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Studies on removal of formaldehyde from industrial wastewater by photocatalytic method

Ezhilkumar. P[1*], Selvakumar.K.V[1], Jenani R[1], Koperun Devi N[1], Selvarani M[1], V. M. Sivakumar[2]
[1]Department of Chemical Engineering, Adhiyamaan College of Engineering (Autonomous) - Hosur.
[2] Department of Chemical Engineering, CIT, Coimbatore.
***Corresponding author: E-Mail: ezhilfbt2007@gmail.com**

ABSTRACT

Nowadays, there are increasingly stringent regulations requiring more and more treatment of industrial effluents containing Formaldehyde. These can be treated by physical, chemical & biological methods. But chemical & biological processes have their own disadvantage like the aerobic treatment process is associated with production and disposal of large amounts of biological sludge, while wastewater treated by anaerobic treatment method does not bring down the pollution parameters to the satisfactory level and activated charcoal adsorption and air stripping methods simply transfer the pollutants from one medium to another. They either transfer it to the atmosphere, which causes air pollution, or to a solid which is often disposed off in landfills whereas physical process consumes more time & less effective. Therefore, Photo catalytic degradation were investigated for treatment of industrial effluents containing formaldehyde, by the formation of highly reactive free radical (OH^-) & converting it into biodegradable compound. In this study, the photocatalytic reaction of formaldehyde in an industrial effluent was studied in a batch reactor, using titanium di-oxide and zinc oxide as a catalyst. The industrial effluent was characterized. The photo catalytic performance for the reduction of COD level was verified for various initial concentration level of 500 to 4000 mg/liter by UV light. A maximum COD level of 98% from the effluent was achieved in 5 hours, at a pH of 7, low concentration of 500 mg/liter& power of UV lamp is 6 W. The reaction was influenced by the process parameters such as catalyst loading, initial pH and initial formaldehyde concentration, reaction time. In this study, photocatalytic process was identified as an alternative method for the treatment of formaldehyde containing waste water was proved to be feasible and effective.

KEY WORDS: Formaldehyde removal, Photo catalytic degradation, TiO_2 & ZnO, UV light, and COD level.

1. INTRODUCTION

Chemical industries are rated as one of the major polluting industries with discharge of effluents. Numerous treatment techniques have been practiced for treating chemical effluents like chemical coagulation, precipitation, co-precipitation, air floatation, flocculation, adsorption (Sivakumar, 2012; 2014), ion exchange process, membrane process, electro-dialysis (Sivakumar, 2014), biological process (Sivakumar, 2014), bioremediation (Sivakumar, 2014), phyto-extraction, constructed wetland (Sivakumar, 2014) etc. However, these treatments are cost extensive and do not reduce the pollutants to satisfactory level.

The low volatile compounds are organic chemicals that have a high vapor pressure at room temperature, this high vapor pressure have low boiling point, which causes large number molecules to evaporate from liquid or solid form of the compound and enter the surrounding air. Among the many chemical compounds usually present in polluted air, there is one that can be considered paradigmatic because of its omnipresent: formaldehyde. It is a major industrial chemical, especially used as an intermediate; production of urea and phenol-formaldehyde resins, polyoxymethylene plastics, 1,4-butanediol, and methylene diphenyl diisocyanate are its primary destinations, other products includes paints, adhesives, cleaning products, fertilizers, coating cosmetics and also found as a typical product in smoke. At room temperature, formaldehyde is a colorless gas with strong pungent odour.

These can be treated by physical, chemical & biological methods. But chemical & biological processes have their own disadvantage by causing pollution whereas physical process consumes more time & less effective. Among the individual treatment systems proposed, photo catalytic systems received greater attention due to the reputations and it helps in removing formaldehyde from waste water which is present in a greater concentration.

