Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27903

243 (2021) 206–210
December

Degradation of formaldehyde from wastewater by batch re-circulation process using a photocatalytic reactor

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Received 28 April 2021; Accepted 1 October 2021

ABSTRACT

The most abundant component in industrial effluent is the carcinogenic formaldehyde. The presence of formaldehyde in industrial waste water is increasing day by day. It can be removed by various processes viz., photocatalytic reaction, electrochemical methods, and biological methods. This study involves the degradation of formaldehyde by photo catalytic method. In the biological method, the maximum percentage reduction of formaldehyde was achieved at low initial formaldehyde concentration range of 100–300 mg/L. For higher concentration more than 300 mg/L, the most efficient method is the photo catalytic degradation. The experiments were conducted in a UV photo catalytic reactor and it was a batch reactor with recirculation process. It was carried out at various initial formaldehyde concentrations such as 500; 1,000; and 1,500 mg/L and the feed flow rate was adjusted 4, 8, and 12 LPH. The flow rate of the feed was controlled by using peristaltic pump. The pH of the feed solution maintained was 7 and the catalyst dosage was fixed to 0.3 g/L. The sample was collected at each 1 h interval and analyzed by UV-Visible spectrophotometer at 410 nm by using Hantzsch reagent method. For initial concentration of 1,000 mg/L at 8 LPH, the maximum efficiency of 76% was obtained when compared to other concentration. From the study, it was predicted that photo catalytic method is most feasible for higher concentrations.

Keywords: Formaldehyde; Photocatalytic degradation; Zinc oxide; UV spectrophotometer

1. Introduction

Water is the major component used in the chemical industry. For the welfare of the environment, we have to remove harmful component present in the effluent waste water. The waste water contains many harmful agents such as heavy metals, acids, salts, and organic toxic pollutants such as volatile organic compounds (VOCs). VOCs are major toxic chemicals which are harmful to humans and environment [1]. Environmental pollution caused by volatile organic compounds, such as formaldehyde, is most serious problem at present [2]. Formaldehyde is one of the carcinogenic contents present in industrial wastewater that could harm our environment and human. Most industries use formaldehyde for produce materials such as urea formaldehyde resin, melamine resin, and phenol formaldehyde resin. Industries such as textile, plastic, automobile, and wood processing uses formaldehyde. Usage of formaldehyde in medicine, pesticides, and biocides is predominant. Therefore, chance of formaldehyde in varying quantity may be prevalent in industrial waste water [3].

Chemical and biological treatments have been followed till now, but these treatment methods have their own drawbacks. Formaldehyde concentration ranging from 10 to 100 mg/L can be toxic to the microbial community of wastewater treatment plants as a result of the rapid

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interaction of formaldehyde molecules with DNA and RNA of the microorganisms [4,5]. Thus, biodegradation of formaldehyde using biological wastewater treatment technologies is ineffective to achieve a desirable effluent characteristics. Various physico-chemical techniques such as electrochemical and adsorption processes have been used to degrade formaldehyde in aqueous solutions. But the application of advanced oxidation processes (AOPs) has fascinated environmental researches with more attention due to the generation of hydroxyl radical (OH^-) as the most powerful oxidant for decomposition formaldehyde [6]. Among different AOPs, photocatalytic processes have been widely used in recent years due to their high potential to degrade various organic pollutants [7].

Photocatalytic method is regarded as one of the most promising technologies for purification of waste water. Photocatalysis involves removal of water contaminants that are chemically stable and resistant to biodegradation. Photocatalysis is technological solutions that involve oxidative degradation of a wide range of organic pollutants in gas or liquid phase [8]. Photocatalysis is a method which can oxidize the VOCs into CO_2 and H_2O at room temperature and atmospheric pressure [9]. The photocatalytic method has wide applications in the waste water treatment, due to high availability of OH in water. The photocatalytic processes offer a number of advantages for the removal of pollutants from water, complete mineralization, and use of low cost catalyst system. Photo catalytic systems do not require additional resources except electricity to power the sources irradiation. Photo catalytic method works at the temperature of ambient environment which excludes the need for heating of the treated emissions [10].

The ideal photo-catalytic method should possess the following properties.

- Photo activity, low cost, and non-toxic nature: for large scale environmental cleanup operations, the photo catalyst has to be available at low cost without toxic properties to flora and fauna especially, when used at large concentrations.
- Biological and chemical inertness: the catalyst used in the process of substrate treatment must not promote the formation of other complex and undesirable products.
- Stability toward photo-corrosion: the catalyst must not undergo corrosion under prolonged light exposure; it has to be stable to tolerate the long light exposure which will be persistent throughout the process.
- Suitability toward visible or near UV light: an excitation source which is essential for initiation of reaction must be of low energy in the visible of near UV region so that the high radiation energy is not required.

