



Thermal Catalytic Treatment (Thermolysis): An Effective Process for the Removal of COD and Color from Industrial Wastewater

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Abstract

Nowadays, water pollution control is one of the global concern areas of scientific research. To meet stringent regulating measures set by various regulatory authorities for effluent discharge, it is a challenging task for various industries. Various processes such as adsorption, biological process, thermal catalytic, membrane technology, electrochemical etc. are reported for the treatment of industrial wastewater. Amongst all the above processes, thermal catalytic process has appeared as an advance process for the treatment of highly polluted wastewater originating from various industries. In this paper, mechanism of thermal catalytic (thermolysis) process towards the pollutant removal has been discussed. This paper provides information about the recent research on thermal catalytic process for the treatment of synthetic and real industrial wastewater. In addition to this, a case study on the treatment of tannery wastewater using thermolysis process has also been investigated. The obtained results showed that maximum 65.25% COD and 72.65% color were reduced using copper sulphate salt with catalyst mass loading of 2 kg/m³ at pH of 4.

Keywords: Chemical oxygen demand, Color, Wastewater treatment, Tannery wastewater, Thermal catalytic process

1 Introduction

Water is one of the most precious compounds of nature for living life on earth. All living organism must have water in order to survive. There would be no life on earth without water. It covers more than 71% of the earth surface, whereas less than 1% of water is for drinking purpose as per international standards. Thus, major global challenge for the 21st century to have drinkable water (1, 2). Human health is affected by water quality typically due to the presence of contaminants in drinking water from highly polluted wastewater. With Strictest regulation standards set by different regulatory authorities and increasing environmental awareness industries faces challenges, it requires appropriate waste water treatment technologies (3-4). Several industries such as food processing, textiles, distilleries, pulp and paper industries, tanneries and many other industries are continuously polluting aquatic medium in numerous different ways, either discharge directly and/or from the treatment plants of wastewater that do not fulfill their obligation; as they contains hardly degradable organics substances. Traditional biological treatment methods are incapable to treat such larger complex compounds (5, 6). In the past years, several researchers have studied on the various treatment technologies such as electrochemical methods (7-9), Adsorption (10, 11), biological process (12), membrane processes (13), Advance oxidation process (14) and combination of biological and advance oxidation process (15, 16) for the treatment of wastewater. In the recent years, thermal

catalytic process has gained attention for the treatment of wastewater discharge from different industries. This novel process not only creates the desirable transformation but also decreases the total processing cost and has been found to be more energy efficient in comparison to many other conventional techniques. Thermal catalytic treatment offers immense potential for the removal of hardly degradable organic pollutant from various industrial effluents (17). Thermal catalytic process is an attractive destruction process for the treatment of wastewater in which organic and/or inorganic substances in aqueous/synthetic solutions gets decomposed and form precipitate at moderate or an elevated temperatures and self (autogenous) pressure in the absence of air/oxygen with or without metal salt catalysts like copper sulphate, copper oxide, magnesium oxide, ferric chloride etc. (18, 19). Due to its ease in operation, relatively simple equipment design, less maintenance and low energy consumption, thermal catalytic process can be applied almost all types of waste water. The main advantages and disadvantages of thermal catalytic process are given in Table 1. This process has been successfully applied in different type of industries such as pulp and paper mills (20), textile (21-22), alcohol distillery (17-18,23) waste water, Petrochemical wastewater (19), sugar industry waste water (24). Further thermal catalytic treatment process may be used as a pre-treatment, post-treatment, or even as the main treatment of wastewater because of versatility of the treatment process (25).

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Table 1: Advantages and disadvantages of thermal catalytic treatment process

S.No.	Advantages	Dis-advantages
1.	Simple equipment required, low maintenance, easy to operate.	1. Need of cleaning of the reactor wall at Periodic interval since charred/solid residue gets attached to reactor wall.
2.	Efficient for reduction in the COD, color, odor, TDS etc.	2. Requirement of acidic resistant reactor since the process is generally effective under acidic conditions.
3.	Less sludge generated.	3. Required physicochemical monitoring of the effluent.
4.	Residue generated after thermolysis process has good calorific value.	
5.	Operating cost is low since no nutrient and air are required.	
6.	Small space required for the treatment.	
7.	Good sludge settling and easy dewatering due to presence of Metallic oxides/hydroxides.	

It may be economical and a better supplement to the biological and oxidation processes. In this process, organic substrate precipitates in the form of solid, can be used as a fuel and the ash obtained may be mixed with organic manure for use in agriculture/horticulture. The major objective of the present study is to provide the detailed information about the recent research on the thermal catalytic process towards the treatment of industrial wastewater. The mechanism of thermal catalytic process has also been discussed. A case study on the treatment of tannery wastewater has also been studied in order to check the efficiency of the thermal catalytic process.

