UNIVERSITI PUTRA MALAYSIA

DEGRADATION OF 2-CHLOROPHENOL IN WATER USING ADVANCED OXIDATION PROCESSES

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Dedicated to mum, dad and pei ching, with love

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements of the degree of Master of Science

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The presence of endocrine disruptor chemicals (EDCs) in treated wastewater lately, is alarming. Chlorophenols, an endocrine disruptor chemical compound is hardly eliminated in water using conventional treatment. In this study, contaminated water containing 2-Chlorophenol was treated using the Advanced Oxidation Processes (AOPs) reactor (anolyte solution/ozone/UV) and anolyte solution alone. Various conditions such as initial pH values, ozone dosages, reaction time and initial 2-Chlorophenol concentrations were tested to achieve the optimum degradation of 2-Chlorophenol. Possible intermediates and by-products in each treatment effluents were investigated. Results showed that almost 90% of 2-Chlorophenol (5mg/L) degraded in water with initial alkaline pH values (11-12) using AOPs reactor (anolyte solution (0.4L)/Ozone 50% (0.51 mg/L)/UV). Complete (100%) degradation of 2-Chlorophenol

in water was achieved when initial concentration of 2-Chlorophenol was 0.04 mg/L in neutral pH condition. On the other hand, at least 70% of the 2-Chlorophenol degraded when treated with anolyte solution in all initial pH values and initial 2-Chlorophenol concentrations. Complete (100%) degradation of 2-Chlorophenol occurred when the initial concentration of 2-Chlorophenol was 1.0 mg/L in original pH condition. All effluent samples had acidic pH value except those 2-Chlorophenol solutions with initial alkaline pH values. Comparison between two treatments showed that anolyte solution was more effective to degrade 2-Chlorophenol than AOPs reactor at original and neutral pH conditions. The degradation of 2-Chlorophenol compounds in water was achieved up to 100% using anolyte solution compared to the AOPs reactor at higher 2-Chlorophenol concentration in most cases. The 2-Chlorophenol degraded intermediates and by-products using AOPs reactor and anolyte solution were mainly alkenes, alkanes, carboxylic acid, ketones and ether functional group compounds.

Keywords: *Degradation, 2-Chlorophenol, Advanced Oxidation Processses (AOPs), Anolyte solution*

Abstrak yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

DEGRADASI 2-KLOROFENOL DI DALAM AIR DENGAN MENGGUNAKAN PROSES PENGOKSIDAAN LANJUTAN

Oleh

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Pengerusi: **Profesor Azni Idris, PhD**

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Kehadiran bahan kimia gangguan endokrin di dalam air yang telah dirawat baru-baru ini amat membimbangkan. Perawatan air yang konvensional tidak mampu untuk menyingkirkan Klorofenol yang merupakan salah satu ahli kumpulan bahan kimia gangguan endokrin. Dalam kajian ini, air buangan sintetik yang mengandungi 2-Klorofenol telah dirawat dengan menggunakan proses pengoksidaan lanjutan (kombinasi cecair 'anolyte'/ozon/lampu ultraungu) dan cecair 'anolyte' sahaja. Pelbagai keadaan telah dikaji seperti nilai pH awal, dosej ozon, masa tindakbalas dan kepekatan awal 2-Klorofenol untuk mencapai keadaan optimum degradasi 2-Klorofenol. Sampel yang telah dirawat dari setiap proses perawatan tersebut dikenalpasti bahan perantaraan dan degradasinya. Keputusan menunjukkan hampir 90% daripada 2-Klorofenol (5mg/L) di dalam air yang berkeadaan nilai pH awal beralkali (11-12) telah didegradasikan dengan menggunakan reaktor proses pengoksidaan lanjutan (cecair 'anolyte' (0.4

