REMOVAL OF CHLOROPHENOLIC COMPOUNDS FROM AQUEOUS SOLUTION BY ADSORPTION ONTO VARIOUS ACTIVATED CARBONS PRODUCED FROM OIL PALM SHELL

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by

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LIST OF SYMBOLS

		Unit
A	Arrhenius factor	molec./ cm^2 s
A_i	Spectrometry absorbance	-
A	Constant for Temkin isotherm	L/g
B	Constant for Temkin isotherm	J/mol
b	Constant for Langmuir isotherm	L/mg
b_c	Path length of the cell	cm
C_{ad}	Difference between inlet/initial and outlet/equilibrium concentration	mg/L
C_{de}	Concentration of adsorbate desorbed	mg/L
C_e	Concentration of adsorbate at equilibrium	mg/L
C_i	Constant for Intraparticle diffusion model	mg/g
C_t	Concentration of adsorbate at time, t	mg/L
C_0	Initial/inlet adsorbate concentration	mg/L
D_p	Average pore diameter	nm
E_a	Arrhenius activation energy of adsorption	kJ/mol
k_f	Adsorption or distribution coefficient for Freundlich isotherm	$(mg/g)\ (L/mg)^{1/n}$
k_{pi}	Adsorption rate constant for intraparticle diffusion model	$mg/g\ h^{1/2}$
k_1	Adsorption rate constant for pseudo-first-order kinetic model	1/min
k_2	Adsorption rate constant for pseudo-second-order kinetic model	g/mg h
K_D	Distribution coefficient of the adsorbent, is equal to q_e/C_e	L/g
n	Constant for Freundlich isother	-
q_{max}	Adsorption capacity for Langmuir isotherm	mg/g
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium	mg/g

q_t	Amount of adsorbate adsorbed per unit mass of adsorbent at time, *t*	mg/g
$q_{t,cal}$	Calculated adsorption at time, *t*	mg/g
$q_{t,exp}$	Experimental adsorption at time, *t*	mg/g
R	Universal gas constant	8.314 J/mol K
R^2	Correlation coefficient	-
R_L	Dimensionless constant for Langmuir isotherm	-
T	Absolute temperature	K
t	Time	h
V	Solution volume	L
W	Dry weight of adsorbent	g
$\Delta G°$	Changes in standard free energy	kJ/mol
$\Delta H°$	Changes in standard enthalpy	kJ/mol
$\Delta S°$	Changes in standard entropy	J/mol K
$\mathcal{E}_\lambda$	Molar absorptivity coefficient of solute	L/mol cm

LIST OF ABBREVATIONS

AC	Activated carbon
ACs	Activated carbons
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BOD	Biochemical Oxygen Demand
CAC	Commercial Activated Carbon
4C2MP	4-chloro-2-methoxyphenol
COD	Chemical Oxygen Demand
2CP	2-chlorophenol
CPs	Chlorophenols
24DCP	2,4-dichlorophenol
EDX	Energy Disperse Analysis through X-ray Spectroscopy
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared
GAC	Granular activated carbon
IR	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
MSDS	Material Safety Data Sheet
OPS	Oil palm shell
OPSAC	Oil palm shell Activated Carbon
OPSACs	Oil palm shell Activated Carbons
OPSAC-K_2CO_3	Oil palm shell Activated Carbon with Potassium Carbonate
OPSAC-KOH	Oil palm shell Activated Carbon with Potassium Hydroxide
OPSAC-NaOH	Oil palm shell Activated Carbon with Sodium Hydroxide
PAC	Powdered activated carbon
pH_{pzc}	pH point of zero charge
rpm	Rotation per minute
SEM	Scanning electron microscopy
246TCP	2,4,6-trichlorophenol
TGA	Thermogravimetric analyzer
USA	United States of America
WHO	World Health Organisation

PENYINGKIRAN SEBATIAN KLOROFENOL DARIPADA LARUTAN AKUEUS MELALUI PENJERAPAN KE ATAS PELBAGAI KARBON TERAKTIF YANG DIHASILKAN DARIPADA TEMPURUNG KELAPA SAWIT