Though several catalysts have been studied, but ZnO and TiO_2 have been found to be the most commonly used photo catalyst in heterogeneous photocatalysis, due to good stability, non-toxicity, and insolubility. Compared to TiO_2, the ZnO has been considered as a promising photocatalyst because of its low cost, with wide band gap (3.37 eV), and high potential to adsorb UV irradiation with a large exciton binding energy of 60 meV. The most important advantages of ZnO are absorbing bigger fraction of the solar spectrum and also more active in sunlight than TiO_2. Electron hole pair also limits the efficiency of TiO_2 due to rapid recombination. Moreover, ZnO is more stable in high temperatures [11]. The generation of OH^- during aphotocatalytic process conducted with ZnO as below:

$$ZnO + hv \rightarrow ZnO\left(e^- + h^+\right) \quad (1)$$

$$h^+ + H_2O \rightarrow OH^- + H^+ \quad (2)$$

In this study, the degradation of formaldehyde from waste water by batch re-circulation process using photo-catalytic reactor was performed with experimental studies to reveal the effect of initial concentration and flow rate on percentage reduction.

2. Materials and methods

2.1. Sample preparation

The synthetic effluent containing formaldehyde used in the experiment was prepared by using the distilled water at varying concentration such as 500; 1,000; and 1,500 mg/L. Formaldehyde and other chemicals used in the study were of analytical grade were procured from Hi Media Laboratories Pvt., Ltd., India. Zinc oxide (ZnO) was used as a catalyst with a dosage concentration of 0.3 g/L.

2.2. Reagents preparation

2.2.1. Reagent with pentane 2,4-dione

Pentane 2,4-dione reagent was prepared by dissolving 15 g of ammonium acetate in 70 mL of distilled water and 0.3 mL of acetic acid was added. Then, 0.2 mL of pentane 2,4-dione was added in the solution and made to 100 mL

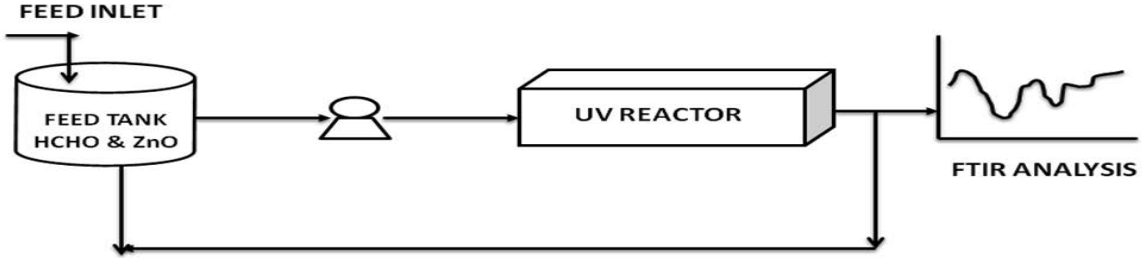

Fig. 1. Batch recirculation process.

by adding distilled water. The pH of solution was adjusted to 7 and monitored using the pH meter [12].

2.2.2. Reagent without pentane 2,4-dione

Pentane 2,4-dione reagent was prepared by dissolving 15 g of ammonium acetate in 70 mL of distilled water and 0.3 mL of acetic acid was added and made to 100 mL by using distilled water.

2.3. Batch recirculation process

In batch recirculation process, the feed stream after degradation recirculated to the main stream (Fig. 1) for the purpose of higher efficiency.

The present study focuses on photocatalytic degradation of formaldehyde with ZnO as catalyst at constant pH. The dosage of the catalyst was optimized and fixed. Initial formaldehyde concentration of the feed and the flow rate were varied for optimization of the parameters for degradation of formaldehyde.

2.4. Photo-catalytic reactor

The experiments were conducted in a UV-photo catalytic reactor (Flow and Force Engineers, Bengaluru) as shown in Fig. 2. The reactor used is a batch type with recycle process. The reactor is made up of a glass tube of 500 mL and is jacketed by an outer jacket. The outer jacket consists of two openings, one for the inlet of the water and the other for the outlet of the water. The outer jacket was circulated with cooling water to avoid the excess heat and the ambient temperature was maintained inside the reactor. The opening at the top of the reactor is meant to insert the UV light of 6 W which can be fit firmly in the space provided. The outer jacket is being opaque and it avoids the passage of light to the surrounding.

