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REMOVAL OF TOXIC CONTENT FROM EFFLUENT USING ECO FRIENDLY TECHNIQUE

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ABSTRACT

Industrial plants generate increasing amounts of wastewater contaminated with toxic and hazardous organic compounds, which cause severe problems for the environment. These industrial wastewaters must be treated in order to meet the specifications for discharge or recycling in the process. Catalytic wet air oxidation (CWAO) removal of organic pollutants in the liquid phase via complete oxidation using an oxidizing agent gas such as oxygen or air in the presence of a catalyst has received considerable interest over the last three decades. Among the different investigated advanced oxidation methods, the highest degradation efficiencies were observed for catalytic wet air oxidation systems. Homogeneous catalysts have been synthesized and tested in the last decade, based either on metal oxides (Cu, Zn, Co, Fe, Mn and Bi) or supported noble metals. CWAO can be accomplished with temperature as low as 250 °C as compared to temperatures ranging from 600 to 1000 °C.

INTRODUCTION

Wastewater treatment is a multi-stage process to renovate wastewater before applied to the land or reused. The goal is reduce or

remove organic matter, solids, nutrients, disease causing organisms and other pollutants from wastewater (Zhou and Smith, 2002). The purpose of wastewater treatment is to remove the contaminants from water and treated water to meet the acceptable quality standards. The quality standards usually depend upon whether the water will be reused or discharged into a receiving stream.

The waste water coming out of any industry is required to be treated before discharging them into the environment. The variety of wastewater is often visible after discharge to the environment. Wastewater treatment plant operates at a critical point of the water recycle from excessive pollution. In general, the numerous unit operations and processes to remove wastewater contaminants are grouped together to provide various levels of treatment. Sharma et al., (2015) have explored the potential of wet air oxidation (WAO) for pretreatment of mixed lignocelluloses biomass to enhance enzymatic convertibility. Rice husk and wheat straw mixture (1:1 mass ratio) was used as a model mixed lignocelluloses biomass. Post-WAO treatment, cellulose recovery in the solid fraction was in the range of 86% to 99%, accompanied by a significant increase in enzymatic hydrolysis of cellulose present in the solid fraction.

HOMOGENEOUS CATALYST

Homogeneous catalysts in wet air oxidation systems have been studied to significantly enhance the destruction of organics with copper salts showing high reaction rates. Reactors chosen for homogeneous catalytic systems are similar to non catalyzed wet air oxidation. Both homogeneous and heterogeneous catalysts can be applied. The major issue of the homogeneous catalytic system however, is the need to recover/remove the catalyst from the effluent after treatment. This necessitates an additional processing step and increased capital cost of the system.

Homogeneous catalysis has been used with co-oxidation where an easily oxidized material promotes the rate of oxidation of a more refractory material as well as with radicals promoter working in combination with transition metals. Examples are hydrogen peroxide with Fe^{2+} as a catalyst, hydrogen peroxide associated with the generation of free radicals that are able to catalyze the reaction, especially when used with iron or copper salts. Often two or more metal salts act in a synergistic mode.

METHODOLOGY

The research study deals with the fabrication of precious metal catalyst for waste water treatment. The present research describes in detail the experimental equipments, procedures and analysis methods used to

conduct the oxidation experiments. It is worth to mention that for the runs with oxidant, an adaptable high temperature and high pressure experimental set-up, including a reactor made of Stainless steel (SS), was designed and constructed. In a preliminary study catalytic liquid phase oxidation of organic pollutants over catalyst were carried out in an existing small scale autoclave reactor to obtain reference conversions for comparison of performance of the different oxidation techniques tested.

PREPARATION OF CATALYST

Catalytic agents used for oxidation reactions can be divided into three classes: metals, metal oxides, and metal salts and their complexes. A variety of solid catalysts, including metal oxides of Cu, Mn, Co, Cr, V, Ti, Bi, and Zn, as well as noble metals (Ru, Pt and Pd) have been tested as active components of catalysts in the oxidation of organic waste water. Homogeneous catalytic systems, such as the soluble transition-metal salts, are generally more effective than solid catalysts, but the dissolved catalysts are toxic and steps should be taken to separate them from the solution.

RESULTS AND DISCUSSION

The treatment of organic waste water by wet air oxidation technique done the absence of catalyst. At the temperature range from 190 °C to 230 °C, different reaction pressure (25- 37 kg/cm²) and residence time (130 - 210 min.), the oxygen partial pressure was kept at 10 kg/cm² at a reference temperature of 25 °C (Xinhua and Dahui ANG, 2003). As the reaction temperature was increased from 190 °C to 230 °C, a significant increase in the rate of degradation of COD was obtained. The minimum and maximum COD reduction was obtained 33.45% and 55.35%, at 230 °C temperature, 37 kg/cm² and 210 min. residence time.

Table 1: Effect of temperature, pressure and residence time on COD reduction, at initial 998ppm organic content in waste water.

S. No.	Temperature (°C)	Pressure (Kg/cm ²)	Residence Time (Minute)	Mean of COD Reduction	Standard Error
1	190	25	130	33.45	± 0.73
2	200	28	150	37.59	± 0.81
3	210	31	170	43.48	± 0.80
4	220	34	190	49.63	± 0.72
5	230	37	210	55.25	± 0.78

EFFECT OF THE TEMPERATURE ON COD REDUCTION:

In the thermal oxidation of organic pollutants, the temperature is an important parameters affecting the significant removal of organic load. The treatment of organic wastewater by thermal oxidation process was carried out at different temperatures of 190 °C, 200 °C, 210 °C,

220 °C and 230 °C and oxygen partial pressures were kept at 10.0 kg/cm². The result of COD reduction at different temperature is shown in table 2. It has been found that when the temperature from 190 °C to 230 °C, COD reduction significantly increases from 52.41 (± 0.17)% to 54.68 (± 0.10) % at 210 min of residence time.