The low volatile compounds can be discharged to environment from various industrial effluents such as Paint industry, electroplating, pharmaceutical, petrochemical industries, municipal wastewater, paper and pulp wastewater, brackish water, portable water, oil mill wastewater, nitrite effluent, textile dyes, agro industries wastewater and laundry wastewater. VOC's are not actually toxic but have long-term compounding health effects. The effects of formaldehyde exposure to human health ranges from simple headache to nausea and chest tightness. At concentration ranges from 0.01 to 2.0 ppm, it causes eye irritation and concentration from 5 to 30 ppm causes pulmonary effects and carcinogenic problems. It is present at low concentrations, at place where people stay for a long period.

The main advantage of this process is the ability of using sunlight with light sensitivity up to 450 nm, thus avoiding the high costs of UV lamps and electrical energy. These reactions have been proven more efficient than the other processes. The advantages that make photo catalytic techniques superior to traditional methods are the ability to remove contaminates in the range of ppb, no generation of polycyclic compounds, higher speed and lower cost.

1.1. Objectives: To study the degradation potential of photo catalytic process in degrading the low volatile organic compounds present in industrial effluents. To find the optimum operating conditions for the specified treatment scheme. To verify the suitability of available Mathematical models for the process scheme.

1.2. Industrial applications: The textile industry uses resins of formaldehyde as finishers to make fabrics crease-resistant. These treated with phenol, urea or melamine, produces hard thermoset phenol, urea formaldehyde resin and melamine resin respectively. These are permanent adhesives used in plywood and carpeting. Other formaldehyde derivatives like methylene diphenyl diisocyanate, an important component in polyurethane paints, foams and hexamine, are used in explosive RDX. Methylene glycol a type of formaldehyde is used in hair smoothing treatments to straighten wavy/curly hair and make hair less prone to high humid weather.

2. MATERIALS AND METHODS

Photo catalytic methods rely on the formation of highly reactive chemical species that degrade more number of recalcitrant molecules into biodegradable compounds.

The semiconductor may be in the form of a powder suspended in the water or fixed on a support. The most active photo catalyst for this application is the Anastasi form of TiO_2 because of its high stability, good performance and low cost (Andreozzi, 1999). The primary photo catalytic mechanism is believed to proceed as follows:

$$TiO_2 + hv \rightarrow e\text{-}_{CB} + h_{+VB}$$
$$h_{+VB} + H_2O \rightarrow OH^- + H^+$$
$$e_{-CB} + O_2 \rightarrow O_2$$
$$2O_2 + 2H_2O \rightarrow H_2O_2 + 2OH + O_2$$
$$H_2O_2 + e_{-CB} \rightarrow OH^- + OH$$

In solids the electrons occupy energy bands as a consequence of the extended bonding network. In a semiconductor the highest occupied and lowest unoccupied energy bands are separated by a band gap region devoid of energy levels. Activation of semiconductor photo catalyst is achieved through the absorption of a photon of ultraviolet band gap energy which results in promotion of an electron (e-) from the valence band (VB) into the conduction band (CB) with the generation of hole in the valence band. The resulting hole is an oxidizing agent and electron is a reducing agent. In the generally accepted mechanism for the photo catalytic process, the hole can react with water to generate hydroxyl radical and the electron can reduce molecular oxygen, hydrogen peroxide or some other oxidizing agent in the solution. This creates the reactive radicals responsible for the removal of hazardous components from the water.

2.1. TiO_2/ UV process is known to have many advantages: A large number of organic compounds dissolved or dispersed in water can be completely mineralized. The rate of reaction is relatively high if large surface area of the catalyst can be used. TiO_2 is available at a relatively modest price and can be recycled on a technical scale. UV lamps emitting in the spectral region required to initiate the photo catalytic oxidation are well known and are produced in various sizes. Absorption cross-section of TiO_2 can be improved by its surface modifications, e.g. by transition metal ion doping.

2.2. Samples: The synthetic wastewater containing formaldehyde of various concentration range of 500 to 4000 mg/l was prepared by considering the commercial waste water containing formaldehyde.

2.3. Catalysts: TiO_2 was bought and used as in required quantity level. ZnO was bought and used as in required quantity level.

