An Efficient-Green-Catalytic Process For Degradation Of Organic Pollutants In Industrial Waste Waters

Raj Kumar Sharma, Jyoti Sharma, D. V. Rai and Mohammad Zafar

Agri Informatics Engineering, Shobhit University, Meerut (UP), India

Abstract

The feasibility of a catalytic liquid-phase oxidation process using copper sulphate to treat the organic pollutant of industrial wastewater derived from a chemical industry. The effect of the operating parameters such as temperature, pressure, pH, and residence time on COD removal efficiency was studied. The experiments were conducted in a stainless steel autoclave reactor and the maximum of 91.61% of COD removal was achieved after 150 min of reaction time at 230° C temperature and 34 kg/cm² pressure, resulting a significant improvement in organic effluent discharge of industry. An ideal pressure of 31 kg/cm² in reactor was determined that favoured the maximum COD removal of 78.80%. Here, the copper sulphate catalyst was found as an effective homogeneous catalyst for maximum degradation of organic pollutants. This catalytic liquid-phase oxidation technique shows the significant potential for the treatment of organic content of industrial wastewater.

Key words: Homogeneous catalyst; Catalytic liquidphase oxidation; Industrial wastewater treatment; Organic pollutants; COD removal.

1. Introduction

Water is an essential substance for living systems as it allows the transport of nutrients and waste products in living systems. Research shows a clear correlation between diseases and the amount and types of fluids consumed, health-promoting properties of nutrients which can be added to water, optimal intake levels, and consumption patterns [1]. Conventional technologies have been established in removing many chemical and microbial contaminants of concern to public health and the environment. However, the effectiveness of these processes has become limited over the last two decades because of new challenges [2]. Industrial wastewaters containing organic pollutant usually have a very complex and toxic while required several remediation treatment. At present, several physicochemical, thermal and biological technologies used to remove the aqueous pollutants. Although these conventional process do not give satisfactory results, because these organic pollutant are inhibitory and toxic [3]. Some other techniques such as flocculation, precipitation, adsorption and reverse osmosis require a posttreatment dispose of the pollutants from the newly contaminated environment.

Several technologies like Fenton, ozonation, photo catalysis, catalytic liquid – phase oxidation etc. are included in the advanced processes and their main difference is the source of radicals. Catalytic liquidphase oxidation process, which is one of the most economically and technologically viable process for wastewater treatment [4]. Moreover, it shows satisfactory results at relatively mild operating conditions of temperature and pressure, while lead to substantially lower investment and operation cost. It refers to aqueous phase oxidation of organics components at elevated temperatures and pressures using a gaseous source of oxygen (either pure oxygen or air). Elevated temperatures are required to increase the oxidation rate and solubility of oxygen in the aqueous solution, while elevated pressures are required to keep water in liquid state. Water provides an excellent heat transfer medium which enables the process to be thermally self-sustained with relatively low organic feed concentrations [5]. This process involves a number of oxidation and hydrolysis to degrade the hazardous organic compounds into carbon dioxide, water vapours, nitrogen and ammonia. In this process, the reaction can be carried out to pressures from 5 to 200 kg and temperatures comprises between 100 and 320°C using homogeneous catalysts. It is an

efficient process for the treatment of a great diversity of organic pollutant in industrial wastewater. Depending on the conditions (temperature and pressure), two different objectives can be reached: (i) a total mineralization of the polluting agents to CO_2 , N_2 , and H_2O or (ii) an increase of the biodegradability of the polluting agent when orienting the reaction towards the by-product formation is easier to biodegradable **[6]**.

In catalytic liquid – phase oxidation process, organic pollutants can efficiently be removed at much milder conditions in the presence of suitable homogeneous catalyst. This significantly cuts capital and operational costs compared with other established process. The purpose of this study to investigate the performance of a catalytic liquid – phase -oxidation process of organic wastewater derived from chemical industries. This catalytic liquid–phase oxidation process was conducted in a stainless steel autoclave reactor with homogeneous catalyst. The effects of operating conditions such as temperature, pressure, pH, RPM and residence time on COD removal of industrial wastewater was studies.