2 Mechanism of thermal catalytic (thermolysis) process

In thermolysis process, dual mechanisms occur simultaneously. The wastewater is subjected to heat in the presence of metal based catalyst. At the initial stage, the both simple and complex organic compounds present in wastewater

are broken down thermally and chemically and undergo complexation. Finally, it transforms into insoluble particles/molecules which settle down in the reactor. These insoluble particles become precipitate in terms of COD and color removal. Additionally, larger complex compounds are broken down into the smaller soluble compounds. Due to the development of insoluble precipitates, substantial reduction in terms of COD and color from wastewater takes place (26, 24, 27). The steps in the mechanism of thermolysis process have been shown in Fig. 1. Thermal catalytic reaction in the absence of catalyst can be represented as:



Thermal catalytic reaction in the presence of catalyst can be written as:

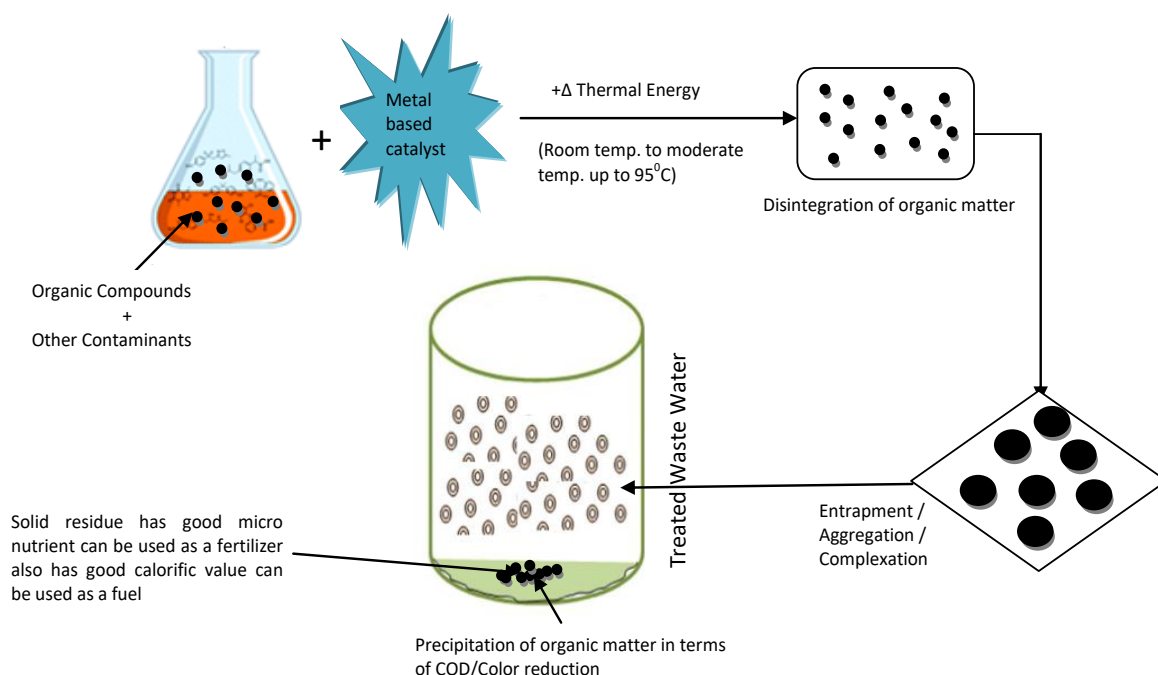
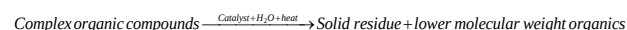


Figure 1: Mechanism of thermal catalytic process

Table 2: An Overview of thermolysis process towards the treatment of industrial wastewater in recent years

