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PHENOLIC WASTEWATER TREATMENT: A REVIEW

Vivek R. Singh[1], Manisha V. Bagal[2], Ronak P. Mota[3]

[1,2,3] *Department of Chemical Engineering, Bharati Vidyapeeth College of Engineering, Navi Mumbai*

Abstract — *Phenols are extremely toxic to humans, plants and other animals. The toxicity of phenol concentrations in industrial effluents is high enough to meet its needs for separation. Advanced oxidation processes can be effectively used for wastewater treatment applications due to the easy operation and simple reactor design. In this review, advanced oxidation processes such as Photocatalysis, Fenton and Cavitation (Ultrasound and Hydrodynamic) have been discussed for effective degradation of Phenol from wastewater. Also hybrid methods based on cavitation coupled with Fenton process, UV and Fenton and sonophotocatalysis (US/UV) for the treatment of Phenolic wastewater have been discussed. It has been observed that the main mechanism for the higher efficiency of degradation using combined process depends on the generation of additional hydroxyl radicals and its proper utilization for the degradation of the pollutant.*

Keywords- *Phenol, Wastewater treatment, Photocatalytic oxidation, Fenton Process, cavitation.*

I. INTRODUCTION

Phenol (hydroxybenzene) is a coal tar derivative. Most of the industrially produced phenol (70%) is used in the production of polycarbonate resins, but the compound is used for explosives, paints, inks, perfumes, wood preservatives (pentachlorophenol), textiles, drugs, and as an antibacterial and antifungal agent and disinfectant as well. In medicine, phenol is used as a topical anesthetic or antiseptic (Paula M. ,2000) [1]. All the industries that produce or use phenol may at some point be responsible for the release of this compound into the environment. The U.S. Environmental Protection Agency (EPA) criterion to protect freshwater aquatic life is 600 ug/l. as a 24-hour average, never to exceed 3.4 mg/L (36 JlM), and the drinking water limit is 1 mg/L (0.01 JlM) (USE1979). It is obvious that, without the proper treatment, industrial wastewaters would be an important source of anthropogenic phenol into the environment**.**

Shohreh Mohammadi et al. (2014) [2] reported that Phenol is a basic raw material for various products such as herbicides, drugs, paints, cosmetics, and lubricants. Minor uses of phenol and its derivatives include a versatile precursor for the production of some drugs such as aspirin and pharyngitis medicines, carbolic soap, one of the constituents of industrial paint strippers in the aviation industry, and cosmetics including sunscreens, hair dyes, and skin lightening products. Therefore, phenol and its derivatives are usually present in the effluents of the relevant industries such as conversion processes, coke ovens, petroleum refineries, fiberglass.
Harmful effects of phenols on humans and animals:

- Short term effects: Respiratory infection, Head-aches, burning eyes, skin rashes.
- Chronic effect (high exposure): Weakness, Muscle pain, anorexia, weight loss, fatigue.
- Long term effects (low exposure): Respiratory cancer, heart disease, weakening of the immune system. Harmful effects of Phenols on agriculture:
- Effects on soil: Porosity of soil decreases,
- Effects on plants: Reduced amount of germination of seeds.
- Effect on groundwater: Groundwater near hazardous sites are contaminated by phenol which seeps in through the soil.

II. Advanced Oxidation Processes

Any organic compound can be degraded by oxidation using generation of OH radicals. This process is known as Advanced oxidation process (AOP). The generation of OH radicals is done using several methods.

- Photocatalysis
- Cavitation: Sonolysis and Hydrodynamic Cavitation
- Fenton’s Process

Conventional processes include Physico-Chemical Processes such as Adsorption, Electrochemical Oxidation and Biological treatment show cost effective solutions but are not efficient in degrading phenol, besides they generate waste which needs to be disposed.

2.1. Photocatalysis Process for Degradation of Phenol

Photocatalytic oxidation process employing catalyst such as TiO_2, ZnO, etc., This process mainly relies on generation of hydroxyl radicals under ambient conditions which are capable of converting organic compounds including the non-biodegradable ones into relatively nontoxic end products such as CO_2 and H_2O. In this process, the combined action of semiconductor photocatalyst, an energetic radiation source and an oxidizing agent governs the destruction of organics. Moreover, the process can be driven by solar UV and visible light. This suggests using sunlight as an economically and ecologically sensible light source. As a result, development of an efficient photocatalytic water purification process for large-scale applications has received substantial interest, but still it remains a challenge.

Advantages:
1. It is most efficient and economical method as compared to all the other methods of degradation.
2. The rate of degradation is comparatively high for photolysis.

Disadvantages:
1. In case of Photocatalysis, the separation of homogenous catalyst from treated water is difficult and clogging takes place also the operating cost increases for treatment of large batches using Ultraviolet light.

Jabeen et al. (2014) [3] has investigated the degradation of the phenol from the waste water in a batch process wherein, the samples were taken in the shaking chamber exposed to the UV radiations using TiO_2 as a catalyst. It was found that the efficiency of the concentration of phenol in terms of % was affected by TiO_2 concentration, pH of the solutions and the exposure time to UV-irradiation. The results showed that degradation yields in 2 hours' period with pH 3, 7 and 11 was 17%, 13% and 30%, respectively.