Table .2: Effect of the temperature on COD reduction of organic waste water at constant pressure and residence time

S. No.	Temperature (°C)	Pressure (Kg/cm ²)	Residence Time (Minute)	Mean of COD Reduction	andard Error
1	190	37	210	52.41	± 0.17
2	200	37	210	53.58	± 0.15
3	210	37	210	53.91	± 0.11
4	220	37	210	54.41	± 0.18
5	230	37	210	54.68	± 0.10

The maximum of 54.68 (±0.10)% of COD reduction was achieved at 230 °C under thermal liquid-phase oxidation process. Significant improvement in COD reduction was noticeable at 220 °C and 230 °C temperatures, however, the reaction temperature of 190 °C and 220 °C are refractory to total oxidation, but are compatible for biodegradable. Hence, the temperature of 230 °C is an economically optimal reaction temperature for COD removal of industrial wastewater. For this configuration, Figure 2 shows the linear relationship between pressure and COD reduction response. The R² (coefficient of determination) value for all calibration curves measured was 0.919.

The wet air oxidation was performed at different temperature ranging from 190 °C to 230 °C with different reaction pressure (25-37 kg/cm²) and residence time (130-210 min.). The reaction temperature, pressure and residence time were fixed in agreement of Jinwook et al. (2009). We found that reduction in COD with incremental of temperature. Similar results were observed by Jinwook. C. when evaluated the COD concentration w.r.t reaction temperature. We have found at comparable temperature reduction in COD with non catalytic wet air oxidation was 52.41 (190 °C), 53.58 (200 °C), 53.91 (210 °C), 54.41 (220 °C) and 54.68 (230 °C). Comparably COD reduction in non catalytic wet air oxidation is less.

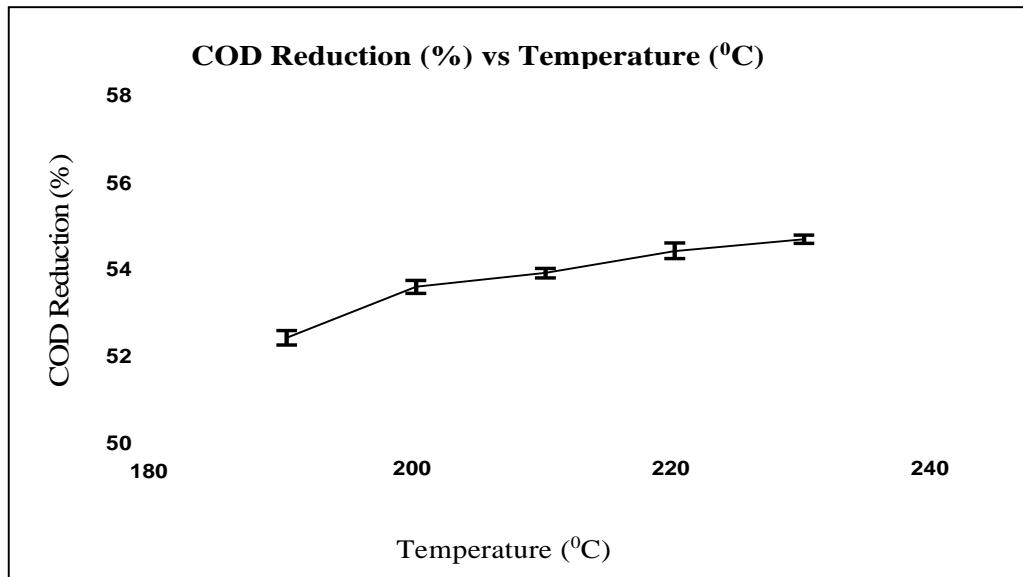


Figure-1: Effect of the temperature on percent reduction of COD

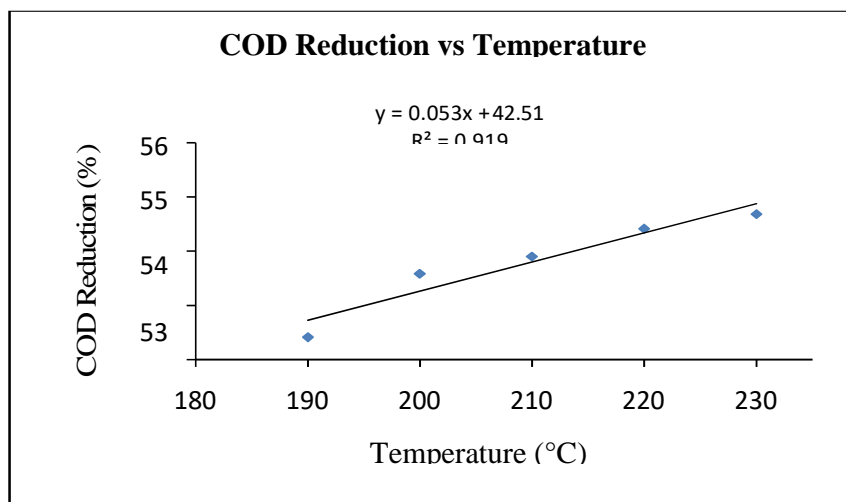


Figure-2: Linear relationship between COD reduction and temperature

EFFECT OF THE PRESSURE ON COD REDUCTION

The treatment of organic wastewater was carried out at five levels of pressure, i.e. 25 kg/cm², 28 kg/cm², 31 kg/cm², 34 kg/cm² and 37 kg/cm² with constant temperature 230 °C and 210 min. residence time. Oxygen partial pressures were kept at 10.0 kg/cm² and a reference temperature of 25 °C. The results of COD reduction at different temperature are shown in Figure 3.