S. No.	Type of wastewater	Initial characteristics of wastewater	Type of catalyst used	Range of Parameters	Optimum process parameters	Important outcomes	References
1	Alcohol distillery wastewater	COD=108 kg/m ³ , BOD=50 kg/m ³ , pH=4.5, color=dark brown	Nil	pH = 1 to 12, temp. = 160 to 250°C	pH=1, Temp.=250°C t _R = 2 h	COD reduction= 59% at pH 1 (temp. 230°C)	Lele et al. (31)
2	Distillery wastewater after biogas generation	COD= 35000 mg/L	Nil	Temp=150°C	Temperature =150°C t _R = 0.6 h	COD reduction =40%, color reduction = 30%	Dhale et al. (33)
3	Pulp and paper mill waste water	COD=7 kg/m ³ Color=dark brown pH=10.8	CuSO ₄ , CuO, activated carbon	pH=5 to 10.5, C _w =1-8kg/m ³ Temp. range=20-95°C	pH= 5, C _w =5 kg/m ³ for COD, C _w =2 kg./m ³ for Color, CuSO ₄ catalyst	COD reduction=63.3% Color removal=92.5%	Garg et al. (20)
4	Bio-digester effluent from alcohol distillery plant	COD= 34000 mg/dm ³ , BOD=6300 mg/dm ³ , pH = 7.8, color = blackish brown	CuO	Temp. =100-140°C C _w =2 to 5kg/m ³ , Pressure range=1-9 bar	pH=1, Temp.=140°C, C _w =3kg/m ³	COD reduction =70%, BOD reduction=83%	Chaudhari et al. (18)
5	Desizing wastewater	COD=2884 mg/L BOD _{3days} at 20°C=3275 mg/L Color=520(PCU)	CuSO ₄ .5H ₂ O, CuO, ZnO, FeSO ₄ .7H ₂ O, Al ₂ (SO ₄) ₃ .16H ₂ O	pH=2-12 Temp.= atmospheric temp. to 95°C Catalyst dose=1-8 kg/m ³	pH=4, C _w =4 kg/m ³ , Temp. = 95°C t _R =4 h, CuSO ₄	COD reduction=71.6%, Color removal=87.2%	Kumar et al. (21)
6	Composite wastewater of a cotton textile mill	COD=1960 mg/L, Color=2250 (PCU), pH= 7	CuSO ₄ , FeSO ₄ , FeCl ₃ , CuO, ZnO and PAC	pH=2 to 12 C _w =1 to 12 kg/m ³ Temp. range =60-95°C	pH=12 C _w = 6 kg/m ³ , t _R =4 h	COD reduction=77.9%, Color reduction=92.85%	Kumar et al. (22)
7	Desizing wastewater	COD=2884 mg/L BOD _{3days} =3275 mg/L Color=520(PCU)	Commercial alum, FeCl ₃ , FeSO ₄ , PAC	pH=2-12 C _w =1-7 kg/m ³	pH=4, C _w =4 kg/m ³ ,	COD reduction=88% Color reduction=96%.	Kumar et al. (44)
8	Alcohol wastewater	COD = 108,400 mg/L, BOD = 48,000 mg/L, Color = Blackish brown, pH = 4.0	CuO	pH=1-10, Temp. range= 100-140°C, C _w = 2-5 kg/m ³	pH=2, Temp.=140°, C _w =3 kg/m ³	COD removal=60%,	Chaudhari et al. (17)
9	Sugarcane based alcohol industry waste water DWW and BDE	(i)DWW COD=108400 mg/L, BOD=48000 mg/L, Color = Blackish Brown, pH = 4 (ii)BDE COD=34000 mg/L, BOD=6300 mg/L, Color = Blackish Brown, pH = 7.58,	CuSO ₄ .5H ₂ O, CuO, MnO, ZnO	pH=1-10, Temp.=80-100°C, C _w =2-5kg/m ³ , t _R =0-12 h	pH=less than 2 Temp.=100°C C _w =4 kg/m ³ t _R =12 h, CuO	(i) For DWW, COD reduction=47, colour reduction =68%, (ii) For BDE, COD reduction=61%, color reduction =78%	Chaudhari et al. (23)
10	Petrochemical wastewater	COD=3320 mg/L, BOD=963 mg/L, pH=5.6	CuSO ₄ , FeSO ₄ , FeCl ₃ .	pH=6-10 C _w = 1-4 kg/m ³ , Temp. range=40-90°C	pH=7, C _w =3 kg/m ³ , T=50°C Time=20 min, Catalyst= FeCl ₃ .	COD reduction=77.2%	Verma et al. (19)

11	Biodigester effluent(BDE) of a molasses based alcohol distillery	COD=34 kg/m ³ , pH=7.8, Color =Blackish brown	CuO	pH = 1-10, C _w =2-5 kg/m ³ , Temp. range=100-140°C, t _R =0-6 h	pH=1, C _w =3kg/m ³ , Temp.=140°C t _R =6 h,	COD reduction=70%, BOD reduction=83%	Chaudhari et al. (51)
12	Synthetic Dye wastewater	COD=120 mg/L, color=530PCU, pH=6.4	CuSO ₄ .5H ₂ O, CuO, MgSO ₄ .7H ₂ O, FeCl ₃ , CaCl ₂ and FeSO ₄ .7H ₂ O.	pH=2-12, C _w =1-10g/L, Temp. range=60-90°C, t _R =0-3 h	pH =11, C _w =4 g/L, Temp= 60±2°C, t _R =90 min, CuSO ₄ . 5H ₂ O	COD reduction=95%, Color reduction=67.59%	Kumar et al. (46)
13	Sugar industry waste water	COD=3682 mg/L, Color=dark yellow, pH=5.5	CuSO ₄ , FeSO ₄ , CuO, MnO	pH=2-10, C _w =2-5kg/m ³ Temp.=55-95°C, t _R =0-9 h	pH=10, C _w =4 g/dm ³ , Temp. = 75°C t _R =9 h, CuO	COD reduction=74%, Color removal=80%.	Sahu et al. (24)
14	Rice grain-based biodigester effluent (BDE)	COD=11500 mg/L, Color = Blakish Brown, pH=7.8	CuO, CuSO ₄ , FeSO ₄	pH=3.5-9.5, C _w =1-5g/dm ³ , T emp. = 65-100°C, t _R =0-9	pH=5, C _w =4 g/dm ³ , Temp. = 95°C t _R =9 h, CuO	COD reduction=80.4%, Color removal=72%	Prajapati et al. (26)
15	Cibacron Blue in aqueous solution (reactive dye)	Reactive Dye three main groups anthraquinone, benzene and triazine groups	CuO,copper sulphate,ZnO	pH=1-12 C _w =1-8 g/L Temp.=40-95°C	pH=2 C _w =5 g/L, T=95°C CuSO ₄	Color removal=65.35%	Su et al. (47)
16	Sugarcane industrial effluent	COD=3682 mg/L, Color= 350 PCU, (Dark Yellow), pH = 5.5	CuO,CuSO ₄ , CuCl ₂	pH=2-10, C _w =2-6 kg/m ³ , Temp.=55-95°C, t _R = 0-9 h	pH=8, C _w =5 kg/m ³ , Temp. =85°C, t _R = 9 h, CuO	COD reduction=73%, Color removal=76%	Sahu et al. (49)
17	Sugar industry waste water	COD=3682 mg/L, Color=350 PCU (Dark Yellow) pH=5.5	CuO, ZnO, FeO, and MnO	pH=1-11, C _w =2-6 kg/m ³ , Temp.=55-95°C, t _R = 0-9 h	pH=5, C _w =5kg/m ³ , T emp.=85°C, t _R = 9h, CuO	COD reduction=84.2% Color removal=89.6%	Sahu et al. (27)
18	Distillery waste water	COD=40-70 kg/m ³ , color = Dark brown	CuO	pH=1-9, C _w =1-4kg/m ³ , T emp. = 80-110°C, t _R = 0-9 h	pH=2, C _w = 4 kg/m ³ , T emp.= 110°C, t _R = 9 h	COD reduction=65%	Sharma et al. (35)