Lathasree et al. (2004) [4] studied the effect of initial concentration (40-100 ppm) on the photocatalytic degradation of phenol using ZnO as the catalyst. The initial rates of photodegradation were high at the lower concentration range but it decreased as concentration increased. The degradation was found to follow first-order kinetics. For chlorophenols, the initial rate was observed to increase with the increase in the initial concentration range 40-60 ppm and decreased as concentration increased further.

Wu et al. (2014) [5] that the efficiency of degradation of phenol increases with an increase in irradiation time giving the degradation to be 32.71% obtained with photocatalysis.

Gomez et al. [6] (2015) investigated the Photocatalytic degradation of phenol under both UV radiation and visible light, using TiO_2 (Degussa P-25) and TiO_2 loaded with some transition metal ions (Co, Cu, Fe and Mo) and concluded that from the series of metal loaded catalysts, Mo/TiO_2 was the most efficient one. In the presence of Mo, neither TiO_2 anatase/rutile fraction nor its pore size diameter has been affected, however Mo made its surface more acidic. It was reported that 2 wt% Mo/TiO_2 was the most effective one. The synergetic effect between SBET, mean pore size diameter, catalyst agglomerates size, band gap, ZPC and the type of Mo_xO_y species on TiO_2 surface, depending on Mo loading, created its Photocatalytic performance.

2.2. Fenton Process for Degradation of Phenol

Based on the oxidant power of hydrogen peroxide (H_2O_2) catalyzed by iron ions to endorse the formation of hydroxyl radicals (•OH), the Fenton's process is a very promising Advanced Oxidation Process (AOP) due to the high mineralization promoted at mild conditions of both temperature and pressure. The Fenton's process efficiency depends on several parameters, such as pH, concentrations and type of iron ions and hydrogen peroxide amounts. It requires short reaction times besides using easy-to-handle reagents. Since Fenton's peroxidation treatment plants design and construction are simple and the process does not imply significant operating problems, its application to real wastewaters becomes of industrial interest.

Advantages:
1. The advantage of the Fenton method is mineralization of the organic substances as compared to conventional methods which generate secondary pollution.

Disadvantages:
1. Relatively high cost of hydrogen peroxide.
2. acidification of the effluent stream
3. the removal of the generated iron sludge.

Fenton's processes are reported to be efficient in the acidic range. Muthukumar et al. (2011) [7] reported that the Fenton process gave the 93 % of degradation of phenol when accompanied with the UV rays, at the optimum pH of 3. The increase in the pH resulted in the decrease of the degradation of phenol, as the Fe^{+3} ions tends to be inactive in the acidic medium.

J. Feng et al. (2017) [8] had studied the effects of pH on degradation of phenol by the Fenton process. It was reported that the degradation of the phenol showed great response under the alkaline conditions, there was a slight floc formation at the pH of 11 in the collection sample, as a result separation of Fe was not possible. Further, at the pH of 8.5 the conversion was reported to be at a greater extent as the flocs were formed by the end of the 60 min and also the separation was quite clear.

W. Wang et al. (2014) [9] has experimented the degradation of phenol by the advanced Fenton process by use of catalyst Fe_3O_4/MCNs and was reported that unlike typical Fenton process which usually requires high acidity, Fe_3O_4 /MCNs effectively catalyzed phenol degradation under pH. varied from 3 to 9.

2.3. Cavitation

2.3.1. Use of Ultrasound for Degradation of Phenol: -

In a sonochemical process, acoustic cavitation bubbles form, develop, and collapse in extremely small intervals of time, releasing large magnitudes of energy (high temperature and pressure) and, thus, producing oxidizing agents, such as H•, HO•, O•, and H_2O_2 via the following chain reaction:

$$H_2O \rightarrow H\bullet + HO\bullet$$
$$O_2 \rightarrow 2O\bullet$$
$$O\bullet + H_2O \rightarrow 2HO\bullet$$

When these oxidizing radicals react with the organic dye molecules, they break the cyclic structure, degrading into simple harmless compounds such as H_2O and CO_2

Advantages:

1. It is most suitable method for higher rate of degradation.
2. There is no possibility of sludge formation or clogging as in photocatalysis and Fenton process since no heterogeneous catalysts are used.

Disadvantages:

1. Industrial scale operation using acoustic cavitation is difficult due to uneven cavitation.
2. higher cost and problems associated with power dissipation

Mahvi and Maleki (2010) [10] has experimented the degradation of phenol by sonolysis and had demonstrated the removal of phenol by the Photo sonochemical process at different pH. It was clearly shown that lower pH values favoured the phenol degradation. The degradation of phenol attained 98% at pH 3, 93% at pH 5, and 75% at pH 7. For samples controlled at pH 11, the extent of phenol degradation was only 52%. Similar results are reported for degradation of 2, 4 dinitrophenol (Bagal et al.,2013) [11]

2.3.2. Use of hydrodynamic cavitation for degradation of phenol: -

Hydrodynamic cavitation (HC) can simply be generated by the passage of the liquid through a constriction such as an orifice plate. When the liquid passes through the orifice, the kinetic energy/velocity of the liquid increases at the expense of the pressure.