Table 3: Effect of the pressure on COD reduction of organic waste water at constant temperature and residence time

S. No.	Temperature (°C)	Pressure (Kg/cm ²)	Residence Time (Minute)	Mean of COD Reduction	Standard Error
1	230	25	210	51.47	± 0.15
2	230	28	210	52.08	± 0.20
3	230	31	210	53.41	± 0.27
4	230	34	210	54.03	± 0.13
5	230	37	210	55.25	± 0.13

It is observed that the increase in pressure, resulting increase in COD reduction of wastewater. At different pressure of 25 kg/cm², 28 kg/cm², 31 kg/cm², 34 kg/cm² and 37 kg/cm², the COD removal rate of 51.47 (± 0.15) %, 52.08 (± 0.20)%, 53.41 (± 0.27)%, 54.03(± 0.13)% and 55.25 (± 0.13)% respectively were achieved. For this configuration, Figure 4 shows the linear relationship between pressure and COD reduction response. The R² (coefficient of determination) value for all calibration curves measured was 0.986.

The wet air oxidation was performed at different pressure ranging from 25 to 37kg/cm² with reaction temperature (230 °C) and residence time (210 min.). The reaction temperature and residence time were fixed in agreement of Jinwook et al. 2009. We found that reduction in COD with incremental of pressure. Similar results were observed by Jinwook. C. when evaluated the COD concentration w.r.t reaction pressure. We have found at comparable reduction in COD with non catalytic wet air oxidation was 51.47 (25 Kg/cm²), 52.08 (28 Kg/cm²), 53.41 (31 Kg/cm²), 54.03 (34 Kg/cm²), and 55.27 (37 Kg/cm²).