2.5. Experimental procedure

Photocatalytic degradation of formaldehyde experiments were carried out at different initial formaldehyde concentrations such as 500; 1,000; and 1,500 mg/L. For each concentration, the feed flow rate was varied at 4, 8, and 12 LPH by using peristaltic pump (Ravel Hiteks Pvt., Ltd., Chennai). The pH of the feed solution was maintained at 7 and the dosage of catalyst was fixed to 0.3 g/L [13]. The photo treated sample (Fig. 3) was collected at each 1 h interval and filtered using Watsmann filter paper for the complete removal of ZnO catalyst. The samples were analyzed by UV-Visible spectrophotometer (Elico Ltd., Hyderabad) at 410 nm by using Hantzsch reagents [14]. Both raw and UV-treated samples were characterized using FTIR analyzer (Brukers – Aplha Series, Germany).

3. Results and discussion

3.1. Effect of flow rate on percentage reduction

It was observed that the reduction of formaldehyde was increasing in logarithmic rate with respect to time as reported in Figs. 4–6. For the flow rate of 4 LPH, after treatment for 12 h with ZnO, the rate of reduction of HCHO for an initial concentration 500 mg/L, was witnessed to be the maximum of 28.4% (Fig. 4) as compared to the other flow rates (8 and 12 LPH). The increase in the flow rate resulted in increased oxidation rate of the formaldehyde [15]. Simultaneously, the rate of degradation of formaldehyde increases with increase in the flow rate. The rate of reduction of HCHO of initial concentration 1,000 mg/L with respect to time is shown in the Fig. 5. For this concentration of HCHO, the maximum reduction of 76% was observed for the flow rate of 8 LPH after treatment for 12 h which is the maximum percentage reduction reported in this study. The rate of reduction of HCHO with an initial concentration of 1,500 mg/L with respect to time is reported in Fig. 6. The maximum reduction of 58.4 was observed for the flow rate of 4 LPH after treatment of 12 h with ZnO catalyst. Decreasing removal efficiency with increasing initial concentration may be due to the limited number of active sites for the subsequent generation of hydroxyl radicals to degrade

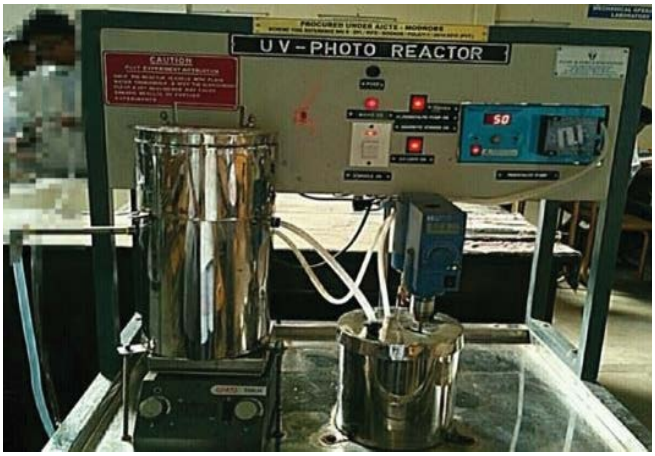

Fig. 2. Photo catalytic reactor with UV-light source.

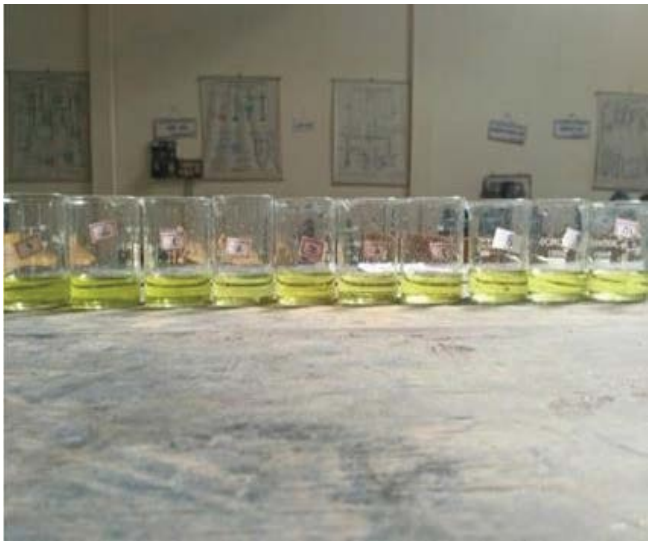

Fig. 3. Photo treated samples after reaction.

high initial concentrations at specified short reaction time [16]. Additionally, the amount of formaldehyde removed via photocatalytic process is directly corresponding to the probability of the generation of OH^- and subsequently the probability of the interaction between OH^-, and the formaldehyde molecules. Moreover as the flow rate decreases, the residential time should be increased. Therefore, for initial concentration of 1,500 mg/L, the maximum removal efficiency was achieved for 4 LPH. The optimal flow rate of the feed for the degradation of formaldehyde was observed as 8 LPH after the treatment time of 12 h using ZnO at constant dosage of 0.3 g/L at constant pH7 [11].

