2007, 46, 4007-4033
- [9]. Hornes, A.; Gamarra, D.; Munuera, G.; Conesa, J. C.; Martinez-Arias, A., "Catalytic properties of monometallic copper and bimetallic copper-nickel systems combined with ceria and Ce-X (X = Gd, Tb) mixed oxides applicable as SOFC anodes for direct oxidation of methane" *Journal of Power Sources* 2007, 169, (1), 9-16.
- [10]. Francesco Arena , Roberto Di Chio, Bianca Gumina , Lorenzo Spadaro , Giuseppe Trunfio "Recent advances on wet air oxidation catalysts for treatment of industrial wastewaters" *Inorganica Chimica Acta* (2015)
- [11]. Fortuny a, C. Bengoa b, J. Font b, F. Castells b, A. Fabregat, " Water pollution abatement by catalytic wet air oxidation in a trickle bed reactor" *Catalysis Today* 53 (1999) 107-114
- [12]. Jie fu, George z. kyzas , "Wet air oxidation for the decolorization of dye wastewater: An Overview of the last two decades" *chiness jornoul of catalyst* 35 (2014) 1-7
- [13]. Dong-Jang Chang, I-Pin Chen, Ming-Ten Chen, Shiow-Shyung Lin, " Wet air oxidation of a reactive dye solution using CoAlPO4-5 and CeO2 catalysts" *Chemosphere* 52 (2003) 943-949
- [14]. Gabriel Ovejero, Araceli Rodríguez, Ana Vallet, Juan García Catalytic wet air oxidation of a non-azo dye with Ni/MgAlO catalyst *Chemical Engineering Journal* 215-216 (2013) 168-173
- [15]. Yin Xu, Xiaoyi Li, Xiang Cheng, Dezhi Sun, and Xueye Wang, "Degradation of Cationic Red GTL by Catalytic Wet Air Oxidation over Mo-Zn-Al-O Catalyst under Room Temperature and Atmospheric pressure" *Environ. Sci. Technol.* 2012, 46, 2856-2863
- [16]. F. Stuber, J. Font, A. Fortuny, C. Bengoa, A. Eftaxias, and A. Fabregat "Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater" *Topics in Catalysis* Vol. 33, Nos. 1-4, April (2005)
- [17]. Kyoung-Hun Kim, Son-Ki Ihm, "Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: A review" *Journal of Hazardous Materials* 186 (2011) 16-34