3 An overview of thermolysis process for the treatment of industrial wastewater

Thermal catalytic process has been recognized as an effective process towards the industrial wastewater treatment. Most of the studies have suggested this process for the treatment of organic compounds present in wastewater (17-18, 22-24). In addition to this, thermolysis process has shown its efficiency towards the removal of COD and color by numerous researchers. In recent years, performance of thermolysis process has been widely evaluated by many authors for the treatment of different industrial wastewater which have been summarized in Table 2.

3.1 Distillery wastewater

In India, Alcohol is manufactured by the fermentation process from sugar cane molasses, grains etc. which generates 8-15 L of high strength wastewater for each liter of alcohol produced. The effluent from distilleries is known in several ways as distillery spent wash (DSW), distillery wastewater (DWW), stillage, slope, vinasse etc. depending on the distillery unit (17). India is the 4th largest producer of ethanol over the world which creates 40.4 billion liters of wastewater per annum with the production of 3.25 billion liter of alcohol by 319 distilleries (3). Distillery industries have been recognized in the "Red Category" industries by the Ministry of Environment and

Forests (MoEF) (28). The distillery wastewaters released into the aquatic environment without proper treatment can cause harmful effects in the aquatic life by hindering the light penetration (29).

In the context of thermolysis process for the treatment of wastewater, Daga et al. (30) have checked the efficiency of catalytic thermal process for the treatment of distillery wastewater for the first time. In their work, they have performed with COD value in the range of 95- 100 kg/m³ at temperatures range of 150-230°C. The COD removal was found to be an increase with an increase in temperature and autogenously pressure. The 30% COD was removed at 150°C and 50% COD reduction was achieved at 230°C in 6 h treatment. The obtained result indicated that the process of degradation kinetics was described by two stages COD reduction with the first stage being faster than the second one. The experimental data was fitted for first order kinetics with a k value of 9.72, 12.96 and 14.35 min⁻¹ at 150, 170 and 190°C for the first stage, and 1.46, 1.32 and 1.66 min⁻¹ for the second stage, respectively (30). They reported that an increase in temperature resulted in an increase in COD reduction. The results indicated that the COD removal efficiency was favorable at under acidic conditions. Lele et al. (31) conducted thermolysis experiment for treatment of distillery wastewater having a COD value of 1,08,000 mg/L at temperatures over the