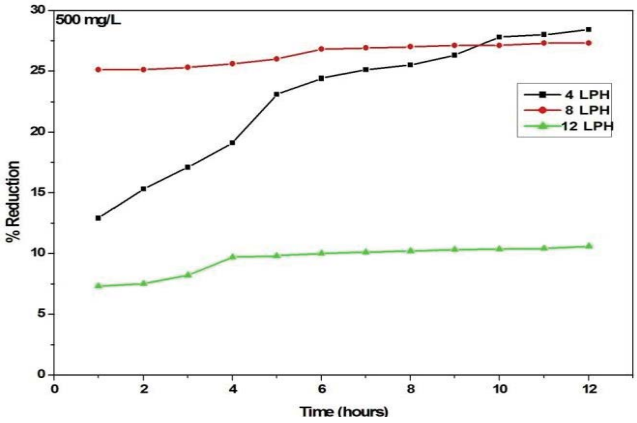

Fig. 4. Effect of flow rate on HCHO degradation at 500 mg/L initial concentration.

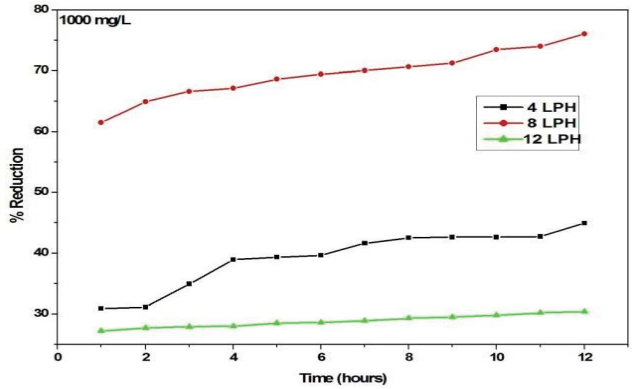

Fig. 5. Effect of flow rate on HCHO degradation at 1,000 mg/L initial concentration.

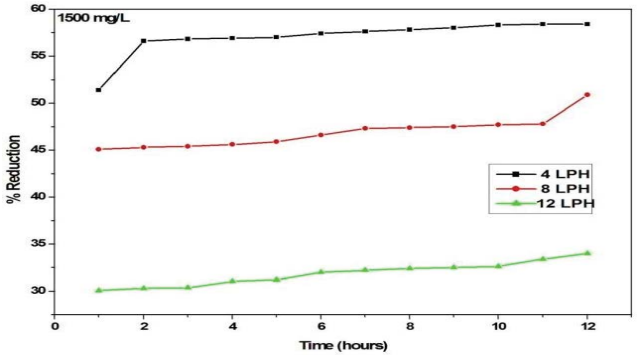

Fig. 6. Effect of flow rate on HCHO degradation at 1,500 mg/L initial concentration.

3.2. Effect of initial concentration of HCHO on percentage reduction

Initial formaldehyde concentrations of 500; 1,000; and 1,500 mg/L were selected to evaluate the efficacy of the photocatalytic process with ZnO catalyst under different formaldehyde concentrations. Fig. 7 represents the effect of initial concentration on the reduction of HCHO after treatment with ZnO. The maximum reduction was observed at 1,000 mg/L concentration after the treatment of ZnO for 8 and 12 LPH. As shown in Fig. 7, the removal efficiency of formaldehyde declined as the initial concentration of formaldehyde increased. Increasing the formaldehyde concentration from 500 to 1,000 mg/L at a flow rate of 8 LPH resulted in an increase in the removal efficiency from 27.3% to 76.0%, respectively, at a reaction time of 12 h, while increasing the concentration to 1,500 mg/L led to decrease in a removal efficiency of about 25.1% within the same reaction time. The results indicated the need for more time to achieve the appropriate removal efficiency of formaldehyde at higher concentrations [11]. The higher the initial formaldehyde concentration, the longer the time needed to reach acceptable removal efficiency. Decreasing removal efficiency with increasing initial concentration may be due to the limited number of active sites for the subsequent generation of hydroxyl radicals to degrade high initial concentrations at specified short reaction time. Additionally, the amount of formaldehyde removed via photo-catalytic process is directly corresponding to the probability of the generationof OH^- and subsequently the probability of the interaction between OH^-, and the formaldehyde molecules. Therefore, increasing the initial concentration of the formaldehyde caused an evident decrease in the interaction of OH^- with formaldehyde molecules [17].