L)/50% ozon (0.51 mg/L)/lampu ultraungu). Degradasi 2-Klorofenol sepenuhnya (100%) di dalam air dapat dicapai apabila kepekatan awal 2-Klorofenol berada pada 0.04 mg/L dalam keadaan nilai pH neutral. Sementara itu, sekurang-kurangnya 70% 2-Klorofenol dapat didegradasikan apabila dirawat dengan menggunakan cecair 'anolyte' di dalam semua keadaan nilai pH awal dan semua kepekatan awal 2-Klorofenol. Degradasi 2-Klorofenol sepenuhnya (100%) di dalam air dapat berlaku apabila kepekatan awal 2-Klorofenol berada pada 1.0 mg/L dalam keadaan nilai pH yang asal. Semua sampel yang telah dirawat oleh kedua-dua proses berada dalam keadaan berasid kecuali sampel yang nilai pH permulaannya beralkali. Cecair 'anolyte' didapati lebih efektif dalam mendegradasikan 2-Klorofenol di dalam air berbanding reaktor proses pengoksidaan lanjutan pada keadaan nilai pH asal dan neutral. Degradasi 2-Klorofenol dapat dicapai 100% pada kepekatan awal 2-Klorofenol yang lebih tinggi oleh cecair 'anolyte' berbanding dengan menggunakan reaktor proses pengoksidaan lanjutan dalam kebanyakan kes. Hasil bahan perantaraan dan degradasi yang telah dirawat oleh kedua-dua proses tersebut terdiri daripada kumpulan berfungsi alkena, alkana, asid karbosilik dan eter.

***Kata kunci**: Degradasi, 2-Klorofenol, Proses pengoksidaan lanjutan, Cecair 'anolyte'*

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LIST OF ABBREVIATIONS

2,4,5,-T	2,4,5-Trichlorophenoxyacetic acid
2,4-D	2,4-Dichlorophenoxyacetic acid
2,4-DCP	2,4-Dichlorophenol
2-CP	2-Chlorophenol
4-CP	4-Chlorophenol
AOPs	Advanced Oxidation Processes
BDD	Boron-doped Diamond
BOD	Biological Oxygen Demand
CAS	Conventional Activated Sludge
Cl_2	Molecular Chlorine
DBCP	Dibromochloropropane
DBP	Disinfection By-Products
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DNA	Deoxyribonucleic Acid
ECA	Electrochemical Activation
EDCs	Endocrine disruptor chemicals
EEDRI	European Endocrine Disruptors Research Inventory
GC-FID	Gas Chromatography-Flame Ionization Detector
GC-MSD	Gas Chromatography-Mass Spectrometric Detector
HOCl	Hypochlorus Acid

HPLC	High Performance Liquid Chromatography
HRT	Hydraulic Retention Time
IARC	International Agency for Research on Cancers
K_a	Dissociation Constant
K_{ow}	Partition Coefficient
NHE	Normal Standard Hydrogen Electrode
OCl^-	Hypochlorite Ion
OI	Oxidation Index
PCP	Pentachlorophenol
PVC	Polyvinyl Chloride
RO	Reverse Osmosis
SBR	Sequencing Batch Reactor System
S-N-K	Student-Newman-Keuls
SPE	Solid Phase Extraction
TOC	Total Organic Carbon
UPUM	Unit Perundingan Universiti Malaya
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

Water is essential to every living thing on earth. Water can be mean of life or dead. In some places, water is abundant while others water shortage is likely to occur. Today, there are approximately 1.2 billion people are lack of access to safe water consumption and 3 billion have insufficient sanitation (Ashraf, 2003). Thus, water is valuable and some even naming water as "Blue Gold" where water is scarcely found. Despite water is cost free and natural gifts, most of us taken for granted and our activities have violated water causing severely water pollution. Those impurities in the water are wide-ranging from substantially nutrient to heavy metal and eventually organic compounds.

The discovery of endocrine disruptor chemicals (EDCs) in the treated wastewater lately is being concerned. EDCs compounds sources are mainly from the synthetic chemicals, which have the ability to disrupt the healthy endocrine systems. Most of the EDCs compounds are xenobiotic and complex organic compounds. They are highly toxic and persistent to environment. Chlorophenols such as 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) and pentachlorophenol (PCP) are categorized as one of the group compounds belong to EDCs and have been named as priority pollutants by the USEPA (Rao et al., 2003). The stability of the C–Cl bond in halohydrocarbons is responsible for their toxicity and persistence in the biological environment (Rao et al., 2003).

The intrusion of 2-Chlorophenol to the aquatic environment via various of discharges from production of higher chlorinated phenols plants manufacturing, paper-mills as by-product of chlorine-based bleaching, disinfection of sewage industrial wastewater with chlorine, by-products as a results of slow microbial breakdown of herbicides and coal extraction industries (Rao et al., 2003).

In Malaysia, contamination of phenolic compounds is found in the rivers and streams. Recently, UPUM (2003) reported that most of the wastewater discharged from industries along the Sungai Langat River is polluted with phenolic compounds. This wastewater contained extensively phenolic compounds, which is exceeded the standard limits (0.001 mg/L - Standard A) of environmental regulations. Those highly toxic compounds are consequently harmful to humans, animals, and fish once they entered to the rivers and streams.