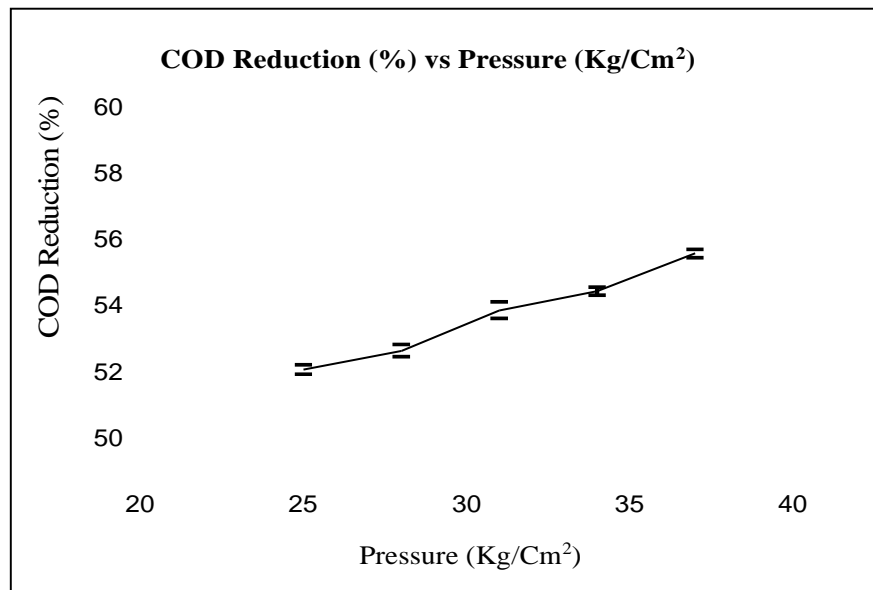


Figure-3: Effect of the pressure on percent reduction of COD

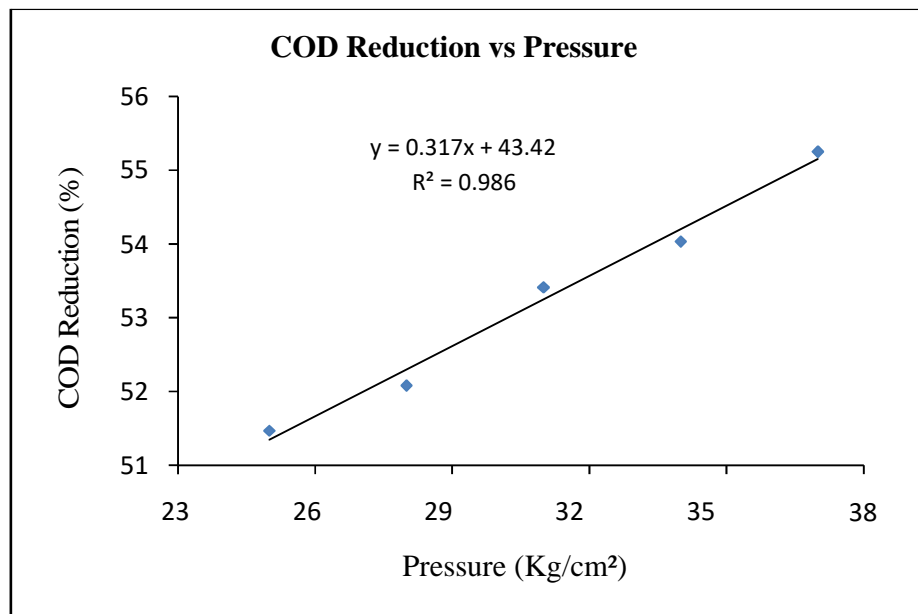


Figure-4: Linear relationship between COD reduction and pressure

EFFECT OF THE RESIDENCE TIME ON COD REDUCTION

The COD reduction experiments were conducted at different residence time, i.e. 130 min., 150 min., 170 min., 190 min., and 210 min. with constant pressure 37 kg/cm² and 230 °C temperature. Oxygen partial pressures were kept at 10.0 kg/cm² and a reference temperature of 25 °C. The results of COD reduction at different temperature are shown in Fig.5. It is observed that COD reduction in organic waste water significantly affected by residence time.

Table 4: Effect of the residence time on COD reduction of organic waste water at constant temperature and pressure

S. No.	Temperature (°C)	Pressure (Kg/cm ²)	Residence Time (Minute)	Mean of COD Reduction	Standard Error
1	230	37	130	51.6	± 0.16
2	230	37	150	53.00	± 0.10
3	230	37	170	53.78	± 0.15
4	230	37	190	55.08	± 0.09
5	230	37	210	55.41	± 0.27

The COD reduction increased rapidly during initial hours of reaction time, maximum of 55.41 (± 0.27)% was observed after 210 min and further decreased to 55.08 (± 0.09)%, 53.78 (± 0.15)%, 53.00 (± 0.10)% and 51.60 (± 0.16)% with increase in residence time of 130 min, 150 min, 170 min and 210 min respectively. For this configuration, Figure .6 show the linear relationship between pressure and COD reduction response. The R² (coefficient of determination) value for all calibration curves measured was 0.969.

The wet air oxidation was performed at different residence time ranging from 130 min to 210 min with reaction temperature (230 °C) and reactor pressure (37 kg/cm²). The reaction temperature and pressure were fixed in agreement of Jinwook et al. we found that reduction in COD obtained with incremental of residence time. Similar results were observed when evaluated the COD concentration w.r.t residence time. We have found at comparable reduction in COD with non catalytic wet air oxidation was 51.60 (130 min), 53.00 (150 min), 53.78 (170 min), 55.08 (190 min.), and 55.41 (210 min).

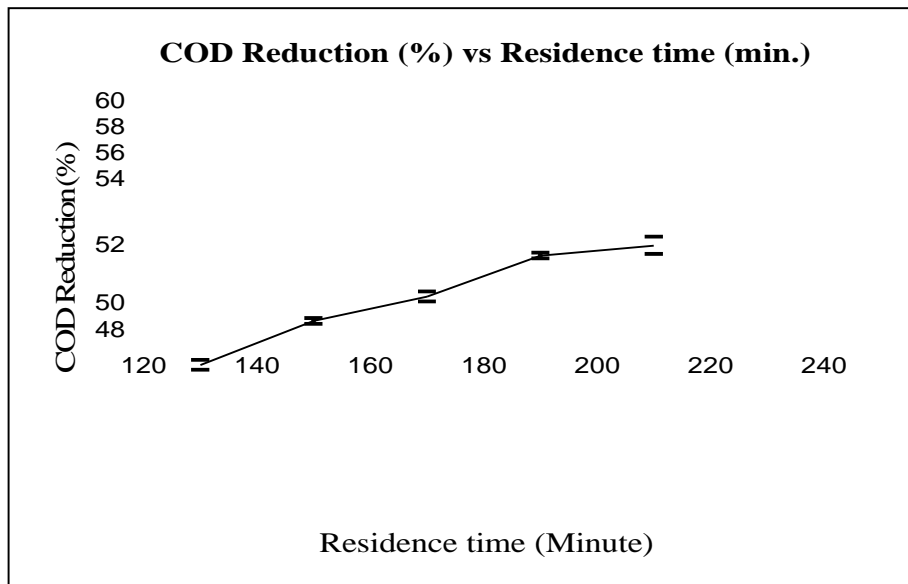


Figure. 5: Effect of the residence time on percent reduction of COD

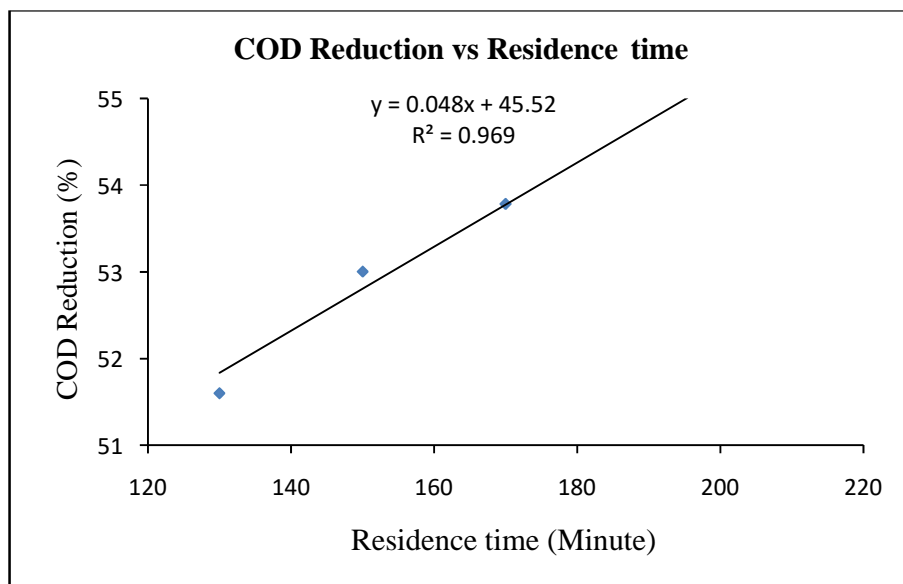


Figure. 6: Linear relationship between COD reduction and residence time.