ABSTRAK

Kajian ini bertujuan meneroka kemungkinan menyediakan karbon teraktif berliang meso daripada tempurung kelapa sawit, yang merupakan hasil sampingan pertanian yang banyak terdapat di Malaysia. Proses pengaktifan fisikokimia dengan natrium hidroksida, kalium hidroksida dan kalium karbonat serta pengisitepuan dengan gas nitrogen dan karbon dioksida digunakan untuk menyediakan karbon teraktif. Hasil eksperimen menunjukkan bahawa suhu dan masa pengaktifan serta nisbah pengisitepuan agen kimia merupakan faktor yang secara ketara mempengaruhi hasil karbon teraktif dan kecekapan penjerapan bagi sebatian klorofenol. Semua karbon teraktif yang dihasilkan daripada tempurung kelapa sawit adalah mesoliang dengan luas permukaan tinggi (1571-2247 m^2/g) dan diameter liang purata 2.2 - 2.7 nm. Mikrograf SEM menunjukkan banyaknya liang homogen yang teratur terbentuk pada karbon teraktif. Analisis FTIR menunjukkan kehadiran kumpulan berfungsi yang berbeza pada permukaan karbon teraktif. Penjerapan klorofenol meningkat dengan pertambahan masa sentuh dan kepekatan awal (30-225 mg/L). Kecekapan penyingkiran tertinggi klorofenol (CP) ke atas karbon teraktif adalah pada pH 2 manakala kecekapan penyingkiran terendah adalah pada pH 12. Penjerapan 4-kloro-2-metoksifenol yang paling sesuai untuk semua karbon teraktif adalah yang diberikan oleh model isoterma Langmuir. Sebaliknya, bagi penjerapan 2-klorofenol, 2,4-diklorofenol and 2,4,6-triklorofenol adalah lebih sesuai dengan model Freundlich and Temkin. Penjerapan

semua klorofenol dapat dijelaskan dengan baik oleh model kinetik tertib pseudo-kedua. Secara umum, nilai tenaga pengaktifan adalah lebih rendah daripada 40 kJ/mol bagi semua proses penjerapan, yang mewakili mekanisme fisijerapan. Nilai ΔG° (0.01-5.29 kJ/mol) dan ΔH° (0.77-12.14 kJ/mol) negatif diperoleh dalam semua kes bagi semua klorofenol, menunjukkan sifat spontan dan eksoterma bagi proses penjerapan. Sebaliknya, nilai ΔS° (0.03-17.44 J/mol K) positif yang diperoleh menunjukkan afiniti karbon teraktif bagi CP dan mempertingkatkan kerawakan pada antara muka larutan-pepejal. Penyahjerapan etanol adalah satu teknik yang munasabah untuk menjana semula karbon teraktif terpakai.

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ABSTRACT

This study seeks to explore the possibility of preparing mesoporous activated carbons from the oil palm shell agricultural by-product abundantly available in Malaysia. Physiochemical activation processes using sodium hydroxide, potassium hydroxide and potassium carbonate and impregnated with nitrogen and carbon dioxide gases were used to prepare the activated carbons. The experimental results showed that the activation temperature and time and the impregnation ratio of the chemical agents were significant factors affecting the yield of the activated carbons and adsorption efficiency for chlorophenolic compounds. All the activated carbons derived from oil palm shell were mesoporous with high surface areas (1571-2247 m^2/g) and with the average pore diameters 2.2 - 2.7 nm. SEM micrographs demonstrated many orderly and developed homogeneous pores of the activated carbons. FTIR analyses illustrated the presence of different functional groups on the activated carbon surfaces. The adsorption rates of the chlorophenols increased with increasing contact time and initial concentrations (30-225 mg/L). The highest removal efficiency of the chlorophenols (CPs) onto the activated carbons was at pH 2 while the lowest removal efficiency was at pH 12. Adsorption of 4-chloro-2-methoxyphenol on all activated carbons was best fitted by the Langmuir isotherm model while adsorption of 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol were better fitted by the Freundlich and Temkin models. Adsorption of all chlorophenols was best described by the pseudo-second-order kinetic model. In general, the values of the activation energies were lower than 40 kJ /mol of all the adsorption processes, which represented

physisorption mechanism. The negative values of ΔG° (0.01-5.29 kJ/mol) and ΔH° (0.77-12.14 kJ/mol) were obtained in all cases for all chlorophenols, indicating the spontaneous and exothermic nature of the adsorption process whereas the positive values of ΔS° (0.03-17.44 J/mol K) obtained demonstrated the affinity of the activated carbon for CPs and the enhancement of randomness at the solid–solution interface. Ethanol desorption was a feasible technique for regenerating the exhausted activated carbons.

CHAPTER ONE

INTRODUCTION

1.1 Industrial Wastewater and Water Pollution

Drinking water supports life on earth and as such, we should do everything within our power to safeguard its quality. Although the greater part of earth is covered with water, only a small percentage is appropriate for drinking. According to WHO estimates, one quarter of the world′s population lacks access to hygienic drinking water. In addition, the industrial production of various goods results in the discharge of many organic compounds to the aquatic environment. Among them, chlorophenols constitute a group of contaminants that have been designated as priority pollutants by the U.S. EPA (Poulopoulos et al., 2008).

In many countries, the economic, social, and political problems have increased due to the rapid industrial development and urbanization, resulting in unpleasant effects on the quality of life.

