

DEGRADATION OF PHENOLIC COMPOUNDS BY ADVANCED OXIDATION TECHNIQUES

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Abstract-

In this paper, one of the Advanced Oxidation Techniques (AOT) that is Catalytic Ozonation is being studied and discussed for degradation of phenolic compound p-nitrophenol with ZnO as catalyst. The parameters studied are initial concentration, pH of p-nitrophenol and catalyst loading. These parameters are studied using COD analysis. From the results, it was found that the optimum conditions were at initial concentration 50 ppm, 0.25 g of catalyst loading.

Keywords: p-nitrophenol, Advanced Oxidation Techniques, Phenol, COD.

1. INTRODUCTION:

Phenolic compounds are widely present in aqueous effluents from several industries like petroleum refineries, petrochemicals, pharmaceuticals, resin manufacturing, dyestuff, paint, pesticide, pulp, paper and wood products [1]. Untreated discharge of these compounds can pose serious health risks to humans, animals and aquatic systems. Phenolic compounds tend to persist in the environment, accumulate and exert toxic effects on humans and animals [2,3]. Due to its hazardous character and growing social concern on environment, emphasis is being laid on treatment of these compounds before being discharged. As most organic compounds are resistant to conventional chemical and biological treatments, advanced oxidation techniques have emerged as effective strategies for wastewater treatment [4]. AOPs are aqueous phase oxidation processes in which highly reactive unstable hydroxyl radicals are formed which destroys the target pollutants. AOPs offer wide range of advantages like fast reaction rates, efficient degradation and complete mineralization [5].

Ozonation is one of the most widely used oxidation processes for industrial wastewater pre-treatment. Ozone molecules break down the organic compounds into smaller harmless molecules. However, the high energy requirement for ozone generation is one of the major drawbacks of this process. Also, in some cases, incomplete oxidation and incomplete mineralization leads to lowered efficiency of the process. These drawbacks of ozonation process can be overcome by using catalytic ozonation process [6]. Catalytic ozonation uses catalysts to increase the ozone decomposition and thereby forming highly reactive free radicals. Many catalysts including metals, metal oxides such as TiO₂ Pt/Carbon nanotube (CNT), Mn/TiO₂, Mn/Co, Fe₃O₄/CoO, ZnO, Fe₂O₃, Fe₂O₃/CeO₂, activated carbon (AC), etc. are widely used for enhancing the activation of the ozonation process [7]. Controlled decomposition of ozone and hydroxyl radicals' formation is also achieved. However, the exact mechanism of catalytic ozonation is unknown. Researchers have developed two representative mechanisms. In interfacial reaction mechanism, catalyst acts as an adsorbent. It adsorbs organic pollutants and provides active adsorptive sites. They combine with organics to form the chelate of lower activation energy that can be degraded by ozone or HO• radical easier. The HO• mechanism proposes that the metal oxide catalysts can increase the solubility of ozone and initiates the ozone decomposition. Soluble ozone in aqueous solution is adsorbed to the surface of the catalyst, a series of radical chain transfer are occurred to generate much HO•, which hold a high oxidation potential and can oxidize the organic pollutants in wastewater [5].

In this study, phenolic compound para-nitrophenol (PNP) was subjected to catalytic ozonation for 120 minutes. ZnO was used as catalyst. This research focuses on degradation of PNP by catalytic ozonation process and influence of parameters like initial concentration of PNP, catalyst loading and initial pH of solution on degradation efficiency. The process was optimized so as to attain enhanced degradation.

2. MATERIALS AND METHODS:

Chemicals used are p-Nitrophenol (AR grade purchased from Research Lab), ZnO (Extra pure purchased from SD Fine- Chem Limited), Sodium Hydroxide (NaOH), Sulphuric acid (H₂SO₄). Ozonator (ozone generator) is also used. 1000 ml Stock solution of p-Nitrophenol of concentration of 500 ppm was prepared by using 0.5 g of p-Nitrophenol. 500 ml solution of known concentration was made by diluting the stock solution. Known amount of catalyst is added to the solution. The glass reactor was placed on a magnetic stirrer that offered continuous stirring. Ozone generator was used for ozonation. A pipe was connected to the output of the generator and was used to pass ozone inside the cylinder continuously. The experiments were carried out for 120 mins. At regular interval of time, 10 ml sample was collected. The collected sample was subjected to COD analysis. The above procedure was repeated for studying the effect of different parameters.

3. RESULTS AND DISCUSSION:

3.1. Results

EFFECT OF INITIAL CONCENTRATION:

500 ml of PNP solution of varying initial concentration was subjected to catalytic ozonation with 0.25 g catalyst loading and pH of 6.3 for 120 mins. By varying initial concentration of PNP, graph of COD versus Time was plotted. It was observed that the rate of degradation of PNP followed the order 10 ppm > 50 ppm > 100 ppm (Chart-1).

