EFFECT OF pH ON DEGRADATION OF PENTACHLOROPHENOL (PCP) USING GAMMA RADIATION

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ABSTRACT

EFFECT OF pH ON DEGRADATION OF PENTACHLOROPHENOL (PCP) USING GAMMA RADIATION. Effect of pH on degradation of PCP using gamma radiation has been studied. PCP of 10 ppm was irradiated at various pHs i.e. 5, 6, 7, and 8 with dose of 0-2 kGy on dose rate of 1 kGy/h. After irradiation, the changes of the spectrums and pH solutions were measured using spectrophotometer uv-vis and pH meter, respectively. Degradation products were analyzed using HPLC. It was found that degradation of PCP could be achieved at pH 7 and dose of 2 kGy. Degradation product that could be detected using HPLC was oxalic acid.

Key words: pentachlorophenol, gamma radiation

INTRODUCTION

Pentachlorophenol (PCP) was used to control termites and to protect the things against fungal rats and wood-boring insect timber [1]. PCP or its sodium salts have also been used as a herbicide and desiccant for forage seed crop, a herbicide for non-food vegetation control, a biocide in the post harvest washing fruits, and as an insecticide for use in beehives, seed plots and green houses [1-3].

In wood processing, the waste that discharges into the environment contains 0.05 up to 2760 ppb of PCP, where in chemical plant PCP was found to be 5400 ppb [1]. Since PCP is one of the hazardous compound and toxic to plants, animals and human, the waste that contains PCP should be good handled before discharges into the environment. Its biodegradation is low, on the other hand physical and chemical treatment remains undestroyed, therefore an alternative method is needed to degrade PCP into another compound which is less toxicity. The use of gamma ray to degrade PCP has been done by several researchers i.e He et al [4] and Fang et al [5]. Their result is promising because PCP could be degraded using gamma rays in combination with ozone. Since PCP was affected by the pH, therefore the effect of pH on the degradation of PCP must be studied using gamma radiation to obtain the optimum pH. The intensity of PCP spectrum increased with the increase of dose both in acidic or basic pH, therefore optimum pH to degrade them will necessary to study.

In this paper the effects of pH and doses on PCP degradation and the degradation products will be discussed.
EXPERIMENT

Reagents
PCP (99%), ethanol, NaOH, H_2SO_4, H_3PO_4 0.005%, (COOH)_2
(as a standard for measuring degradation products using HPLC), buffer
standards of pH 4 and 7.

Preparation of solutions
The solutions of 500 ppm PCP were prepared by dissolving 50 mg of
PCP into 100 ml of ethanol. The solution containing 10 ppm PCP in various
pH of 5, 6, 7, and 8 were prepared from 500 ppm PCP by diluted the solution
in pure water. pHs were adjusted using NaOH and H_2SO_4.

Irradiation procedures
Irradiation was done using cobalt-60 gamma rays at room temperature
with various dose of 0, 0.5, 0.75, 1, 1.5, and 2 kGy. The dose rate of 1 kGy/h
was determined by a Fricke dosimeter. The activity of gamma rays
was 22,000 Ci in July 2001. The air was introduced into the solution
during irradiation.

Analysis
The optimum pH and doses were determined from this experiment.
The absorbance and the pH of the solution were measured by HP 8453
spectrophotometer uv-vis and Methrom 620 pH-meter, respectively.
The degradation products at optimum pH and doses were determined by a
High Pressure Liquid Chromatography (HPLC LC 5A) using uv detector and
Shodex Pax column. The measurement of degradation products after
irradiation of PCP solution was carried out by HPLC using Shodex RS-pak
column and H_3PO_4 0.005% as a solvent. The degradation products that can be
measured is assumed to be an oxalic acid. Calibration curve were made by
injecting the oxalic acid standard at a certain concentration and measuring the
height of the spectrum. By matching a retention time of the samples and
standard, calculation was made.

RESULTS AND DISCUSSION
The effect of pH on the degradation
PCP has a clear absorption band at 220 nm and weak absorption at
250 nm and 320 nm in the uv-vis spectra as shown in Fig1. The first
absorption is considered to be the main absorption assigned to their substituted aromatic rings, the second and third absorptions can be assigned to conjugated system of PCP molecules and free electron of oxygen or chlor atoms. The spectrum of PCP at pHs 5, 6, 7, and 8 could be seen from Fig. 1, 2, 3, and 4, respectively. Figs. 1, 2, and 4 show the absorbance at 220 nm shifted into shorter wavelength, hypsochromic shift, the shift of absorption to a shorter wavelength due to substitution or solvent effect, a blue shift [6]. This blue shift may be caused by the change of the medium and shifted of the conjugated system. The change of the medium is the most possible since the pH of PCP after irradiation decreased into acid condition. It is indicated that in the solution, hydrogen radicals increased, from these situations. It can be assumed that hydrogen radicals will replace the chlor ions in PCP molecules as illustrated as follows:

Because of chlor ions have high electronegativity and free electron, so that PCP spectrum could be shifted into longer wavelength, on the other hand hydrogen ions have no free electron therefore hydrogen atoms in PCP molecules would cause hypsochromic effect.

The intensity at 220 nm decreased at dose of 0.75 kGy, and then increased up to dose 2 kGy. This increase in intensity is influenced by several factors such as: molar extinction coefficient ($\epsilon$), concentration of solute and and path length through the sample. Since the concentration of solute and path length through the sample remains the same, the main factor that influenced is the molar extinction coefficient ($\epsilon$). The $\epsilon$ value also influenced by the probability of electron transition and absorption system. One of the factors that influenced $\epsilon$ value is the overlapping of $\pi$ orbital in the electronic excitation of benzene from PCP molecules. Electronic excitation of PCP molecules in the formed of molecules is bigger than that PCP in the formed of ions. The equilibrium between PCP molecule and ions in water is as follows:
The existence of electron in oxygen atoms will be dislocated to the carbon atoms in the benzene ring, this will cause pentachlorofenolat has small transition probability. Therefore when pentachlorofenolat was irradiated it is difficult to excite.

