Catalytic Oxidation of Toxic Organics in Aqueous Solution for Wastewater Treatment: a Review

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Abstract – The paper reviews catalytic oxidation for the treatment of wastewater that contains toxic organics from industry or domestics which have to be treated before returning into the aquatic environment. Conventional or individual wastewater treatment often cannot degrade organic compounds completely. Therefore, advanced wastewater treatment process is needed, which combines several methods such as catalyst, oxidant and photocatalytic. From the previous studies, advanced process proved to improve the degradation efficiency of organic pollutants from the effluents.

Keyword: Catalytic oxidation, Toxic organics, Oxidants, Photocatalytic
1. Introduction

Industrial activity produces large amount of organic wastewater containing products hazardous to the environment, which have to be processed before discharge into water bodies. There are many types of organics in wastewater; however, one of the most common important class of environmental water pollutants are phenol and its derivatives due to their toxicity to many living organism even at low concentrations [1]. These pollutants have been considered on the EPAs priority since 1976 [2]. The phenol and its derivatives can be found from many industries as by products such as petroleum refining, petrochemical, pharmaceutical, plastic and pesticides chemical industries [3, 4]. There are many typical of wastewater treatment including combination from few techniques which are physical, biological and chemical methods [5-7]. However the chemical processes are promising and attractive because they can degrade pollutants efficiently and economically [8]. These processes are including chemical oxidation, thermal oxidation, wet air oxidation etc. or commonly known as Advanced Oxidation Process (AOPs) [9].

2. Combination of wastewater treatment processes

Wastewater treatment using single or individual process could not provide good results to remove organic and inorganic content from those wastes. There are many researches showing that combinations of wastewater treatment provide highly efficiency than conventional ones. Beltran et.al. (1997) investigated that direct photolysis could not degrade easily organic content of wastewaters, however with combination process with ozone and hydrogen peroxide could degrade much better. Other researchers reported that by means of combining the light and ozone better results of phenol degradation than individual light with rate of 92.6% and 24.2% respectively could be achieved [11]. Moreover, study in decomposition of organophosphoric acid by combination of ozone and vacuum ultraviolet showed that rate of degradation is higher than individual vacuum ultraviolet with rate of degraded 75% and 50%, respectively [12].

Furthermore, other publications by other researchers have reported that photocatalytic system could completely degrade 2-chlorophenolns, 2-nitrofenol in 2 hours [13]. Trichloroethylene and toluene mixtures are also reported to be degraded under photocatalytic system [14]. Moreover, many researchers have conducted intensively work in actual industrial effluents and also mixed pollutants by using photocatalytic system [15].

The photocatalytic system is based on the formation of \( \text{OH}^* \) radicals by means of the photolysis of hydrogen peroxide. The reaction mechanism of photocatalysis could be divided into three steps, which are initial, propagation, termination reaction as described below [16].

Initial reaction:

\[
H_2O_2 + h \nu \xrightarrow{k_p} 2\text{OH}^* \\
H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2
\]

(2)

Propagation reaction:

\[
H_2O_2 + \text{OH}^* \rightarrow \text{HO}_2^* + H_2O \]

(3)

\[
H_2O_2 + \text{HO}_2^* \rightarrow \text{OH}^* + H_2O + O_2 \]

(4)

\[
\text{HO}_2^* + \text{HO}_2^* \rightarrow \text{OH}^* + \text{OH}^- + O_2 \]

(5)

Termination reaction:

\[
\text{OH}^* + \text{HO}_2^* \rightarrow H_2O + O_2 \]

(6)

\[
\text{OH}^- + \text{OH}^* \rightarrow H_2O_2 \]

(7)

In order to increase efficiency of degradation of photocatalysis system, many researchers are using either homogeneous or heterogeneous catalysts such as \( \text{TiO}_2 \), \( \text{ZnO} \) for catalysis, whereas \( \text{H}_2\text{O}_2 \) or \( \text{Fe}^{3+} \) for homogenous photochemistry [17]. These metals e.g. \( \text{TiO}_2 \) exposed of light will produce a hole in the valence band and electrons in the conduction band. The holes will react with ion OH to generate hydroxyl radicals (\( \text{OH}^* \)). Furthermore, the \( \text{OH}^* \) will oxidize the organic compounds in wastewater. While the electrons will reduce the heavy metals, which were adsorbed on the surface catalyst [18]. Currently, titanium oxide has been widely used for photocatalytic process. In addition, there are many researchers reporting that different catalysts also could be used in photocatalytic process such as \( \text{ZrO}_2 \), \( \text{ZnO} \), \( \text{SrO}_2 \), \( \text{Fe}_2\text{O}_3 \), and \( \text{CdS} \) [19]. Moreover, an intensive study has been conducted on \( \text{ZnO} \) in effort to find other metal oxides besides \( \text{TiO}_2 \), which act as a catalyst in photocatalytic system. \( \text{ZnO} \) has a band gap of 3.25 eV reported as an effective catalyst for oxidizing of phentachlorophenol, hydrochloric acid and phenol [20].