CATALYTIC LIQUID-PHASE OXIDATION PROCESS

HOMOGENEOUS CATALYST

Catalytic wet air oxidation is an upgraded with the incorporation of suitable catalysts. Copper sulphate is the effective catalyst that works in homogeneous state. The results indicated that homogeneous reaction, presence of catalyst, significantly increases the reaction rate. When 2.0 gm/liter copper sulphate (CuSO_4) catalyst added, the organic waste water

treatment was significantly improved. A significant increase in the rate of reduction of COD was obtained when the wet air oxidation was performed at different temperature ranging from 170 °C to 230 °C with different pressure (25 - 37 kg/cm²) and residence time (60- 140 min.). The minimum and maximum COD reduction was 67.39% and 91.41% .

Table 5: Effect of temperature, pressure and residence time on COD reduction using CuSO₄ catalyst, at initial 998 ppm organic concentration in waste water.

S. No.	Temperature (°C)	Pressure (Kg/cm ²)	Residence Time (Minute)	ean of COD Reduction	Standard Error
1	170	25	60	67.39	± 0.89
2	185	28	80	78.58	± 0.66
3	200	31	100	84.91	± 0.95
4	215	34	120	87.90	± 0.74
5	230	37	140	91.41	± 0.72

EFFECT OF THE TEMPERATURE ON COD REDUCTION

Treatment of organic content in industrial wastewater by catalytic liquid-phase oxidation process was carried out at different temperatures of 170 °C, 185 °C, 200 °C, 215 °C, 230 °C and 245 °C with constant pressure 37 kg/cm² and 140 min. residence time. Oxygen partial pressures were kept at 10.0 kg/cm² and a reference temperature of 25 °C. The results of COD reduction at different temperature are shown in Figure 7 .

Table 6: Effect of the temperature on COD reduction of organic waste water at constant pressure and residence time

S. No.	Temperature (°C)	Pressure (Kg/cm ²)	Residence Time (Minute)	ean of COD Reduction	Standard Error
1	170	37	140	84.52	± 0.11
2	185	37	140	86.40	± 0.17
3	200	37	140	88.41	± 0.13
4	215	37	140	90.39	±0.14
5	230	37	140	91.61	± 0.14
6	245	37	140	91.62	±0.11

Effect of temperature on COD reduction was studies at 170 °C, 185 °C, 200 °C, 215 °C, 230 °C to 245 °C, COD reduction significantly increases from 84.52 (±0.11)%, 86.40 (±0.17)%, 88.41 (±0.13)%, 90.39 (±0.14)%, 91.61 (±0.14)% to 91.62 (±0.11)%.

Improvement in COD removal efficiency was down at 200 °C and 215 °C temperatures. However, the reaction temperature of 215° C are refractory to total oxidation, but are compatible for biodegradable. Hence,

the temperature of 230 °C is an economically optimal reaction temperature for COD removal of industrial wastewater. For this configuration, Figure 8 show the linear relationship between pressure and COD reduction response. The R^2 (coefficient of determination) value for all calibration curves measured was 0.900.

The wet air oxidation was performed at different temperature range from 170 °C to 245 °C with reaction time (140 min) and reactor pressure (37 kg/cm²). The reaction temperature and pressure were fixed in agreement of Lei L. et al. (Lei and Sun, 2000). We found that reduction in COD obtained with incremental of temperature. Similar results were observed by Pradeep kumar et al, 2012. When evaluated the COD concentration w.r.t temperature. The reduction of COD was evaluated by them max. 77% (240 °C). We have found at comparable temperature the reduction in COD with homogeneous catalyst was 84.52 (170 °C), 86.40 (185 °C), 88.41 (200 °C), 90.39 (215 °C), 91.61 (230 °C min) and 91.62 (245 °C).

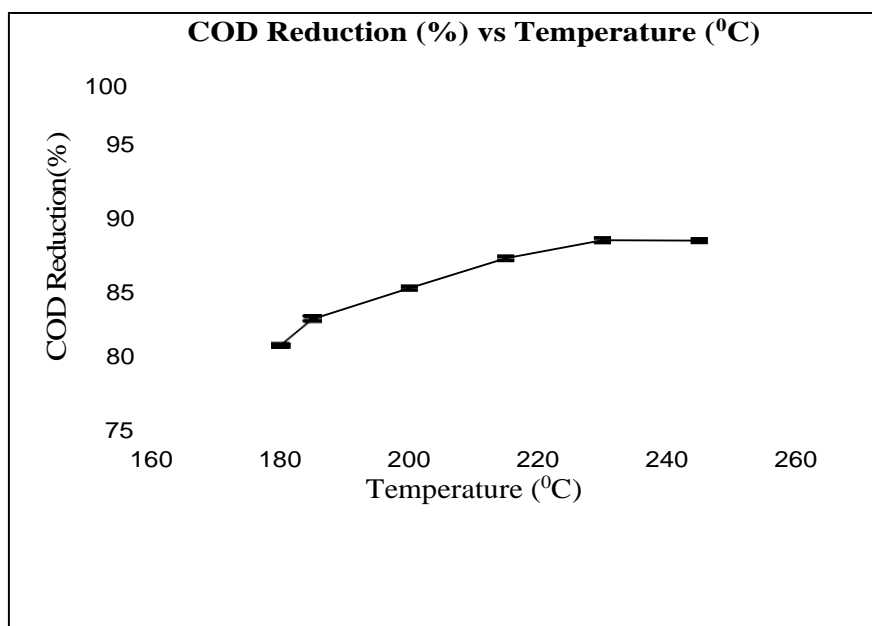


Figure- 7: Effect of the temperature on percent reduction of COD using CuSO₄ catalyst