2.4. Reagents and Chemicals: Reagents used for COD determination are potassium dichromate, mercuric sulphate, silver sulphate, concentrated sulphuric acid, ferrous ammonium sulphate and ferroin indicator. In all the experiments, double distilled water was used.

2.5. Apparatus required: COD Digester, Burette & Burette stand, COD vials with stand, 250mL conical flask (Erlenmeyer flask), Pipettes & Pipette stand, Tissue papers, Wash Bottle.

2.6. Equipment and instruments: The equipment which we used for the treatment of formaldehyde is Immersion Well type Photo Reactor. An immersion well type photochemical reactor made of Pyrex glass equipped with a water-circulating jacket maintaining a temperature of 25°C and an opening for supply of oxygen was used. The photo catalytic reactor is provided with one more inlet (sampling port) through which the samples are taken with the help of syringe from time to time during the experiment. The photo reactor is placed on a magnetic stirrer. An 18W UV lamp is placed in the center of the photo reactor as a source of UV and visible light respectively.

2.7. Process description: Experiment is carried out by adding formaldehyde at various concentrations (500 to 4000 mg/l) of deionized water to simulate waste water. Then, we added TiO_2 (0.2 g) and put the beaker with the solution on a stirring plate. A 6W UV bulb and a second beaker was carefully placed inside the solution to activate the TiO_2. Every 1 hour we took a sample of the solution and centrifuged it to separate the $TiO_2$from the rest of the solution. Next, we made COD analysis for sample solution. Similarly the same procedure was carried out by using ZnO (0.35 g) as catalyst.

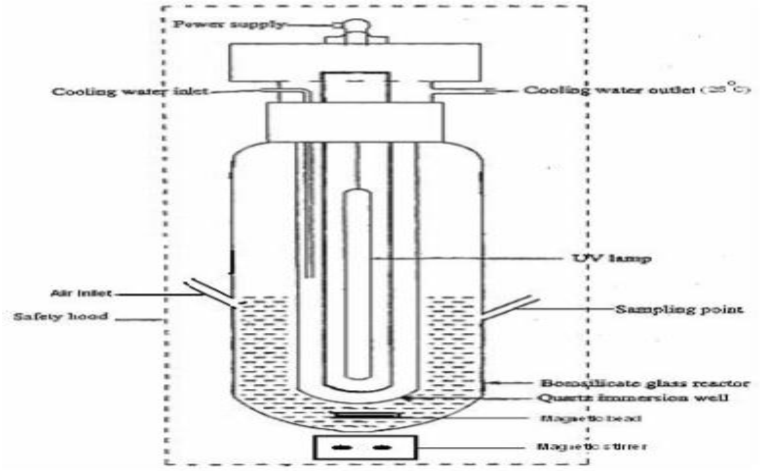

Fig.1. Effects of Formaldehyde Concentration

2.8. Determination of chemical oxygen demand: The chemical demand (COD) test is commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers), making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution. COD is the measurement of the amount of oxygen in water consumed for chemical oxidation of pollutants. COD determines the quantity of oxygen required to oxidize the organic matter in water or waste water sample, under specific conditions of oxidizing agent, temperature, and time. This method covers the determination of COD in ground and surface waters, domestic and industrial waste waters.

The organic matter present in sample gets oxidized completely by potassium dichromate ($K_2Cr_2O_7$) in the presence of sulphuric acid (H_2SO_4), silver sulphate ($AgSO_4$) and mercury sulphate ($HgSO_4$) to produce CO_2 and H_2O the sample is refluxed with a known amount of potassium dichromate ($K_2Cr_2O_7$) in the sulphuric acid medium and the excess potassium dichromate ($K_2Cr_2O_7$) is determined by titration against ferrous ammonium sulphate, using ferroin as an indicator. The dichromate consumed by the sample is equivalent to the amount of O_2 required to oxidize the organic matter.