Freshwater is an important natural resource that can retain its freshness with proper care and treatment. To achieve the sustainability of this resource in the local development level, ensuring the prevention of pollution from domestic, industrial, and agricultural activities is necessary. In Asian developing countries, 785 million people are not able to save fresh water (Sawhney, 2003). The pollution of fresh water properties which results in declining water quality can only worsen the status. Such pollution comes from the discharge of incorrectly treated sewage and industrial wastewater.

The effect of industrial wastewater discharges on the environment is harmful to human population. Some 50 years ago, the *Minatmata* disease spread rapidly because of the presence of methyl mercury wastes in the Yatsushiro Sea and Agano River basin areas. Methyl mercury came from Japan's industrial wastewater (Matsuo, 1999). In 1981 the Malaysian palm oil and rubber industries generated 63% (1460 tons/day) and 7% (208 tons/day) of the biochemical oxygen demand (BOD), respectively. In the Philippines, wastewater from the pulp and paper mills generated 90 tons/day of BOD (Villavicencio, 1987). In Thailand, the Nam Pong River was polluted by the pulp and paper industry wastewater. The pulp and paper industry ranks third in terms of freshwater withdrawal after primary metals and chemical industries and ranks fifth among the major industries in terms of its contribution to the water pollution problem (Jindarojana, 1988).

1.2 Paper Industrial Effluent

Pulp and paper mills are the most important sources of industrial pollution worldwide. Liquid, solid, and gaseous wastes are spread mostly due to the pulping and bleaching processes. Pulping is a process in which the wood raw material is treated mechanically or chemically to separate the cellulose and hemicelluloses fiber from the wood and to improve the paper quality properties of fibers. Different stages and bleaching processes are used for removing the residual lignin to whiten and brighten the pulp.

A large amount of water is used up by the paper industry. Approximately 250−300 m^3/ton of paper are produced and consumed, which generates approximately an equal amount of wastewater having high chemical oxygen demand (COD),

biochemical oxygen demand (BOD), color, and turbidity. Furthermore, pulp and paper mill wastewater contains various amounts of lignin, chlorides, sulphides, and sulphates that are toxic and non-biodegradable. Classic treatment processes like chemical pretreatment lagooning and activated sludge treatment are insufficient. These lead to non-conformance to the regulatory effluent standards for discharging into streams and other bodies of water. Thus, the pulp and paper industry has to use tertiary treating stage to adhere to the effluent discharge standards. In India, the problem is more severe in the small paper mills which use agricultural residues as by-product materials, largely because of the absence of the chemical recovery system. In a small paper mill's wastewater, approximately 215−225 kgs/ton of paper is produced and the pollution caused by the paper mill is almost five times compared with a paper mill of similar capacity with a chemical recovery sector. The wastewaters from the pulp and paper mills contain a large number of organic pollutants that are toxic and undesirable due to their oxygen demand, odor, taste, color, etc. (Allan, 1986, Lawrence and Yang, 2006).

Due to the increase in reforestation activities and demand for paper, the usage of hardwoods and non-woods for making paper has increased worldwide. Eucalyptus is one of the popular short fiber wood by-products used by the Indian paper industry. A reasonably strong paper can be formed when eucalyptus is blended and mixed with some long fiber pulp. Among the various sections in the paper industry, toxicity comes from the bleaching section which gives a high pollution-load. In this section, chemical digestion is needed in bleaching to produce pulps of appropriate brightness prior to additional processing. Many chemical agents are used in the bleaching process. In some developing countries, the use of chlorine and other

chlorinated compounds for hardwood and non-wood materials is widespread (Sharma et al., 1996).

Several studies have been conducted on the identification of chlorinated organic compounds in bleach wastewater. During pulp chlorination, some of the chlorinated phenolic compounds which have lower molecular weights like guaiacols, catechols, phenols, and vanillin have been identified in pulp mill bleaching effluent (Sharma and Kumar, 1999).

Of the 300 various compounds in bleaching pulp mill effluents, approximately 200 different chlorinated organic compounds have been identified. Among these, approximately 75%−80% of organic chlorinated compounds which have large molecular weights are difficult to identify or characterize (Sharma et al., 1999).

1.3 Chlorophenol Sources

Chlorophenols are organic compounds. These belong to a group of chemicals composed of phenols in which between one to five chlorines have been added. Phenol is the simplest aromatic hydrocarbon, derived from benzene where a carbon is separated from hydrogen and replaced by hydroxyl group. There are five essential kinds of chlorophenols: monochlorophenol, dichlorophenols, trichlorophenols, tetrachlorophenols, and pentachlorophenols (Penttinen, 1995, Czaplicka, 2004).

The largest sources of pollutants containing chlorophenols are the wastewaters from pharmaceutics, pesticide, wood-preserving chemicals, paint, solvent, and paper and pulp industries (Quintana and Ramos, 2008).