range of 160-250°C and autogenously pressure in a autoclave. The results showed maximum 50% COD reduction within 2 hrs. Belkacemi et al. (32) carried out thermolysis process for the treatment of mature timothy grass based distillery wastewater which having total organic carbon (TOC) 22,500 mg/L in the temperature range of 473-513 K and autogenously pressure in the absence of catalyst. The result revealed that maximum 54% TOC reduction was obtained at 513 K in 10 min with initial pH of 4.5. They also reported first order kinetic model for TOC reduction incorporated the effect of initiation-deactivation of catalyst during the process. Dhale et al. (33) have studied for the treatment of distillery waste water after bio-gas generation using wet oxidation at the laboratory scale. They have reported that 40% COD and 30% color reduction was obtained at 150°C and pH of 8. Chaudhari et al. (18) have investigated the efficiency of catalytic thermal treatment process in terms of COD removal from a bio-digester effluent of an alcohol distillery plant. They reported that maximum 70% COD reduction was obtained at pH of 1 using CuO catalyst at 140°C with initial COD = 34000 mg/L for the reaction time of 6 hrs. Chaudhari et al. (17) have conducted thermolysis experiments in a batch mode with a 1 dm³ stainless steel pressure reactor for COD removal from alcohol distillery effluent. The observed results showed that maximum COD removal was found as 60% at 140°C, 3 kg/m³ (catalyst loading) and pH of 2. They have also found that the solid residue with a heating value of 21.77 MJ/kg had a C:H atomic ratio of 1:1.08. They have suggested that the obtained residue can be utilized as a fuel in the combustion furnaces and the obtained ash can be mixed with organic manure for the agriculture/horticulture purpose. Chaudhari et al. (23) studied the thermolysis process for the treatment of distillery wastewater (DWW) and bio-digester wastewater (BDE) at atmospheric pressure using various catalysts such as CuO, ZnO and MnO₂-CeO₂. They observed that CuO catalyst had highest removal efficiency as compared to all the other catalysts. The maximum 47% COD with 68% color reduction from DWW and 61% COD with 78% color reduction from BDE was achieved at 100°C with 4 kg/m³ catalyst loading in 12 h. Kadam et al. (34) reported 80% and 92% COD reduction with 60 mg dose FeCl₃ and CuSO₄ catalyst respectively. Prajapati et al. (26) studied on the treatment of rice grain based biodigester effluent of the distillery unit. They have used various catalysts such as copper oxide, copper sulphate and ferrous sulphate during thermolysis process. They have observed that maximum COD and color removal of 80.4% and 72% respectively were found at an optimum temperature of 95°C, catalyst loading of 4 g/dm³ and pH of 5 with CuO catalyst. They have also suggested that the slurry found after thermolysis had good settling characteristics. The obtained residue may be used as a fuel in combustion furnaces. Sharma et al. (35) reported the maximum 65% COD from distillery wastewater was reduced at an optimum pH of 2, catalyst loading of 4 kg/m³, a temperature of 110°C. They also suggested that due to the containing of high organic load in wastewater, thermolysis followed by electrocoagulation may be utilized for the complete treatment of distillery wastewater.

3.2 Textile wastewater

Textile industry is one of the polluting industries over the world, and it consumes approximately 200 L water per kg of fabric processed per day (36-37). All textile industries involve desizing, scouring, bleaching, mercerizing, dyeing operation according to their requirements. These industries generate a huge quantity of wastewater which contains a wide range of pollutants in terms of high turbidity, strong color, pH, high-

salt content, high chemical oxygen demand (COD) and total organic carbon (TOC) and toxic chemicals due to presence of surfactants, scouring agents, oil and grease, reactive dyes (38-41). The wastewater emanates from textile industries creates serious environmental problem such as hinders photosynthesis activity in plant, threat to aquatic life due to existence of metals and chlorine, high color hinders the light penetration and oxygen consumption (42). Therefore it is required to treat textile industry waste water before being allowed to be discharge in to surface waters. The conventional waste water treatment methods are found to be not appropriate for the treatment of high strength complex waste water emanating from textile industry (43). Thermal catalytic process may be an option for the treatment of textile wastewater. This process is very effective in color as well as COD removal. There have been numerous studies described in literature towards the treatment of synthetic dye wastewater and real industrial effluent using thermal catalytic process. In this context, Kumar et al. (21) studied the effectiveness and performance of the thermolysis process for the treatment of desizing wastewaters under moderate temperature and atmospheric pressure conditions. They have used in their study various types of catalysts such as CuSO₄.5H₂O, CuO, ZnO, FeSO₄.7H₂O, Al₂(SO₄)₃.16H₂O. They have found that maximum 71.6% COD and 87.2% color were removed at catalyst mass loading of 4 kg/m³ and pH of 4. It was also found that the pH₀ value of the wastewater have an important effect on the precipitation process. Kumar et al. (22) investigated treatment of dyeing effluent from a cotton textile mill by thermolysis and coagulation process. They also compared the efficiency of different catalysts such as CuSO₄, FeSO₄, FeCl₃, CuO, ZnO and PAC (poly aluminium chloride). It was found that CuSO₄ was found to be most effective catalyst as compared to others. It was found that about 77.9% COD and 92.85% color were reduced using thermal catalytic process at a catalyst mass loading (CuSO₄) of 6 kg/m³, pH 12 and 95°C. It has been reported that 88% COD and 96% color reduction of thermally treated desizing waste water followed by coagulation were achieved using commercial alum at a coagulant dose (1kg/m³) at pH of 4 (44). Man et al. (45) studied thermolysis-coagulation-flocculation process for the reduction of color and COD from aqueous solution. Almost 90% of COD and 98% of color removal were achieved at a final pH of 10.89 and a coagulant dose of 3 g MgCl₂/L of dye solution. Thermolysis followed by Coagulation-flocculation resulted in a removal of 91.26% COD and 98.78% color at final solution pH of 10.89 with a lesser coagulant dosage of 500 mg/L. Kumar et al. (46) investigated the efficiency of catalytic thermal treatment of synthetic dye wastewater in terms of COD and color reduction. They have used in their study various catalysts such as CuSO₄.5H₂O, CuO, MgSO₄.7H₂O, FeCl₃, CaCl₂ and FeSO₄.7H₂O. They have observed that copper sulphate was found to be best catalyst in comparison to others. Almost 95% COD and 68% color from synthetic solutions with copper sulphate loading of 4 g/L in 90 min were achieved at temperature of 60±2°C, pH of 11 and 100 mg/L of initial dye concentration. Another study on dye wastewater using thermolysis process was reported by Su et al. (47), they reported that almost 66.14% color was removed at optimum pH of 2 and catalyst mass loading of 5 g/L.

