PHENOL WASTE TREATMENT USING OZONE-PLASMA HYBRID REACTOR

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Abstract — Phenol is one of the most dangerous ingredients in industrial wastewater, which has acute toxicity and is difficult to degrade in the environment. Therefore, Ozone-Plasma Hybrid Reactor (RHOP) is an effective phenol waste treatment used to test the performance of the treatment of synthetic phenolic compounds. Its working principle is based on the combination of ozonation reaction in the liquid plasma field of the reactor. Ozone as a reagent is produced by the ozonator, which is fed into the RHOP by mixing it with the liquid phase feed in the injector to enable the intensive the reaction of the two-phase mixture react. Furthermore, the two-phase mixture intensifies hydroxyl radicals when the liquid phase is in alkaline condition and continuously exposed in plasma. The results obtained from the performance test carried out on several wastes with high concentrations, showed that the system needed improvement. The improvements were made by changing the reactor system to Dielectric Barrier Discharge (DBD) plasma with wire cylinder configuration, to degrade synthetic waste containing phenolic compounds through active species formed in the reactor. This process has a high oxidation potential and decomposes various organic pollutants in waste. Furthermore, the ozonation technique was applied to the DBD reactor with the aim of increasing the amount of ozone and \( \text{OH}^- \) radicals, therefore maximizing the phenol degradation process.

Keywords: Ozone, Dielectric Barrier Discharge, Plasma, Ozone, Phenols, Advanced Oxidation Processes.

1. INTRODUCTION

Phenol is one of the most dangerous pollutants which produce liquid waste in the chemical industry, such as petrochemical, paint, textile, pesticide industry and many more[1]. In high concentrations, it causes death when swallowed, inhaled or absorbed by the skin. Subsequently, it affects the central nervous system and causes damage to the liver and kidneys. Furthermore, it irritates the skin but has a local anesthetic effect, preventing the pain from been felt at the first contact area, which usually turns white and becomes burnt.

The Advanced Oxidation Processes (AOPs) has been technologically developed and adopted worldwide to carry out several different conditions, such as ozone/UV, ozone/H\(_2\)O\(_2\), ozone/UV/H\(_2\)O\(_2\), H\(_2\)O\(_2\)/UV and ozone at high pH. It encourages the formation of active radical hydroxyl, which has high ability to neutralize organic material. Oxidation occurs through three processes, namely: (1) Hydrogen abstraction, (2) Electron transfer and (3) Radical formations[2].

In liquids, ozone reacts with various compounds in two ways, namely direct reaction with its molecules and reaction with radical species formed when it decomposes in water. In the resonance structure, ozone molecule acts as a dipole, both as an electrophilic and nucleophilic agent. The reaction mechanisms which occur due to these properties are categorized into three, namely cyclic addition, electrophilic reactions and nucleophilic reactions. The electrophilic reaction mechanism describes the reaction between ozone and phenol compounds.
Non-thermal plasma technology is an environmental friendly waste treatment method, which is vast in growth due to the simplicity of its process, effectiveness, low energy consumption, does not require the use of other chemicals and does not produce new waste. Furthermore, various active species, such as O₃, H₂O₂ and hydroxyl (OH, HO₂, H, O•) are formed in the plasma discharge process, which decomposes various organic compounds, including phenol compounds.

Cold plasma occurs in a state of non-thermal equilibrium between electron and gas temperature. This is because, electron temperature is high, while the temperature of gas particles is relatively low due to the slow rate of collision between them. Furthermore, in cold plasma, the neutral ions and atoms or molecules remain in a temperature of about 1000K, while the electrons have a fairly high temperature of about 50000K. Therefore, it is used in microelectronics for the formation of new materials and cleaning of pollutants.

The dielectric discharge barrier (DHF) used in water treatment is usually coated with ceramic or glass and is referred to as dielectric. Its characteristic is the presence of one or more layers of insulation between the metal electrodes.

Ozone-Plasma Hybrid Reactors (RHOP) are formed from electrodes placed in the center of the reactor, while liquid waste samples flow around a tubular glass reactor with borosilica glass material. Therefore, plasma is formed in the gas phase on the water surface. RHOP was chosen because of its advantages, which include electrodes not experiencing relative rise in temperature due to the direct contact between the liquid and electrodes. In addition, the required voltage is also lower when compared to the plasma generated in water, which requires a very high voltage (10-1000 kV)[3]. Therefore, a lower voltage of 12 kV was used in this study. Irrespective of the low voltage used, plasma was formed, starting from the 150 Volt primary voltage regulator, because it was generated from the gas phase and not the water phase. Furthermore, in accordance with its nature, gas was used as an insulator due to its inability to conduct electric current, while water is a good conductor. The electric current in is static,
therefore the movement of electrons formed will be more centered and experience a quick electron jump, enabling the formation of plasma at lower voltage.