Basically, photocatalytic process needs oxidizing species in order to increase the rate of photooxidation [21]. Gratzel et al. (1990) have conducted the research to degrade organophosphorus compounds using photocatalytic/oxidant system, using several oxidants. \( \text{NaIO}_3 \) provides the most attractive effect in enhancing the rate of catalytic activity followed by \( \text{KBrO}_3 \). The ranking of the oxidants are in the following order which are \( \text{NaIO}_3 > \text{KBrO}_3 > \text{H}_2\text{O}_2 > \text{K}_2\text{S}_2\text{O}_8 \) [22].
2.1 Oxidizing Agents

The table below shows a list of oxidizing agents and their oxidation potentials measured in volts, which are often used in AOP. If oxidizing agents have higher oxidation potential, it will have the greater reactivity and oxidation capacity. Some popular oxidants include ozone, hydrogen peroxide, permanganate, chlorine dioxide, and chlorine.

Hydrogen peroxide, which has a standard reduction potential of 2.8 V vs NHE in acidic media, would be able to oxidize almost all organic compounds to carbon dioxide and water, except for some of the simplest organic compounds, such as acetic, maleic and oxalic acids, acetone or simple chloride derivatives [16]. Hydrogen peroxide (H₂O₂) is unstable and readily gives up its extra oxygen atom, it is an excellent oxidizing agent (Noyes, 1994). It has been used to oxidize amines, aldehydes, and cyanide without catalysts. When a catalyst is needed for more-difficult-to-oxidize compounds, ferrous iron (Fe²⁺) is the one most commonly used.

<table>
<thead>
<tr>
<th>No</th>
<th>Oxidant</th>
<th>Standard reduction potential (V vs NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fuerine (F₂)</td>
<td>3.03</td>
</tr>
<tr>
<td>2</td>
<td>Hydroxyl radical (OH)</td>
<td>2.80</td>
</tr>
<tr>
<td>3</td>
<td>Atomic Oxygen</td>
<td>2.42</td>
</tr>
<tr>
<td>4</td>
<td>Ozone (O₃)</td>
<td>2.07</td>
</tr>
<tr>
<td>5</td>
<td>Hydrogen peroxide (H₂O₂)</td>
<td>1.77</td>
</tr>
<tr>
<td>6</td>
<td>Potassium permanganate</td>
<td>1.67</td>
</tr>
<tr>
<td>7</td>
<td>Hypobromous acid (HBrO)</td>
<td>1.59</td>
</tr>
<tr>
<td>8</td>
<td>Chlorine dioxide (ClO₂)</td>
<td>1.50</td>
</tr>
<tr>
<td>9</td>
<td>Hypochlorous acid (HClO₄)</td>
<td>1.49</td>
</tr>
<tr>
<td>10</td>
<td>Chlorine (Cl₂)</td>
<td>1.36</td>
</tr>
<tr>
<td>11</td>
<td>Bromine (Br₂)</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Chlorine is widely used as an oxidant for oxidizing cyanide in industrial wastewater for mining industries. Due to many complex chlorinated compounds produced when chlorine reacts with organic compounds chlorine oxidant is rarely used in oxidation of organic compounds [23]. Chlorine dioxide is different with chlorine oxidation, in which the effectiveness of chlorine dioxide (ClO₂) oxidation is not depending on pH. For instance, when chlorine dioxide is used to oxidize phenols, the byproducts are odorless, while chlorine is highly odorous. In addition, chlorine dioxide can oxidize alcohols, while chlorine cannot.

Other oxidant, Permanganate (MnO₄⁻) compounds is one of the most famous oxidants utilized to wastewater to oxidize inorganic and organic pollutants such as cyanide, hydrogen sulfide, and phenols. Permanganate has also been used to oxidize iron, manganese, and compounds associated with taste and odor. Permanganate obtained from potassium permanganate, which can be stored dry in crystalline form [24].

2.2 Heavy metal catalysts

Homogenous catalytic oxidation has been identified as effective process to degrade toxic organics such as phenol. Fenton’s reagent (H₂O₂ and ferrous ion) and copper cations are mostly effective process to reduce hazardous substance [25, 26]. However, their recovery needs a more process for separation of the catalyst, which requires additional separation cost [27]. Moreover, most of the dissolved metal catalysts are harmful to the environment. This advantage can be overcome by using heterogeneous catalysts in which these catalysts will be easily recoverable and reusable [28]. Heterogeneous catalytic oxidation of aqueous solutions containing organic compounds, such as dyes, phenol and its derivatives, have widely used as a technology for reducing these substances in wastewater from industries [3, 8, 9]. Furthermore, the heterogeneous catalysis can completely convert organics to CO₂ and H₂O or partially oxidize the organic compounds to less toxic intermediates by using hydrogen peroxide as an oxidant agent.

Phenol degradation has been studied in many heterogeneous catalytic investigations [29-31]. Moreover, the literature review shows most the researchers investigated variability in activity and stability among the catalysts. They most often used metal oxides (Cu, Mn, Co, Cr, V, Ti, Bi and Zn) or supported noble metals (Ru, Pt, Rh, Ir, and Pd) [32, 33]. According to Massa et al. (2006) there are still many problems using metal oxides or noble metals such as stability, deactivation, leaching of the active phase (or support) and also forming carbonaceous products which will cover of the catalyst surface.

3. Conclusion

Toxic organics degradation has been analyzed. It is apparent that the most of toxic compounds for which heterogeneous catalyse using oxidant and potocatalytic are feasible because easily recoverable and reusable. Furthermore, the heterogeneous catalysis can completely convert organics to CO₂ and H₂O or partially oxidize the organic compounds to less toxic. However, it needs intensive research for synthesizing a catalyst which has stability and durability.

References