3.3 Sugar Industry Waste water

Wastewater from sugar industry is polluted with various organic and inorganic molecules. The sugar industry wastewaters have been characterized by high COD, BOD and TDS. If untreated waste water is discharged to the natural water

bodies, which makes the water bodies unhealthy for both aquatic and human usages (48). Therefore it is required to treat wastewater before discharging in to the environment. In recent years, thermal catalytic process has been employed towards the treatment of sugar industrial wastewater by many authors (20, 24, 27, 49-51). In this regards, Garg et al. (20) studied thermochemical precipitation for the COD and color removal from pulp and paper mill wastewater using copper sulphate as a catalyst. The obtained result showed that a maximum COD reduction of 63.3% was achieved with a catalyst loading of 5 kg/m³, whereas the maximum 92.5% color was removed using a CuSO₄ loading of 2 kg m⁻³ at an optimal solution pH of 5.0. Sahu et al. (24) investigated the treatment of sugar industry wastewater for the COD and color removal using catalytic thermal process. They found that maximum 74 % COD and 80 % color reduction were obtained using copper oxide as a best catalyst at catalyst mass loading of 4 kg/m³, pH of 10 and temperature of 75°C. Sahu (27) compared the performance of different metal oxides such as copper oxide, zinc oxide, ferrous oxide and manganese oxide towards the treatment of sugar industry wastewater using thermolysis process as pretreatment step. The results showed this process with copper oxide gave 84.2% COD and 89.6% color removal at catalyst concentration of 5 kg/m³, solution pH of 5, reaction time of 9 h and temperature 85°C. It was reported that the obtained sludge after thermolysis has high heating values and can be further used as a fuel (27). Sahu (49) illustrated the reduction of chemical oxygen demand and color from sugarcane industry wastewater using thermolysis and coagulation method. Only thermolysis process gave maximum 73% of COD and 76% color removal from sugar industry wastewater at catalyst (copper oxide) loading of at 5 kg/m³, temperature of 85°C, reaction time of 9 h and pH of 8. Whereas, 97.6% COD and 99.9% color were removed using thermolysis followed by coagulation method at pH of 6.5 and mass loading of 8 mM with copper sulfate salt. It was suggested that thermolysis followed by coagulation method may be an alternative option for the treatment of real industrial effluent. Sahu et al. (50) evaluated the performance of thermolysis and electrocoagulation process on sugar industry wastewater. They reported that maximum 75.6% of COD and 79.2% of color content were achieved using thermolysis process whereas 97.8% of COD and 99.7% of color were obtained with combined thermal and electrocoagulation process under optimum conditions.

In all, it can be concluded that based on above studies, thermolysis process has shown its efficiency towards the treatment of different wastewater. Also, various other processes such as coagulation, electrocoagulation process etc. can be coupled with thermolysis process in order to enhance its performance and efficacy. It can be said that the organic pollutants from wastewater can be treated successfully using thermolysis process, and it can be employed other similar dyes wastewater as well as real industrial effluent. Therefore, a real sample from tannery industry has been taken in order check the performance and efficiency of thermolysis process in subsequent section 4.

4 Treatment of Tannery wastewater using thermolysis process: A case study

4.1 Introduction

The leather industry has a major relevance in Indian economy and contributes significantly towards exports, employment generations. However, these industries are typically recognized as most polluting wastewater generated industries (52). A typical tanning processing comprises of beamhouse operation, tanyard, retanning and finishing process.

The wastewater generated from tanning industries increases aquatic environmental problems due to their complex composition and high concentrations of several organic and inorganic compounds reflected in particular by high chemical oxygen demand (COD), strong color, dissolved and suspended solids, salinity, toxic chemicals etc. (53). The compositions of waste water coming from tanneries are highly fluctuated and depend on the raw materials, tanning route, the processing volume, the amount of water utilized and hide/skin preservation process. The contamination of water bodies with highly concentrated tannery wastewater is a major issue because of hostile effects on aquatic life and human health. Therefore, it is necessary to treat such type of wastewater before discharge in to water bodies. Thermolysis process as an effective treatment option has been taken in this study for the treatment of tannery wastewater. Thermal catalytic process is a chemical process, in which a substance (complex organic compounds + catalyst + H₂O) is decomposed into other substances (solid residue, smaller organic compounds, water, gas) the application of heat (21, 22, 45). The main objective of this study is to evaluate the efficiency of thermal catalytic process in terms of the COD and color reduction from tannery wastewater.