3. RESULTS

Table.1. Effect of various initial formaldehyde concentration on percentage reduction COD

Formaldehyde Concentration (mg/L)	Percentage Reduction of COD
500	62.3
1000	56.4
2000	35.5
3000	22.1
4000	10.8

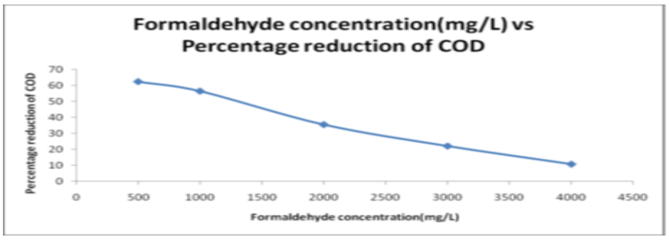

Fig.2. Effects of Formaldehyde Concentration

The experiments were conducted for different initial concentration of formaldehyde. For those parameters the optimum level was identified. The range of initial concentration of formaldehyde was taken as 500 mg/l to 4000 mg/l. The graph shows initial concentration value of formaldehyde as 500mg/l with the percentage reduction of COD was 62.3%. And the final value of formaldehyde concentration as 4000mg/l with the percentage reduction of COD was 10.8%. For the concentration of formaldehyde the optimum level was found to be 500 mg/l and gradually decreases.

Table.2. Effect of various pH on percentage reduction COD

pH Values	Percentage Reduction of COD
1	0
2	12.2
3	18.4
4	33.4
5	52.1
6	54
7	56.6
8	48.8
9	42.1
10	40

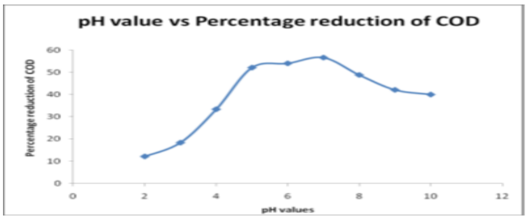

Fig.3. Effect of various initial pH

The experiments were conducted for different initial pH values. For those parameters the optimum level was identified. The range of initial pH values 1 to 10.The graph shows initial value of pH as 1 with the percentage reduction of COD is 12.2%. And the final value of pH as 10 with the percentage reduction of COD is 40%.For the various pH the optimum level was found to be 7 and graph shows increases then gradually decreases.

Table.3. Effect of various reaction times on percentage reduction of COD

Reaction Time (Hr)	Percentage Reduction of COD
1	**5**
2	**11**
3	**24**
4	**35**
5	**38**

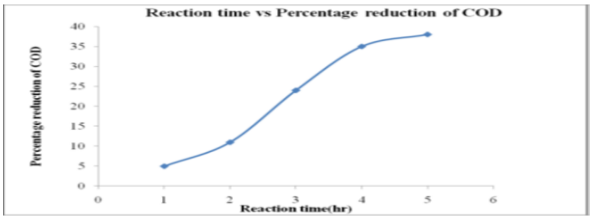

Fig.4. Effect of various reaction time

The experiments were conducted for initial reaction time. For those parameters the optimum level was identified. The reaction time was taken in the range of 1 to 5. The graph shows the initial value of reaction time as 1 with the percentage reduction of COD was 5%. And the final value of reaction time as 5 with the percentage reduction was COD is 38%. For the reaction time the optimum level was found to be 4 to 5 hrs and the graph gradually increases.

Table.4. Effect of catalyst loading ZnO (g) on their percentage reduction of COD

Mass of ZnO (g)	Percentage reduction of COD
0	0
0.05	25
0.10	44
0.15	55
0.20	74
0.25	80
0.30	85
0.35	86
0.40	79

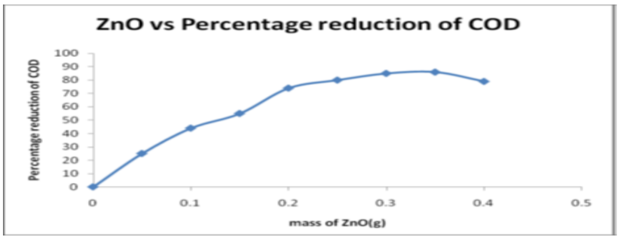

Fig.5. Effect of Catalyst Loading ZnO (g)