In acid medium, pentachlorofenolat will form PCP molecules, the higher the dose the higher the PCP molecules. PCP has high transition probability because of \( \pi \) orbital overlapping. Benzene should contain three \( \pi \) bonds and three \( \pi \) antibondings, the transition of \( \pi \rightarrow \pi^* \) will affect overlapped orbital and will give transition probability of 1.0. PCP molecules have high probability exitation therefore the \( \varepsilon \) value will be high. In accordance with Beer-Lambert law, \( \varepsilon = A/\text{cl} \), at a constant concentration of PCP the intensity of the spectrum will be increased by the increasing of \( \varepsilon \) value. The other possibility that could increase the intensity of the 220 nm wavelength is \( O_2 \) molecules. Oxygen molecules have two free electrons unshared, when oxygen introduced into irradiated PCP solution the oxygen molecules will react with solvation electrons as illustrated \( ^{1}O_2^- + e_{aq} \rightarrow O_2^- \) \( \varepsilon = 1.9 \times 10^{10} \) According to Fang \textit{et al.} (5) \( O_2^- \) reacts slowly with PCP and might reduce some pentachlorofenolat radical to regenerate PCP, therefore the intensity at 220 nm increased.

At pHs 5, 6, and 8 the effect of dose give a different results in intensity of the spectrum at 220 nm. At pH 7 the intensity of the spectrum decreased slowly as the dose increased, therefore experiment was carried out at pH 7. The PCP spectrum at pH 7 could be seen from Fig.4. The intensity of the spectrum at 220, 250, and 320 nm decreased with the increase of the dose. According to He \textit{et al.} 2001 degradation of PCP depends on the dose applied, when the dose applied is higher the intermediet compound will compete with PCP in capturing oxidation species \( \cdot \text{OH} \) atau \( e_{aq}^- \). The existence of oxidation species i.e \( \cdot \text{OH} \) and \( \text{H}_2\text{O}_2 \) should be managed in
In order to get enough to degrade PCP compound. Irradiation was done at low dose and dose rate to maintain the decrease of pH so that the existence of OH radicals could be managed [4].

The absorbance at 250 and 320 nm decreased remarkably as the dose increased. These decreases in intensity are obviously due to the destruction of the conjugated system $\pi \rightarrow \pi^*$ transition and the decrease of free electron of oxygen and chlor atoms $n \rightarrow \pi^*$. 

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>Absorbance at 222 nm</th>
<th>pH 5</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>1.650</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>1.515</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>1.522</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.521</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1.650</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1.867</td>
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</table>

Figure 1. The spectra changes of PCP after irradiated at dose of 0-2 kGy, with dose rate of 1 kGy/h and pH 5.

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>Absorbance at 220 nm</th>
<th>pH 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<tr>
<td>0.5</td>
<td>1.558</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>1.474</td>
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<td>1.0</td>
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<tr>
<td>1.5</td>
<td>1.594</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1.659</td>
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</tr>
</tbody>
</table>

Figure 2. The spectra changes of PCP after irradiated at dose of 0-2 kGy, with dose rate of 1 kGy/h and pH 6.
The change of pH

The pH of PCP after irradiation is decreased as the dose increased the results can be seen in Fig. 5. The decrease of pH indicated that the compound already degraded into acidic compound. At pH 7 and 8 the pH decreased up to dose of 1.5 kGy, and then increased at dose of 2 kGy. This increase suggests that the acidic compound further degraded into CO$_2$, while the hydrogen ions that formed from PCP degradation will react with OH radical and formed H$_2$O.

According to Fang et al. [5] the degradation products of PCP were o- and p-chloranils and they hydrolyse into trichlorohydroxyl-p-benzoquinone and chloranilic acid, these compound will be lowered the pH. In this experiment the degradation products were measured using HPLC. It is found
that oxalic acid is one of the degradation product that could be detected using HPLC. Fang et al. irradiated PCP at low dose (150 Gy) therefore the o- and p-chloranil, trichlorohydroxyl-p-benzoquinone and chloranilic acid were detected. In this experiment the dose applied is from 0.5 up to 2 kGy so those compounds may be degraded into a small compounds.

![Figure 5. The changes of pH after irradiation.](image)

**Measurement of degradation product**

The measurement of degradation product was done using HPLC. The chromatogram of oxalic acid standard and irradiated PCP were shown in Fig 6a and 6b, respectively. The oxalic acid standard has a retention time 5.373 minute and irradiated PCP at 0.5 kGy has a retention time at 5.375 minute. By matching those two chromatograms it is assumed that oxalic acid is one of the degradation product that could be detected by HPLC. Before irradiation oxalic acid was not found, after irradiation at dose of 0.5 kGy oxalic acid is detected. Several researchers reported that PCP at post-irradiated at dose of 1 kGy with the addition of ozon might be decomposed into carboxylic acids. In the photocatalytic process the PCP is degraded into formic acid and acetic acid [7].
CONCLUSIONS

Degradation of pentachlorophenol (PCP) solution can be done at pH 7, at dose of 2 kGy. At pH 5, 6, and 8 the intensity of PCP spectrum at 220 nm increased and shifted to the shorter wavelength after it has been irradiated at dose of 2 kGy. Irradiation is effectively applied to PCP degradation at dose of 2 kGy. The degradation product that could be detected was oxalic acid.

REFERENCES