4.2 Materials and methods

4.2.1 Chemicals

All the chemicals used in this study were of analytical grade (AR) and purchased from Kumar Chemicals, India. Ferrous sulphate (FeSO₄·7H₂O), Ferric Chloride (FeCl₃), Copper Sulphate (CuSO₄·5H₂O), Copper oxide (CuO) and Zinc Oxide (ZnO) were used as catalyst for thermal catalytic treatment process. Potassium dichromate, silver sulfate, ferrous ammonium sulfate heptahydrate, concentrated sulfuric acid, mercuric sulfate and ferroin indicator were used in COD analysis.

4.2.2 Tannery wastewater

The raw effluent was collected from leather industry located in the Kanpur, India (details not provided due to confidentiality issues). The effluent sample was yellowish-brown in color and kept at 4±1°C in the laboratory. The characterization of the wastewater has been shown in Table 3.

Table 3: Characteristics of the tannery wastewater

Parameters	Values	Units
pH	5.8	–
Color	Yellowish brown	–
COD	5970	mg/L
Total solids (TS)	11360	mg/L
Total dissolved solids (TDS)	9740	mg/L
Total suspended solids (TSS)	1620	mg/L
Electrical conductivity	35.2	mS/cm
Turbidity	286	NTU

4.2.3 Analytical Method

The chemical oxygen demand (COD) of the sample was measured as per the standard of APHA method (54). Solution pH was regulated using 1 N NaOH and 1 N H₂SO₄. Total solids (TS) were estimated by drying the effluent sample at 104 °C in hot air oven (Make: Macro Scientific Works Pvt. Ltd.). Total dissolved solids (TDS), conductivity and turbidity were measured using ion meter (Hanna Instruments, USA). Solution pH was determined by a pH meter (Hanna Instruments, USA). To determine the color removal efficiency, absorbances of the sample were measured using a UV–vis double beam spectrophotometer (Model: NSP372) at 475 nm.

4.2.4 Experimental Setup and procedure

The schematic of the thermal catalytic reactor set-up used in the present work is shown in Fig. 2. Thermal catalytic reactor set up consists: (1) a 0.5 L capacity three necked round bottom flask (2) the rotamantle with both heating and speed controlling knob (3) a long vertical water cooler condenser was connected at the center of the atmospheric glass reactor to condense the vapors and recirculate into the glass reactor to prevent any loss of the vapor generated during the reaction (4) a mercury thermometer was inserted into the glass reactor to measure the reaction mixture temperature (5) one neck of the glass reactor was used for sample withdraw. In this study, all experiments were performed for treating 300 ml volume of tannery waste water sample. The effect of solution pH on the removal of COD and color was studied over a pH range of 2.0–11.0 to optimize the pH. The desired amount of the catalyst (2 kg/m^3) was added to the wastewater sample and temperature was kept at 95°C . The reaction time was 5 h for all the experiments. After the start of an experiment five millimeters of the samples were taken from the reactor at a regular interval of time and analyzed for COD and color. The % removal of COD and color was calculated using following Eq. (1):

$$\text{Removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad \text{Eq. (1)}$$

where, C_i and C_f = Initial and final concentration respectively (mg/L).

4.3 Results and discussions

Initial pH is an important parameter in deciding the efficiency of thermolysis process. Thermolysis process strongly depend on the initial pH for the treatment of textile industry wastewater (22), pulp and paper wastewater (20), sugar industry wastewater (24, 50), synthetic dye wastewater (46) and petrochemical wastewater (19). Therefore, in this case study, the effect of initial pH on thermolysis of the wastewater with copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), ferric chloride (FeCl_3), copper oxide (CuO), ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), zinc oxide (ZnO) and without catalyst was investigated in a batch mode at the atmospheric pressure and at 95°C . All the experiments were conducted for a reaction time of 5 h with the catalyst mass loading (C_w) of 2 kg/m^3 . The initial pH was varied in the experiments over a range of 2–12. The obtained results are shown in Fig. 3 and Fig. 4. A sample from treated wastewater was collected after each experiment and sludge was allowed to settle down. Then, the supernatant was taken for the measurement of its COD and color. It can be seen from figure (3) and (4) that all the catalysts i.e. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, FeCl_3 , CuO , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and ZnO exhibited high removal efficiency of COD and color under acidic solution in comparison to basic conditions of the solution. Maximum 65.25% COD and 72.65% color reduction were obtained in case of copper sulphate salt at pH of 4. Ferric chloride has shown 45.36% COD, 58.32% color reduction at pH of 4. Copper oxide provided 47.65% COD and 56.32% color reduction at pH of 6. Ferrous sulphate and zinc oxide have shown 40.25% COD and 45.26% color reductions, and 25.23% COD and 30.25% color reduction at pH of 6 respectively. When the tannery wastewater was heated in the absence of catalysts at the similar conditions, the maximum 12.65% COD and 15.46% color were reduced at pH of 8. The random reduction in COD values was also found for treatment of various industrial wastewaters by numerous researchers (17, 18, 20, 21, 22). It has also been observed that the after the treatment final pH was also measured and found to be a

decrease in pH except for CuO and ZnO . This may be due to the dissociation of sulphate/chlorides and thus creating sulfuric acid/hydrochloride which reduces the pH of the solution (22).