The experiments were conducted for different catalyst as ZnO. For that parameter the optimum level was obtained. The initial mass of ZnO values 0.05 to 0.40. The graph shows the initial value of mass of ZnO as 0.05 with the percentage reduction of COD was 25%. And the final value of mass of ZnO as 0.40 with the percentage reduction of COD was 79%. For the catalyst loading (ZnO) the optimum level was found to be 0.35g and graph shows gradually increases

Table.5. Effect of catalyst loading TiO_2 (g) on their percentage reduction of COD

Initial concentration	Catalyst Dosage(TiO_2), g	Percentage Reduction of COD
1	0.05	28
2	0.10	44
3	0.15	49
4	0.20	50
5	0.25	48
6	0.30	45
7	0.35	41

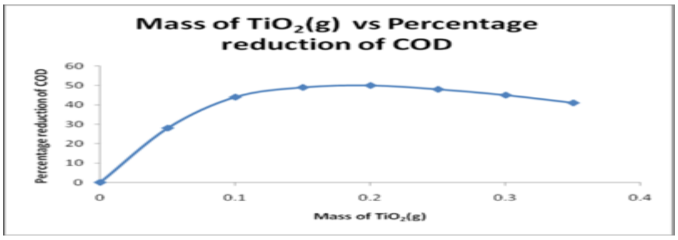

Fig.6. Effect of Catalyst Loading TiO_2 (g)

The experiments were conducted for different catalyst dosage using TiO_2. From the graph the optimum level was obtained. The range of catalyst dosage was taken as 0.05 to 0.35. The graph shows the initial value of mass of TiO_2 as 0.05 with the percentage reduction of COD was 28%. And the final value of mass of TiO_2 as 0.35 with the percentage reduction of COD was 41%. For the catalyst loading (TiO_2) the optimum level was found to be 0.2g and graph shows gradually increases.

4. CONCLUSION

The experiments were conducted for different parameters such as varying formaldehyde concentrations, reaction time, pH values, varying the catalysts as TiO_2 and ZnO. From the experimental value the optimum level of various parameters was obtained.

a) For the initial concentration of formaldehyde the optimum level was found to be 500 mg/l.
b) The optimized pH value was found to be 7.
c) The optimized level of reaction time was found to be 5 hrs.
d) For the catalyst loading (TiO_2) the optimum level was found to be 0.2g.
e) For the catalyst loading (ZnO) the optimum level was found to be 0.35g.

REFERRENCES

Akyol A, and Bayramoglu M, Photocatalytic degradation of Remazol Red F3B using ZnO catalyst. J. Hazard. Mater, 124, 2005, 241–246.

Akyol A, Yatmaz H.C, and Bayramoglu M, Photocatalytic decolourization of Remazol Red RR in aqueous ZnO suspensions, Applied Catal. B: Environ., 54, 2004, 19–24.

Alinsafi A, Evenou F, Abdul Karim E.M, Pons M.N, Zahraa O, Benhammou A, Yaacoubi A, and Nejmeddine A, Treatment of textile industry wastewater by supported photo catalysis, Dyes. Pigm., 74, 2007, 439- 445.

Bauer R, and Fallmann H, The photo-Fenton oxidation—a cheap and efficient wastewater treatment method, Res. Chem. Interned., 23, 1997, 341–354.

Chacon J.M, Leal M.T, Sanchez M, and Bandala E.R, Solar Photocatalytic degradation of azo-dyes by photo-Fenton process, Dyes. Pigm., 69, 2006, 144-150.

Chu W, and Wong C.C, The photo catalytic degradation of dicamba in TiO_2 suspensions with the help of hydrogen peroxide by different near UV irradiation, Water Res., 38, 2004, 1037–1043.

Glaze W.H, Kang J.W, and Chapin D.H, The chemistry of water treatment processes involving ozone, hydrogen peroxide and UV-radiation, Ozone Sci. Eng., 9, 1987, 335-352.

Hachem C, Bocquillon F, Zahraa O, and Bouchy M, Decolourization of textile industry wastewater by the photo catalytic degradation process, Dyes. Pigm., 49, 2001, 117–125.