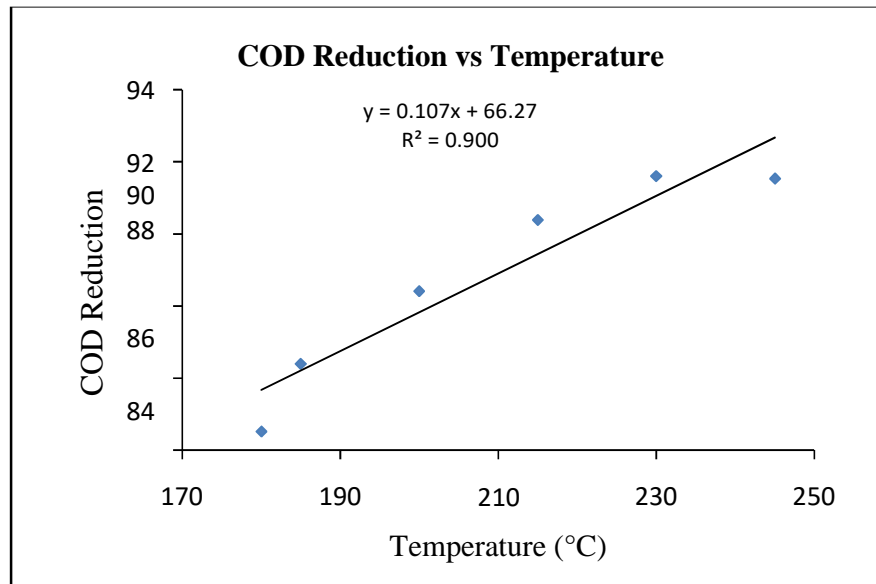


Figure- 8: Linear relationship between COD reduction and temperature

EFFECT OF THE PRESSURE ON COD REDUCTION

The treatment of industrial waste water was carried out at pressure 25 kg/cm², 28 kg/cm², 31 kg/cm², 34 kg/cm², 37 kg/cm² and 40 kg/cm² with constant temperature 230 °C and constant residence time 140 min. Oxygen partial pressures were kept at 10.0 kg/cm² and a reference temperature of 25 °C. The results of COD reduction at different pressure are shown in Fig. 9.

Table 7: Effect of the pressure on COD reduction of organic waste water at content temperature and residence time

S. No.	Temperature (°C)	Pressure (Kg/cm ²)	Residence Time (Minute)	Mean of COD Reduction	Standard Error
1	230	25	140	85.31	± 0.18
2	230	28	140	87.34	± 0.14
3	230	31	140	88.57	± 0.16
4	230	34	140	90.60	±0.10
5	230	37	140	91.73	± 0.09
6	230	40	140	91.75	±0.08

The experimental result shown that the increasing in pressure resulting increase in COD reduction of wastewater. At different pressure of 25 kg/cm², 28 kg/cm², 31 kg/cm², 34 kg/cm², 37 kg/cm² and 40 kg/cm². The COD removal rate of 85.31 (±0.18)%, 87.34 (±0.14)%, 88.57 (±0.16) %, 90.60 (±0.10)%, 91.73 (±0.09)% and 91.75 (±0.08)% were achieved. For this configuration, Figure 10 show the linear relationship

between pressure and COD reduction response. The average R^2 (coefficient of determination) value for all calibration curves measured was 0.948.

However, similar results were observed by Lei et al, 2000 when evaluated the COD concentration w.r.t reaction pressure of degradation of organic material. It is found that the operating pressure is an important parameter affecting the organic material removal from waste water.

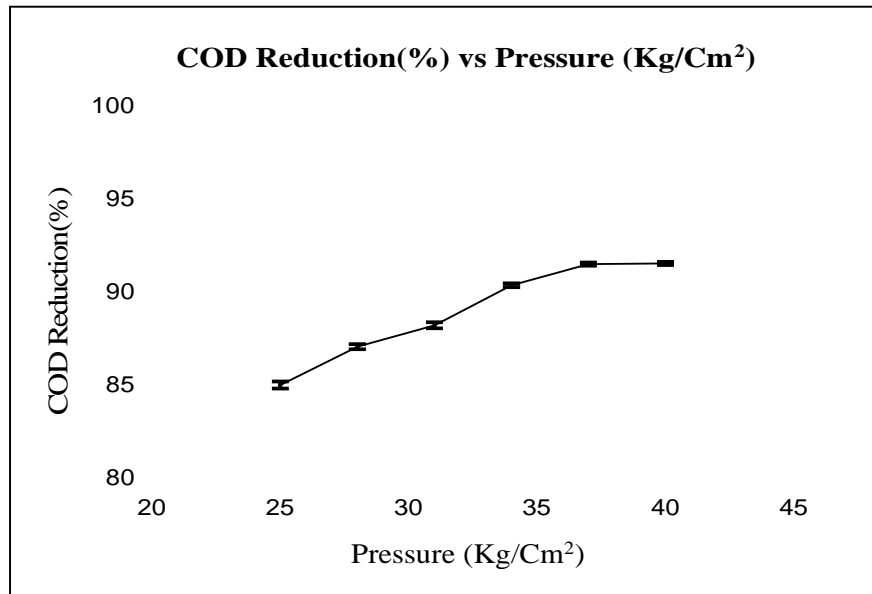


Figure- 9: Effect of the pressure on percent reduction of COD using CuSO_4 catalyst