2. EXPERIMENTAL DETAILS

The chemicals used in this study were obtained from related industries and made artificially according to decided parameters. The plasma was formed in the gas phase on the surface of water. Furthermore, the active species produced dissolved in water and degraded organic matter by oxidation process. Therefore, the plasma reactor used was designed to ensure the flow of liquid waste to be in contact with the plasma simultaneously.

The formation of plasma in the gas phase was greatly influenced by the gas source in the reactor. Therefore, air from the compressor was used as the gas source in the reactor. Furthermore, O\textsubscript{2} was needed, which was converted into O\textsubscript{3} and dissolved in water, leading to an increase in the formation of OH radicals through a decomposition reaction, especially at alkaline pH. This increased the degradation of waste leading to the very short life time of OH\textsuperscript{●}, while the air flow rate used was 10 L/min.

Visually, the amount of energy possessed by the plasma at each voltage was seen from the sound character, colour and shape produced by the plasma. The 225Volt regulator or its equivalent i.e. 12kV (secondary voltage), were the maximum primary voltage used in this study. Consequently, the plasma formed was very effective since the liquid was in direct contact with it at all points therefore, the process occurred optimally. However, the plasma and free radicals produced were still very small therefore, the voltage used was higher and circulation time was prolonged to achieve higher process efficiency.

The reaction mechanism in the plasma reactor was that OH and O are the dominant species in pollutant degradation. The use of O\textsubscript{2} as the gas source for the plasma reactor led to the production of OH and O as the dominant oxidants, which were produced due to the dissociation of electron collisions from H\textsubscript{2}O and O\textsubscript{2} (as the gas source in the reactor)\textsuperscript{[4]} . Based on the results obtained, the reactor was considered as the main oxidizer, namely OH\textsuperscript{●}, O\textsuperscript{●} and O\textsubscript{3} with the following equation:

![Fig 2. Scheme Hybrid Plasma Reactor](image-url)
Where: * shows the magnitude of the energy level, e − is an electron and M is the third particle which may be O2, N2, OH e.t.c.

Furthermore, two things were explained in this study, which include the formation of plasma in the reactor that produces ozone. The Ozone formed was dissolved on the surface of the water and reacted with organic substances in the waste by hydroxyl radicals or other active species. The two hydroxyl radicals formed further combined with each other to produce a stable product with the following reaction:

$$\text{OH}^\bullet + \text{OH}^\bullet \rightarrow \text{H}_2\text{O}_2$$

H2O2 can also be produced from the reaction below:

$$2\text{H}_2\text{O} + e^-* \rightarrow \text{H}_2\text{O}_2 + \text{H}_2 + e^-$$

Plasma Physical Test was carried out to observe the physical plasma phenomena in the DHF reactor visible to the naked eye. When the slide regulator voltage was set to 220volts, a moderate intensity discharge was observed, which created a thin orange discharge. Meanwhile, in the configuration of the reactor, there was an area between the inner and outer electrode, which was called the discharge gap. This was the main area of plasma material formation, due to the electron jump from both electrodes, colliding with atoms and molecules originating from the flowing air. Furthermore, the formation conditions occurred randomly and continuously along the electrode, leading to electrons coming in from the source of the electric current. The interactions that occurred include ionization, recombination, excitation and de-excitation. High-energy electrons struck atoms or molecules from the air and converted kinetic energy into ionization energy which led to excited species. Subsequently, the absorption of the collision energy by the electrons led to the transfer of electrons from a lower to higher energy level by a process called the excitation. Furthermore, excitation took place temporarily and electrons returned to their original energy level, which was accompanied by the emission of photons. This interaction was continuous in other for the emissions to yield the appearance of a plasma discharge in the reactor.

3. RESULT AND DISCUSSION

In alkaline conditions, there are two reaction mechanisms that occur during the oxidation of phenolic compounds, which include reaction with the ozone molecule itself and reaction of hydroxyl radicals with phenol compounds. Due to the high potential of OH^∗ radicals, they are able to break the
organotoxin compounds in the liquid. Furthermore, with a high concentration of radicals, the degradation of phenol compounds will be faster since they are quickly oxidized.