Harrelkas F, Paulo A, Alves M.M, Khadir L.E, Zahraa O, Pons M.N, and Vanderzee F.P, Photocatalytic and combined anaerobic–photo catalytic treatment of textile dyes, Chemosphere, 72, 2008, 1816-1822.

Konstantinou I.K, and Albanis T.A, TiO_2-assisted Photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations A review, Applied Catal. B: Environ., 49, 2004, 1–14.

Muneer M, Bahnemann D, Qamar M, Tariq M.A, and Faisal M, Photo catalysed reaction of few selected organic systems in presence of titanium dioxide, Appl. Catal. A: Gen., 289, 2005, 224–230.

Munter R, Advanced Oxidation Processes- Current Status and Prospects. Proc. Estonian Acad.Sci.Chem., 50, 2001, 59-80.

Muruganandham M, and Swami Nathan M, Solar Photocatalytic degradation of a reactive azo dye in TiO_2-suspension, Sol. Energy. Mat. Sol. C., 81, 2004, 439–457.

Neelavannan M.G, Revathi M, and Ahmed Basha C, Photocatalytic and electrochemical combined treatment of textile wash water, J. Hazard. Mater., 149, 2007, 371–378.

Pera-Titus M, Garcia-Molina V, Banos M.A, Gimenez J, and Esplugas S, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Applied Catalysis, B47, 2004, 219-256.

Riga A, Soutsas K, Ntampegliotis K, Karayannis V, and Papapolymerou G, Effect of system parameters and of inorganic salts on the decolourization and degradation of Procion H-exl dyes, Comparison of H_2O_2/UV, Fenton, UV/Fenton, TiO_2/UV and TiO_2/UV/H_2O_2 processes, Desalination, 211, 2007, 72–86.

Saien J, and Soleymani A.R, Degradation and mineralization of Direct Blue 71 in a circulating upflow reactor by UV/TiO_2 process and employing a new method in kinetic study, J.Hazard.Mater., 144, 2007, 506–512.

Silva C.G, Wang W, and Faria J.L, Photocatalytic and photochemical degradation of mono-di- and tri-azo dyes in aqueous solution under UV irradiation, J. Photoch. Photo bio. A, 181, 2006, 314–324.

Sivakumar D, Gayathri G, Nishanthi R, Vijayabharathi V, Sudeshna Das, and Kavitha R, Role of fungi species in colour removal from textile industry wastewater, International Journal of ChemTech Research, 6, 2014, 4366–4372.

Sivakumar D, Murugan N, Rajeshwaran R, Shobana T, Soundarya C, and Vanitha V.S, Role of rice husk silica powder for removing Cr (VI) in a tannery industry wastewater, International Journal of ChemTech Research, 6, 2014, 4373–4378.

Sivakumar D, Shankar D, Dhivya P, and Balasubramanian K, Bioaccumulation study by *lemna gibba* lin., Pollution Research, 33, 2014, 531–536.

Sivakumar D, Shankar D, Gomathi V, and Nandakumaar A, Application of electro-dialysis on removal of heavy metals, Pollution Research, 33, 2014, 627–637.

Sivakumar D, Shankar D, Kandaswamy A.N, and Ammaiappan M, Role of electro-dialysis and electro-dialysis cum adsorption for chromium (VI) reduction, Pollution Research, 33, 2014, 547–552.

Sivakumar D, Shankar D, Vijaya Prathima A.J.R, and Valarmathi M, Constructed wetlands treatment of textile industry wastewater using aquatic macrophytes, International Journal of Environmental Science, 3, 2013, 1223–1232.

Sivakumar Durairaj, and Shankar Durairaj, Colour removal from textile industry wastewater using low cost adsorbents, International Journal of Chemical, Environmental and Pharmaceutical Research, 3, 2012, 52–57.

Tang C, and Chen V, The Photocatalytic degradation of reactive black 5 using TiO_2/UV in an annular photo reactor, Water Res., 38, 2004, 2775–2781.