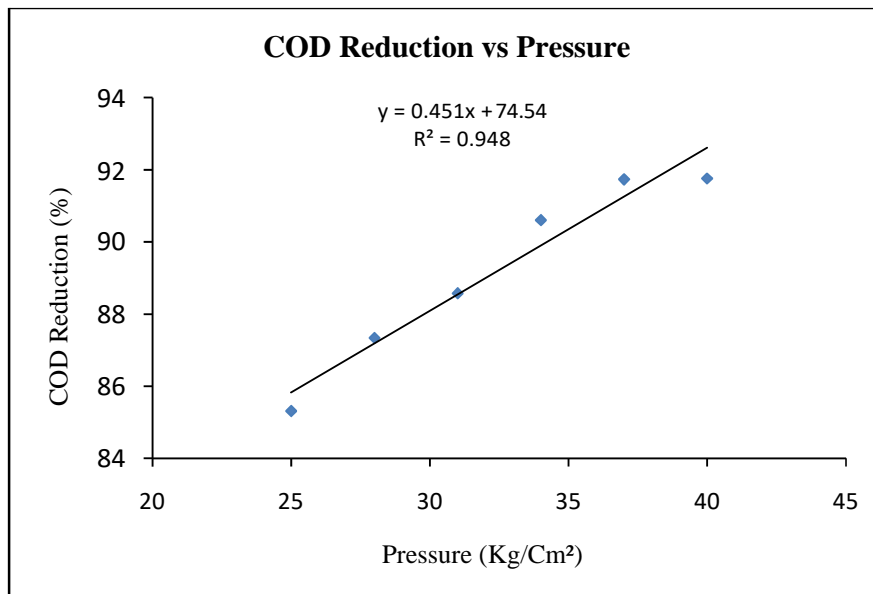


Figure- 10: Linear relationship between COD reduction and pressure.

EFFECT OF THE RESIDENCE TIME ON COD REDUCTION

The COD reduction experiments were conducted at different residence time, i.e. 60 min., 80 min., 100 min., 120 min., 140 min. and 160 min. with constant temperature 230 °C and constant pressure 37 kg/cm². Oxygen partial pressures were kept at 10.0 kg/cm² and a reference temperature of 25 °C. It is observed that COD reduction in waste water significantly affected by residence time in pressure reactor. The results of COD reduction at different residence time are shown in Figure 11.

Table 5.8: Effect of the residence time on COD reduction of organic waste water at constant temperature and pressure

S. No.	Temperature (°C)	Pressure (Kg/cm ²)	Residence Time (Minute)	Mean of COD Reduction	Standard Error
1	230	37	60	81.77	± 0.11
2	230	37	80	83.69	± 0.13
3	230	37	100	85.67	± 0.21
4	230	37	120	87.91	±0.11
5	230	37	140	91.33	± 0.20
6	230	37	160	91.33	±0.16

The COD reduction increased rapidly during initial hours of reaction time, maximum of 91.33 (±0.16)% was observed at 160 min, and further decreased to 87.91 (±0.11)% with residence time of 120 min. and 81.77 (±0.11)% COD reduction with 60 min. residence time. For this configuration, Figure 12 show the linear relationship between pressure and COD reduction response. The average R² (coefficient of determination) value for all calibration curves measured was 0.969.

The reaction rate is depends on temperature and reactant concentrations. However, the increasing residence time lead the increase the reaction rate of COD reduction.

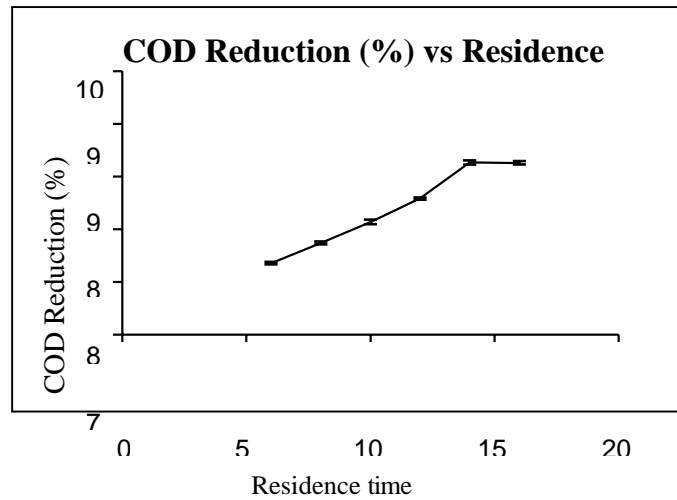


Figure-.11: Effect of the residence time on percent reduction of COD using CuSO_4 catalyst