3.3. FTIR analysis before and after treatment

Figs. 8 and 9 represent the FTIR spectra of HCHO of 1,000 mg/L of HCHO before treatment with ZnO and after treatment with ZnO. The samples were characterized before UV-treatment, showed peak intensity at wave number of

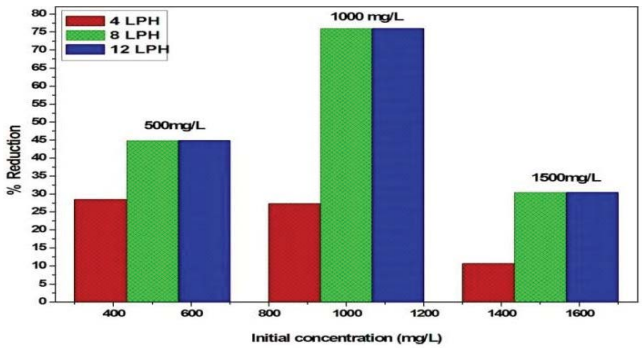

Fig. 7. Effect of initial HCHO concentration on % reduction.

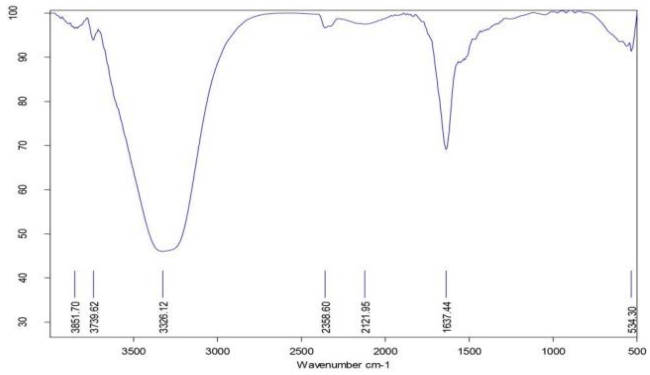

Fig. 8. FTIR analysis before treatment.

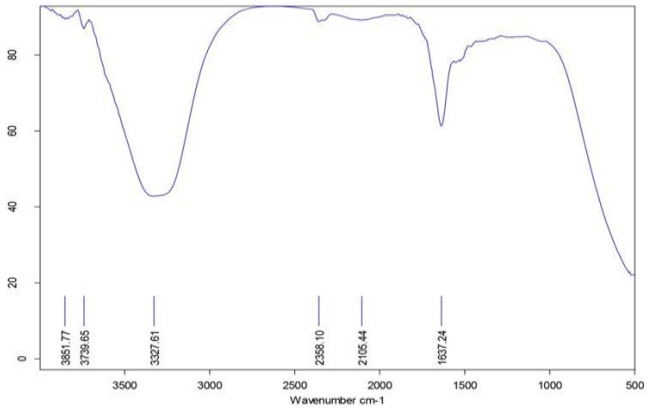

Fig. 9. FTIR analysis after treatment.

1,739.82 cm^{-1}, which may be due to the presence of aldehyde group (Fig. 8). It is attributed to C=O stretching in aldehyde group. This region reveals changes in intensity and shifts in the peaks position due to biodegradation in the sample after treatment (Fig. 9). Both samples (before and after formaldehyde biodegradation) showed two major absorption bands at 1,637 cm^{-1} and between 3,326 and 3,328 cm^{-1}. The bands in the range of 1,650–1,580 cm^{-1} are attributed to the N–H bending in amine group. The bands in the range of 3,500–3,200 are attributed to the hydrogen-bonded OH group of alcohols and phenols [6,18].

4. Conclusion

A batch process with recirculation was performed with photo-catalytic reactor for the photo-catalytic degradation of formaldehyde from waste water effluent under different experimental conditions of feed rate and initial concentration of formaldehyde. The experimental results confirmed that percentage reduction of formaldehyde increases, if solution reaches a maximum at a fixed catalyst dosage of 0.3 g/L and reported as 76.0% for the initial concentration of 1,000 mg/L and flow rate of 8 LPH at pH 7.

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