EFFECT OF CATALYST WEIGHT:

While maintaining the same reaction conditions, the catalyst loading was varied. The concentration of solution was kept 50 ppm. It was observed that the rate of degradation was not much affected when catalyst loading was changed from 0.25 g to 0.5 g (Chart-2). However for 1 g of catalyst, it was observed that catalyst deposited on the wall of reactor indicating that it was excess.

EFFECT OF pH:

50 ppm concentration solution was subjected to ozonation with 0.25 g catalyst loading. The pH of the solution was varied between 5 to 9 pH and its effect was observed. It was seen that the rate of degradation was highest for 8pH (Chart-3). 60% COD removal was obtained.

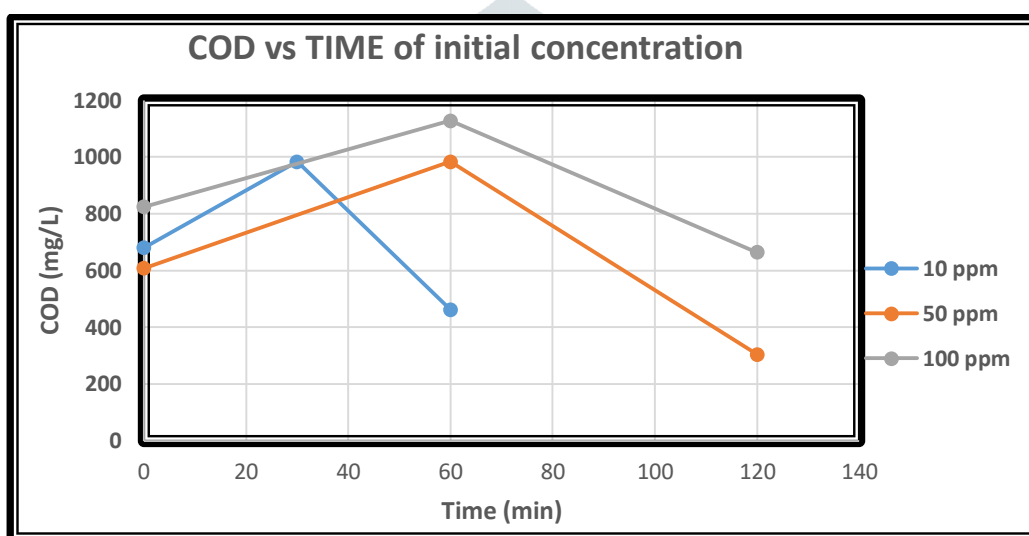


Chart-1: COD Vs Time (Effect Of Initial Concentration)

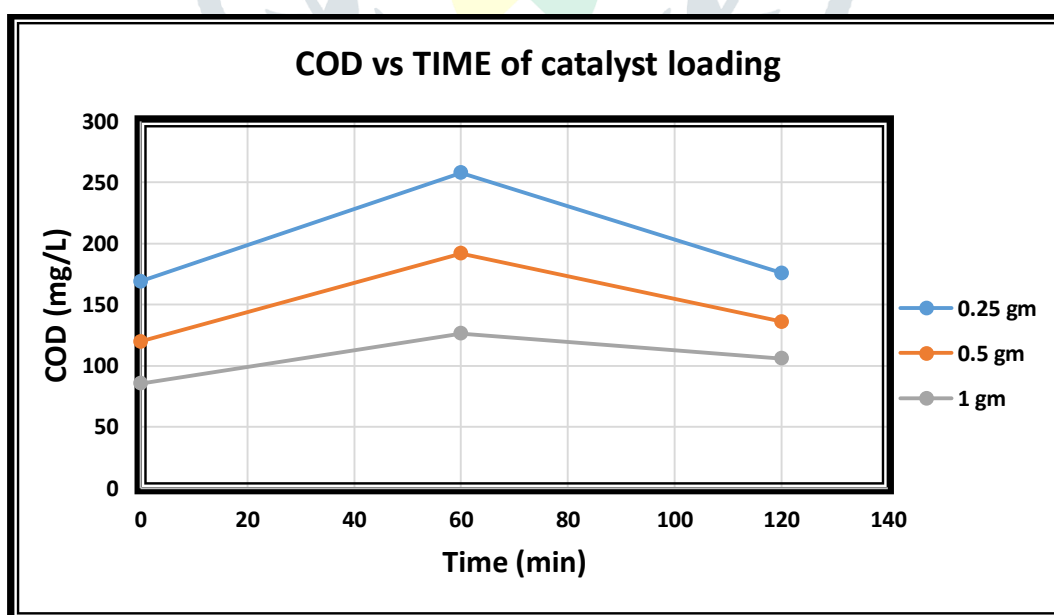


Chart -2: COD vs time (effect of catalyst loading)