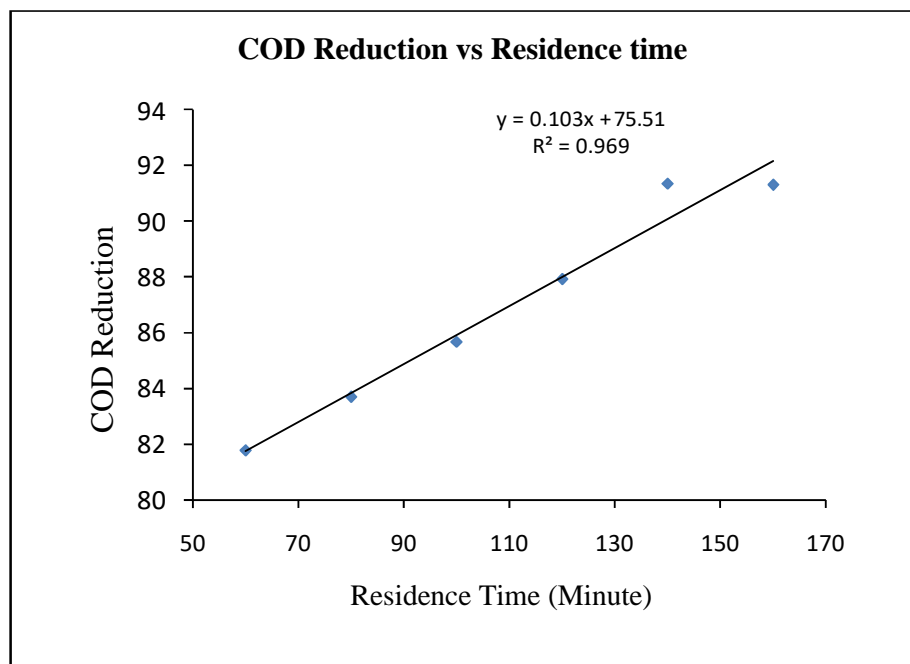


Figure-.12: Linear relationship between COD reduction and residence time.

Experiments were performed over a range of temperature, pressure, residence time and catalyst loading. The catalyst quantity is same in all experiments. With 2.0 gm/liter catalyst, the COD reduction was improved in organic waste water. Performance evaluation of some homogeneous catalyst done with organic waste waters. Results are summarized in Table 9.

Table .9: Summary of some oxidation reaction with Homogeneous Catalyst

S.No	Catalyst	COD before treatment (ppm)	Initial pH	Temperature (°C)	Pressure (Kg/cm ²)	Residence time (Minute)	COD after treatment (ppm)	Final pH	% COD Reduction
01	CuSO ₄	998	9.70	230	37	140	84	7.49	91.58
02	Cu(NO ₃) ₂	998	9.70	230	37	140	284	8.56	71.54
03	FeSO ₄	998	9.70	230	37	140	173	8.17	82.66
04	Co ₂ O ₃	998	9.70	230	37	140	301	8.69	69.84
05	Fe(NO ₃) ₃	998	9.70	230	37	140	232	8.38	76.75

Dudukovic et al., (2002) proposed models with varying degrees of sophistication, based on molecular scale to reactor scale. Most commonly, reactor design is largely empirically because of the complexity of the WO waste treatment. Polaert et al., (2002) developed process based on the use of activation carbon as an adsorbent in the first step and as an oxidation catalyst in the second step, for which only a small quantity of liquid has to be heated and pressurized, thus reducing heat consumption. The two step adsorption – oxidation process appears to offer good potentials for treating moderate flow rate of waste water, especially when the effluent is dilute.

Vidya et al., (2002) used tery-butyl alcohol as an inhibitor, during WO of phenol. They found that the presence of tert butyl alcohol, the rate of phenol WO decreased, indicating the phenol WO occurs via free radical reactions. Eftaxias et al., (2003) studies on (i) the multiphase nature of CWO reactions (two-phase for homogeneous reaction and three phase homogeneous phase reaction), the temperature & pressure of reaction and the radical reaction mechanism. Thus, multiphase reactions are greatly influenced by diffusion kinetics as the various interfaces in multiphase systems act resistances in CWO, generally lowering the reaction rates.

Adrian et al., (2003) shows that formaldehyde is a carcinogen compound and one of the most important pollutants contained in wastewaters. Three different treatments were evaluated in a high-pressure batch reactor for the total organic carbon (TOC) degradation of formaldehyde solutions: thermolysis, non catalytic wet oxidation and catalytic wet oxidation over a CuO - ZnO/Al₂O₃ catalyst.

Arezoo et al., (2011) studies on CWO and WO were carried out for

oxidizing different industrial wastewaters of pharmaceutical production, at 230 °C and 250 °C and total pressure of 50 bar, with oxygen, in stainless steel autoclaves. The catalysts were titania supported precious metal (Pt, Pd, Ru, Rh) oxides and copper sulfate. Samples were analyzed with respect to their TOC, COD (BOD) content. The tested wastewaters, some of them mother liquors, could be oxidized, but with rather different conversions.

CONCLUSION

This process is usually applied for the treatment of high strength waste water with components that are difficult or uneconomical to treat via conventional biological treatment or incineration. Catalysts play a major role in pollutants abatement from liquid effluents. In this study, the impact of various operating parameters such as temperature, pH, pressure, and reaction residence time on the feasibility of wastewater treatment in a thermal liquid oxidation process was evaluated. The process was successfully demonstrated as an efficient treatment method for organic content in industrial wastewater. This process can be operated under medium pressure and temperature. The final COD reductions in the industrial effluent using homogeneous catalyst were observed to be 91.61%, 80.0% and 99.1% respectively. The operating temperature and pressure therefore, it will reduce the operation risk resulting from high pressure and high temperature within conventional oxidation process.

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