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2. Material and methods Experimental Setup, process variable, and catalyst

The catalytic liquid – phase oxidation process of organic wastewater was carried out in a 1.0 L stainless steel batch autoclave (Fig. 1) equipped with automatic temperature control, an adjustable speed stirrer, a valve for sampling and a pressure gauge. The reactor was equipped with a mechanically driven-stirrer ensuring good mass-transfer from gas to the liquid phase. The gas inlet and off-gases release valve, cooling water feed line, pressure gauge, and rupture disk were situated on the top of the reactor vessel. A chilled water condenser was fitted to the sample valve exit line to avoid flashing during the sampling.

The reactor was purged with nitrogen prior to the start of the experiment to ensure an inert atmosphere inside the reactor and to check the gas-leakage. The speed of agitation and reaction temperature was set as per the experimental design. After feeding the wastewater and catalyst, the reactor was heated with an electrical heating jacket under pressure, while agitator continuously solution. A stirrer the constant temperature was maintained with an electronic controller. Air was used as the oxidizing agent, obtained from an air cylinder connected to the reactor. After reaching the desired reaction temperature, oxygen was forced into autoclave. At appropriate time intervals, an aliquot of the solution was drawn and sample was analyzed [7].

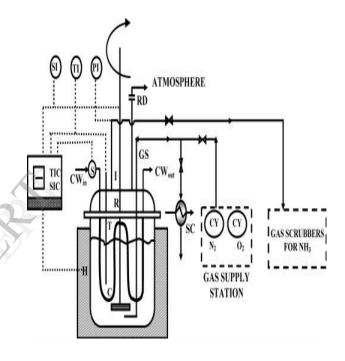


Figure 1: Schematic diagram of the experimental setup for the catalytic liquid–phase oxidation

[Note: PI- pressure indicator; TI- temperature indicator; SI- speed indicator; R- reaction vessel/autoclave; T- thermocouple; H- electric heater; RD- rupture disk; I- impeller; GS- gas sparger; SC- sample condenser; CY- gas cylinder; C- cooling coil; CW_{in} - cooling water inlet; CW_{out} -cooling water outlet; and S- solenoid valve].

The experiments were performed with varying concentration of copper sulphate (0.1 g) as catalyst to investigate the effect of the homogeneous catalyst on the conversion of organic pollutant in the industrial waste water [8]. The metal salts used in the experiments was analytical grade, and was not further

purified. The experiments were conducted using 500 mL of wastewater. The physical parameters of reactors were varied as: temperature, 200° C , 215° C and 230° C; pressure, 28, 31 and 34 kg/cm²; time, 90, 120 and 150 min; and agitation rate, 600, 750 and 900 rpm. The effect of pH was also determined by varying the pH of the process reaction from 7.9 to 9.8.

3. Results and Discussion

3.1. Effect of the temperature on COD removal

Treatment of organic content in industrial wastewater by catalytic liquid–phase oxidation process was carried out at different temperatures of 200 ^oC, 215 ^oC and 230 ^oC, and oxygen partial pressures were kept at 10.0 kg/cm² and a reference temperature of 25 ^oC. The results of COD reduction at different temperature are shown in **Fig. 2**.

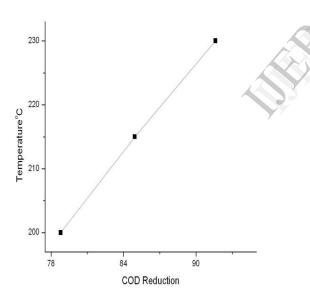


Fig. 2: Effect of temperature on COD removal

It has been found that when the temperature from 200 0 C, 215 0 C to 230 0 C, COD removal significantly increases from 78.80%, 84.93% to 91.61%. Improvement in COD removal efficiency was down at 200 0 C and 215 0 C temperatures. However, the reaction temperature of 215 0 C are refractory to total oxidation, but are compatible for biodegradable. Hence, the temperature of 230 0 C is an economically optimal

reaction temperature for COD removal of industrial wastewater.