Oxidation of phenolic compounds by ozone forms acidic compounds such as maleic acid, muconic acid, oxalic acid, glyoxalic acid and formic acid\(^5\), leading to a decrease in pH at the beginning of the process. However, at the end of the process, CO\(_2\) will be formed, which ensures that the pH is more stable and a decrease will not be significant.

Plasma is an ionized gas therefore, ionization is always present \(^6\). Plasma is formed due to fluid ionization around the electrodes and a very high voltage difference between them. The mechanism of formation is as follow:

- Ionization of neutral atoms or molecules in Media at very high voltage to produce positive ions and free electrons
- Separation of electrodes, prevention of the combination of both positive ions and electrons and movement of electrons towards the positive electrode.
- Movement of electrons collected at the electrode at very high speed and large energy, which leads to hitting of neutral atoms, causing Ionization, dissociation and excitation processes.

The elimination of phenolic compounds in this study was carried out by using synthetic p-chlorophenol solution with an initial concentration of 50mg/L. The parameter taken was the final concentration from process, which showed the degradation value of phenolic compounds. Furthermore, the p-chlorophenol used had a PH of 10.8 which is alkaline, due to the fact that oxidation reaction of phenolic compounds takes place optimally at a pH between 9 and 11\(^6\).

In addition, data was obtained when exposure time was very influential in reducing the p-chlorophenol concentration as shown in figure 3 and 4.

![Fig 3. Degradation of p-chlorophenol during exposure in RHOP](image-url)
From figure 3, it is seen that circulation time and quantity of p-chlorophenol degraded was in direct proportion. This was due to the presence of ozone which binds to the liquid and produces free radicals to break the bonds in phenolic compounds. As a result, the concentration of p-chlorophenol, which was originally 50mg/L, with exposure time of 2 hours decreased.

![Image](fig4.jpg)

**Fig 4.** The percentage of degradation of p-chlorophenol waste concentration in the RHOP exposure process

From the two figures above, it was observed that the concentration of p-chlorophenol after exposure for 120 minutes using RHOP and ozonator degraded by 89.86% i.e. 5.07mg/L. This shows that the degradation process was carried out using RHOP. Although, it took a longer time to reach the quality standard value and further improved other processes. From Figure 4, it is observed that at higher phenol concentrations, the degradation of p-chlorophenol increased. Therefore, the concentration of p-chlorophenol is directly proportional to its degradation rate. However, the decrease in concentration retarded or tends to be constant. This was due to the reduction in the concentration of phenol compound which retard the rate of degradation.

![Image](fig5.jpg)

**Fig 5.** COD value of p-chlorophenol in the exposure process in RHOP

In measuring the COD value, it was observed that the value before processing was 640mg/L, which became 270mg/L after experiencing exposure for two hours in RHOP. This shows that RHOP was able to work in reducing other parameters such as COD. The COD value provided an overview of
the presence of organic compounds in the waste. Furthermore, from figure 5, it showed a decrease, which was in line with the reduction in p-chlorophenol concentration. This implies that during the oxidation process, the phenol decomposition products were broken down and other organic substances that were not completely decomposed were present. However, in this study, the value of COD as a result of processing did not reach the quality standard. Therefore, to achieve this, the number of circulation was increased.

From the active species formed, OH radicals are the main active species in degrading phenol\(^{[6]}\). The initial reaction of phenol degradation was an electrophilic aromatic substitution reaction. The \(\text{OH}\) radicals attacked the para and ortho steering groups, producing hydroquinone and catechol as initial intermediate compounds. The intermediate compounds were further oxidized to form p-benzoquinone and o-benzoquinone, due to the difference in electronegativity between O and H atoms. The oxidation of these compounds caused the breakage of the rings (cyclination) and formation of acidic compounds, such as muconic and maleic acid. In addition, when the discharge time was long enough, the acid compound was mineralized to become \(\text{CO}_2\) and \(\text{H}_2\text{O}\). The mechanism of phenol degradation reaction is illustrated in Figure 6.

![Fig 6. Phenol degradation reaction mechanism](image)

4. CONCLUSION

The Ozone-Plasma Hybrid Reactor and the RHOP system designed have proven to be useful in degrading waste with a certain circulation time, which can be upgraded. Furthermore, the percentage of p-chlorophenol removed was 83.98% at pH 10.8 in RHOP and the reduction in COD was up to 42.19%. In addition, the types of waste, circulation time and ozone levels played a very important role in degrading phenolic wastes in liquids.
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