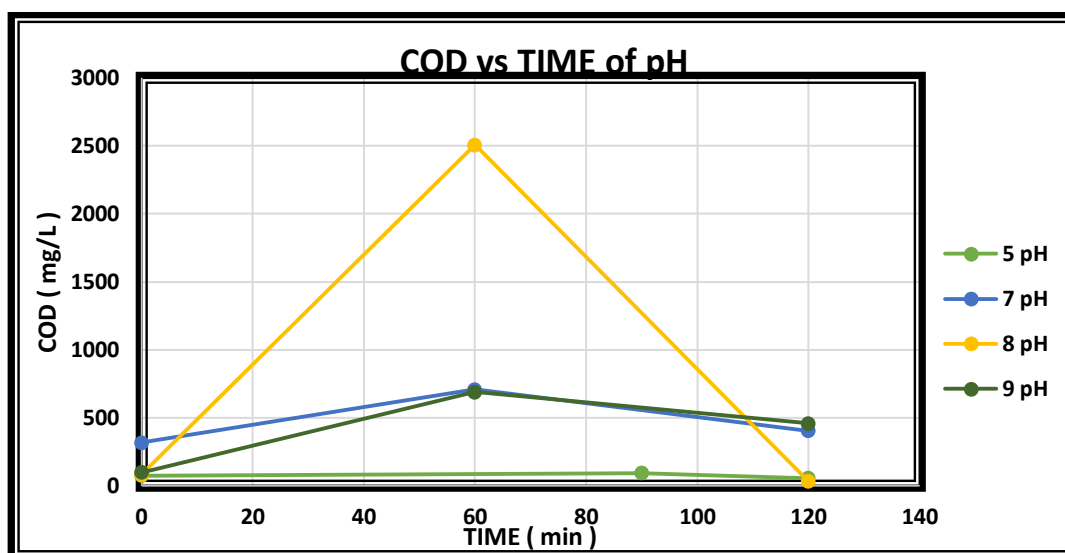


Chart-3: COD vs time (effect of pH)

3.2. Discussion

From the results, we could see that optimum COD was at conditions: 50 ppm, 0.25 gm and 8 pH. Also, peak was seen in COD values at 60 min followed by decrease in COD values as time progressed. This could be attributed to the mechanism of catalytic degradation of PNP.

As per the mechanism, aromatic compounds react rapidly with ozone and form some hydroxylated aromatics and small amount of ring-cleavage products in stage 1 (0-50 mins). In stage 2 (50-100 mins), almost all aromatic compounds are converted to unsaturated acids, aldehydes and saturated acids, such as glyoxylic acid, formic acid and oxalic acid. In stage 3 (100-180 mins), saturated acids, like formic acid and oxalic acid, comprise the appreciable amount of TOC that still remains in solution. These compounds are quite resistant to oxidation by ozone, so the mean oxidation state of organic carbon remains constant with time [8].

Acid detection:

1. After an ozonation run, decolourisation of PNP solution was observed, indicating presence acids, as PNP is a pH indicator. A solution of PNP appears colourless below pH 5.4 and it turns dark yellow above 7.5.
2. A run at pH 6, was conducted and pH was checked after a small interval of time. It was observed that there was a decrease in pH as time progressed.
3. Acid detection test was done, where a pinch of sodium bicarbonate was added to PNP solution taken at time 60 mins. A mild effervescence was observed detecting small amount of acid present at that time period.

4. CONCLUSION:

From literature, it was evident that advanced oxidation techniques are the future of waste water treatment. This is because of wide range of advantages like short residence time, variety of organic compounds can be degraded simultaneously, formation of harmless by-products, etc. offered by AOPs. Ozonation can degrade phenolic compounds to harmless by-products in short period of time. It also offers additional advantage of disinfection and odor removal. But limitations of ozonation like high energy requirement and incomplete mineralization led to development of catalytic ozonation. Catalytic ozonation uses catalysts to increase the ozone decomposition and thereby forming highly reactive free radicals.

On studying the effect of different concentrations of p-nitrophenol degradation by catalytic ozonation, we can conclude that as concentration of PNP increased the rate of degradation decreased. pH highly influences the rate of degradation. Optimum conditions for maximum degradation from the results obtained were initial concentration of 50 ppm with 0.25 gm catalyst and 8 pH. 60% COD removal was obtained under the optimum conditions. The high molecular weight compound, PNP breaks down into smaller fractions of lower molecular weight which are still persistent in the solution. For further degradation of these fragments to achieve complete mineralization, nano-catalysts can be used. Varying ozone flowrate may also help in better degradation. PNP is not readily biodegradable and requires strong maintenance of operating conditions to undergo biodegradation. The acidic products obtained after catalytic ozonation are readily biodegradable. So using catalytic ozonation system in series with biological treatment methods can enhance the removal of organics.

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