Hence, in this critical environment, the conventional treatment such as biological treatment is hardly eliminating those impurities (Papadaki et al., 2004). Thus, formation of new treatment must fulfill at least the initial requirement, which is to degrade those compounds into simplified ones is vital, in order to maintain the entire water bodies into a sustainable environment. The emergence of Advanced Oxidation Processes (AOPs) treatment are believed to be effectively against these intractable compounds (Shu and Chang, 2005).

In this study, 2-Chlorophenol is selected as surrogate EDCs compounds and spiked into distilled water as contaminated water, which then treated using AOPs. The objectives of the research are:

1. To evaluate the possible degradation of 2-Chlorophenol using AOPs reactor, which consisted of anolyte solution, ozone and UV lamp and to determine the optimum condition for 2-Chlorophenol degradation considering parameter such as initial pH values, ozone dosages, reaction time and initial 2-Chlorophenol concentrations.

2. To evaluate the possible degradation of 2-Chlorophenol using anolyte solution alone and to determine the influence of the initial pH value and initial 2-Chlorophenol concentrations on degradation efficiency.

3. To identify the by-products of the reaction and to propose pathway of 2-Chlorophenol degradation in water after each treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Endocrine Disruptor Chemicals (EDCs) Issue

The endocrine system consists of a set of glands that communicates in a more diffuse fashion, transporting information through the circulation from one tissue to another via chemical messengers or hormones (Witorsch, 2002). These chemicals messenger or hormones help to guide the development, growth, reproduction, and behavior of animals including human beings. Some of the endocrine glands include all important functions of an organism, such as the pituitary, thyroid, and adrenal glands, the female ovaries and male testes.

Endocrine disruptors are defined as " an exogenous substance or a mixture, that alters functions of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny or (sub) populations"(European Commission, 1996).

Endocrine disruption refers to the interference of endocrine system function by environmental chemicals. Endocrine disruptors may interfere with the normal functioning of hormones in several ways. Ordinarily, a hormone binds exclusively to its receptor on or inside a cell, like a key fitting into a lock. It then activates a chain of events that results in a biological response. They act by modulating the levels of,

responses to hormones. These effects can be induced according to various mechanisms (Dawson, 2000).

An endocrine-disrupting substance, however, may be shaped enough like the hormone to bind to its receptor. There, it may activate the receptor, initiating the chain of events as if the hormone were there. Or it may simply occupy the hormone's usual binding site, preventing normal hormone activity. Endocrine disruptors may also interfere with serum hormone-binding proteins that regulate the availability and activity of hormones. They may change the number of hormone receptors present in specific tissues, the amount of a hormone produced, or the rate at which hormones are broken down and excreted. In summary, these substances augment, prevent, or otherwise alter the normal activity of hormones.

To date, most research on endocrine disruption has focused on synthetic chemicals that perturb the normal activity of estrogens, androgens, and thyroid hormones, but some chemicals disrupt other hormonal pathways as well. Some sources and potential endocrine disruptor substances in our environment are shown in Table 2.1.

Table 2.1 Some sources and potential endocrine disruptor substances in our environment (Environment Canada, 1999)

Sources	Category (Uses)	Substances
Incineration, Landfill	Polychlorinated compounds (from industrial production or by- products of mostly banned substances)	Polychlorinated dioxins, Polychlorinated biphenyls
Agricultural runoff/atmospheric transport	Organochlorine pesticides (Found in insecticides, many now phased out)	DDT, dieldrin, lindane
Agricultural runoff	Pesticides currently in use	Atrazine, trifluralin, permethrin
Harbours	Organotins (found in antifoulants used to paint the hulls of ships)	Tributyltin
Industrial and municipal effluents	Alkylphenolics (Surfactants – certain kinds of detergents used for removing oil – and their metabolites	Nonylphenol
Industrial effluent	Phthalates (found in plasticizers)	Dibutyl phthalate, butylbenzyl phthalate
Municipal effluent and agricultural runoff	Natural Hormones (produced naturally by animals); Synthetic steroids (found in contraceptives)	17 β-estradiol, estrone: testosterone, ethynyl estradiol
Pulp mill effluents	Phytoestrogens (Found in plant material)	Isoflavones, ligans, coumestans, Phenolic compounds