Hence, it can be concluded from the above case study that the thermolysis process may be an effective process for the treatment of real industrial wastewater. Thus, on the basis of above result found in this work with earlier studies for the treatment of industrial wastewater using thermolysis, it has been proven that thermal catalytic process has potential towards the treatment of the highly polluted industrial wastewater.

5 Conclusions

The thermolysis process is found to be an environmental friendly process for the treatment of industrial wastewater. It can be signified as an effective tool for the treatment of organic, inorganic and larger complex molecules present in various industrial wastewaters.

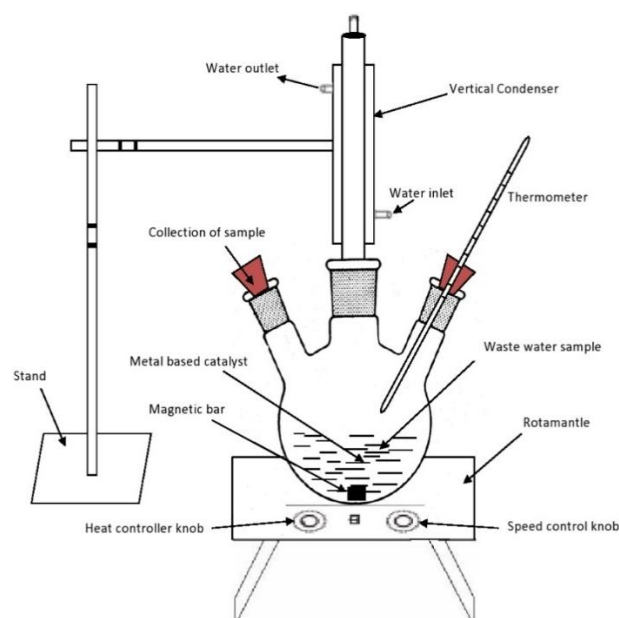


Figure 2: Experimental set-up of thermal catalytic process

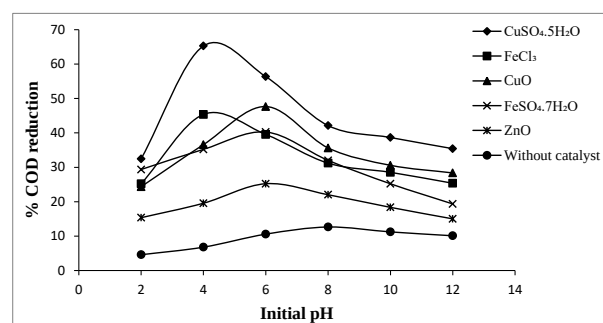


Figure 3: Effect of solution pH on COD reduction of the tannery wastewater by thermolysis (Experimental conditions: $\text{COD}_0 = 5970 \text{ mg/L}$, temperature = 95°C , reaction time = 5 h, catalyst mass loading (C_w) = 2 kg/m^3)

This paper provides information about the recent research on thermal catalytic process for the treatment of synthetic as well as real industrial wastewater. In a case study presented in this paper, the treatment of tannery wastewater using thermolysis process shows that it can degrade and mineralize the organic molecules which are hardly treatable by

conventional treatment techniques. The obtained results based on case study (treatment of tannery wastewater using thermolysis) showed that maximum 65.25% COD and 72.65% color were reduced using copper sulphate salt with catalyst mass loading of 2 kg/m³ at pH of 4. In all, it can be said that thermolysis process can be used as an effective treatment process for the treatment of other synthetic as well as real industrial wastewater.

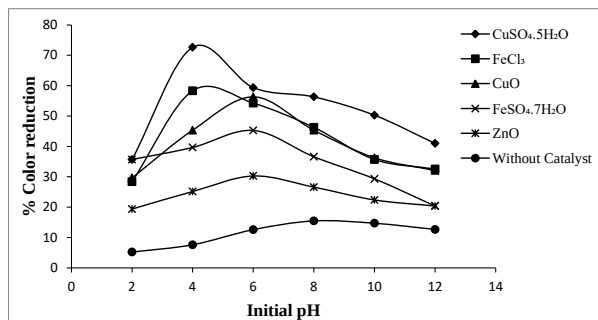


Figure 4: Effect of solution pH on color reduction of the tannery wastewater by thermolysis (Experimental conditions: COD₀ = 5970 mg/L, temperature = 95°C, reaction time = 5 h, catalyst mass loading (C_w) = 2 kg/m³)

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