3.2. Effect of the pressure on COD removal:

The treatment of industrial wastewater was carried out at pressure 28 kg/cm^2 , 31 kg/cm^2 and 34 kg/cm^2 with supply of partial oxygen fixed at 10 kg/ cm2 (**Fig. 3**).

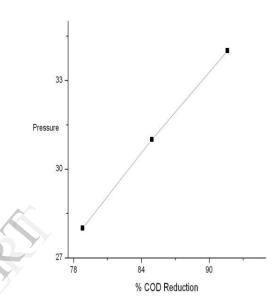
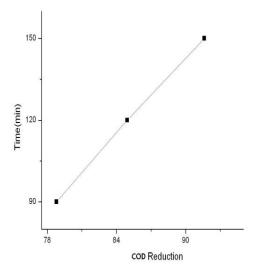


Fig. 3: Effect of pressure on COD removal

It is observed that the increase in pressure resulting in increase in COD removal from wastewater. At different total pressure of 28 kg/cm², 31 kg/cm², and 34 kg/cm², the COD removal rate of 78.80%, 84.93 % and 91.61% were achieved .

3.3 Effect of the reaction residence time on COD removal

The industrial wastewater COD conversion experiments were conducted at different temperature ranged 200 0 C, 215 0 C, and 230 0 C and at pressure from 28 kg/cm², 31 kg/cm² and 34 kg/cm² (**Fig. 4**).



9.6 E ^{8.8} 8.0 -78 84 90 % COD Reduction

Fig. 4: Effect of temperature on COD removal

The COD removal increased rapidly during initial hours of reaction time, maximum of 91.61% was observed after 150 min, and further decreased to 84.93 % with residence time of 120 min. and 78.80% COD reduction with 90 min. residence time. The reaction rate is depends both on temperature and reactant concentrations. As the reaction proceeds, the concentration of organic matter of wastewater decreases and resulting the reaction rate decreases.

3.4. Effect of pH on COD removal

pH is defined as the negative log of hydrogen ion concentration. It indicates the acidity and alkalinity of waste water. The effect of pH on COD removal from wastewater is illustrated in **Fig.5**.

Fig. 5: Effect of pH on COD removal

It is found that the COD removal is more sensitive to pH of wastewater. It is observed that the increase in the pH decreases the COD removal rate and maximum COD removal of 91.61% was observed at pH 7.9 followed by decrease 84.93%, 78.80% at pH 8.8 and 9.8. At high pH value probably the reaction mechanism changes and the formation of OH⁻ radicals may interfere with the oxidation of organic pollutant of industrial wastewater.

3.5. Effect of agitation on COD removal

The effect of stirring on COD reduction of organic pollutant in industrial waste water studies at 600 RPM, 750 RPM and 900 RPM.

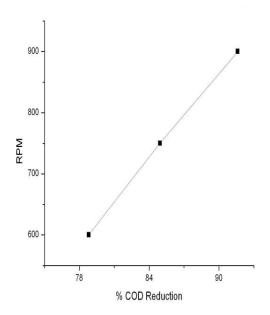


Fig. 6: Effect of agitation on COD removal

The plot of COD reduction vs stirring were drawn (**Fig.6**) for copper sulphate catalyst [9]. Maximum 91.61 % COD reduction achieved at 900 rpm, At 750 RPM and 600 RPM COD reduction was 84.93% and 78.80%, resp. achieved.

4. Conclusions

The following conclusions were drawn from the present study. The impact of various operating parameters such as temperature, pH, pressure, and reaction residence time on the feasibility of wastewater treatment in liquid- phase oxidation process was evaluated. This process was successfully demonstrated as an efficient treatment method for organic pollutant in industrial wastewater. This process can be operated under medium pressure and temperature using homogeneous copper sulphate catalyst. Therefore, catalytic liquid – phase oxidation process will reduce the operation risk resulting from high pressure and high temperature.

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