Advantages:

- Higher rate of degradation.
- Energy efficient process as compared to other advanced oxidation processes.

Disadvantages:

- Uneven cavitation and problems associated with power dissipation.
- High Pressure drop

Yiyu et al. (2012) [12] has experimented the degradation using hydrodynamic process using pH 3.0, initial concentration of H_2O_2 300 mg·L^{-1}, initial phenol concentration 100 mg·L^{-1}, confining pressure was 0.5 MPa, cavitation time 60 min, and pump pressure 20 MPa and observed that 99.85% of phenol has been mineralized, which was the best condition of removal phenol.

III. Combination of Advanced Oxidation Processes

It is reported in literature that the methods operating individually needs to combine with other advanced oxidation processes for the effective destruction of the complex industrial streams. The combination of these processes may be used to overcome the disadvantages of the individual technique.

3.1. Degradation of Phenolic waste using Sonophotocatalysis (UV and US)

Wu et al. (2014) [5] studied the combined effect of both US and UV for the degradation of phenol. The parameters considered by them were, effect of pH, effect of $NaHCO_3$, Fe^{2+} ions. It is observed that the rate of reaction gets doubled when both the methods were combined. They found that effective degradation occurred at the pH of 6.75. Also iron enhances the degradation by 10 % and sodium bicarbonate decreases the reaction rate by 5 %. The maximum degradation obtained were 95% and the synergistic index they found were 1.06.

Mahvi and Maleki (2010) [10] studied the efficiency of the sonochemical effect in conjunction with a photochemical irradiation and the effects of parameters such as pH, ultrasound frequency (35 and 140 kHz), and initial concentration on the degradation processes were considered. The oxidation of a model pollutant, phenol, was carried out in Photosonochemical reactor. 98% degradation was seen using US and UV both for 300 min. The optimum pH was 3 with the ultrasound frequency of 135 Hz with 85 ppm phenol concentration.

3.2. Degradation of Phenolic waste using UV and Fenton

The combined effect of UV and Fenton was studied by Villota et al (2016). [13] Phenol (100 ppm) concentration was taken in a batch reactor and a mercury lamp for UV purpose. 20 ppm of iron particles are mixed. Residence time was 1 hour. It was observed that the reaction was almost completed in 30 min due to the higher oxidation rate under Fe^{2+} ions.
Kavitha and Palanivelu (2004) [14] studied the role of ferrous ions on Fenton, solar Fenton and UV Fenton using a batch reactor. The parameters studied were pH, peroxide and ferrous ion concentration. At optimum conditions, different Fenton-related processes were compared for the degradation of phenol. Increased degradation and mineralization efficiency were observed in Photo-Fenton processes as compared to conventional Fenton process. The maximum mineralizing efficiency for phenol with Fenton, solar and UV-Fenton processes were found to be 41%, 96% and 97% respectively. The optimized pH was found to be 3, peroxide concentration as 1 ml/L and ferrous ion as 20 mg/l.

3.3. Degradation of Phenolic waste using Sono-Fenton (US and Fenton)

Sono-Fenton utilizes the advantages of these two methods to generate more hydroxyl radicals and can be effectively used for the degradation rate of organic pollutants. Also cavitation gives additional mechanism in terms of pyrolysis in the system, which can help in removing some of the chemicals which are refractory to hydroxyl radicals (Bagal and Gogate, 2014). [15].

Liang et al. (2007) [16] have reported complete degradation of 2-chlorophenol by combination of ultrasound generated cavitation and Fenton chemistry at pH 3.

Ranjit et al. (2008) [17] have reported a reduction in the required Fe^{2+} concentration (50%) and H_2O_2 concentration (31%) for the Sono- Fenton method as compared to conventional Fenton process and also established that this method could be applicable even at pH 5.0 instead of pH 2.5 required for conventional Fenton Process. Kinetic studies for the degradation of DCP proved that the degradation of DCP tends to follow pseudo first order reaction.

IV. Conclusion

Advanced oxidation processes have been widely used for the destruction of complex organic pollutants at laboratory scale. Hybrid technique (Cavitation/Fenton) can be used to overcome the disadvantages of individual processes. Advanced oxidation processes prove to be energy efficient as it utilizes the advantages of generation of hydroxyl radicals and improves the degradation rate of organic pollutants. The present work has highlighted the advantages and disadvantages of Photocatalysis, Cavitation and Fenton. Overview of work done in the area of phenolic wastewater degradation using individual (Photocatalysis, cavitation and Fenton) processes as well as combined processes such as UV coupled with Fenton (UV/Fenton), Sonophotocatalysis (US/UV), and Sono Fenton (US/Fenton). Overall it can be said that phenolic wastewater can be effectively treated using advanced oxidation processes.

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