Chlorophenols are synthetic organic compounds, obtained by chlorinating phenol or hydrolyzing chlorobenzene. Chlorophenols also exist as an intermediate product during several stages of 2,3-dichlorophenoxyacetate acid production, or during wood pulp bleaching. This process is described in detail by Lindstrom and Nordin (1976) based on the formation of the chlorophenols in the pulp bleaching process (Penttinen, 1995).

The main source of chlorophenol formation is probably the natural reactions associated with humic acid chlorination. Investigations have associated the formation of 2,4,6-trichlorophenol due to the addition of chloroperoxidase, potassium chloride, and hydrogen peroxide to the fungi *Culduriomyces fumugo*. In addition, some aromatic compounds such as phenols and humic materials become chlorinated due to chloroperoxidase catalysis (Hodin et al., 1991).

Other sources of chlorophenol formation in the environment include microbial degradation of herbicides, especially of 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, and pesticides that produce variable chlorophenols as intermediate metabolites during their decomposition. When drinking water is disinfected with chlorine, some chlorophenols are probably formed in small amounts in such forms as monochlorophenols and dichlorophenols. This was also observed in the emissions from fossil fuel combustion, urban waste incineration, and chlorination

or disinfection of water. Emissions include phenol or definite aromatic acids with hypochlorite (Czaplicka, 2004).

1.4 Toxicity of Chlorophenolic Compounds

Phenols are persistent pollutants and thus, extremely harmful to the environment. In fact, the content of phenol has been listed as programmed waste in Malaysia where a strict disposal standard must not be greater than 0.001 mg/L and 1.0 mg/L for standard A and standard B effluent, respectively (Mohd Din et al., 2009). They have been identified as priority pollutants by the US EPA (Hameed and Rahman, 2008).

In 1976, the US EPA has selected both 2-chlorophenol (2CP) and 2,4-dichlorophenol (24DCP) as priority pollutants. Their use has been severely controlled, but discharge into water of these compounds from different industrial sources, as well as from pulp and paper industry effluents persists. 2,4,6-trichlorophenol (246TCP) is a toxic, carcinogenic, and mutagenic contaminant. At present, the use of 2,4,6-trichlorophenol is being limited because of its toxicity, except in the synthesis of some fungicides. It has been reported to cause bad effects on human nervous and respiratory systems such as cough, altered pulmonary function, and chronic bronchitis (Tan et al., 2009).

1.5 Removal of Chlorophenols from Water

Chlorophenols are among the most widespread organic pollutants of wastewater. Proper treatment should be applied before discharge into the water stream (Quintana and Ramos, 2008). Due to their high toxicity, structural

stabilization, carcinogenic properties, and perseverance in the environment, the elimination of chlorophenols is vital (Tan et al., 2009).

Different treatment methods have been used to eliminate chlorophenols from aqueous solutions. These are biological treatment using anaerobic granular sludge and fungus, catalytic wet oxidation, adsorption technology using activated clay, and use of activated carbons prepared from various precursors and other treatment technologies, which include air stripping, solvent extraction, ion exchange, and incineration (Hameed et al., 2008b).

The bio-resistant organochlorine compounds in aqueous systems need to be converted into harmless types. Biological oxidation needs longer preservation time and is not appropriate for high concentrations of pollutants or for persistent pollutants.

Photochemical methods used to treat 2-chlorophenol in aqueous solutions are ultraviolet radiation, use of hydrogen peroxide, and photo-Fenton reaction (Poulopoulos et al., 2008). Related literature show that different studies have been conducted concerning the oxidation of phenol and chlorophenols using UV/H_2O_2 (Al Momani et al., 2004), photocatalysis (Rao et al., 2003), and the photo-Fenton process (Xu et al., 2003).

The removal of such organic substances such as phenol from water solutions has been studied through the combination of reverse osmosis with oxidation of organic pollutants with hydrogen peroxide in the presence of $FeCl_2$ (Goncharuk et al.,

2002). Previously, phenol has been weakly discarded by reverse osmosis membrane, the kind which is very retentive to inorganic salts (Murthy and Gupta, 1998).

1.6 Preparation of Activated Carbon with Desired Properties

The high removal of chlorophenols from wastewater by adsorption and easy regeneration by thermal desorption or combustion of activated carbon is the most effective among all treatment technologies.

Adsorption is a well-recognized technique and offers great performance for treating domestic and industrial effluents. Activated carbon is commonly used as adsorbent, whether in powder or granular form. The structure consists of a network of interconnected micropores, mesopores, and macropores and demonstrates a good ability for the adsorption of organic molecules because of its high surface area. The chemical characteristics of adsorbate and the structure of the surface chemistry of activated carbon determine the nature of bonding mechanisms which in turn, depends on properties such as polarity, functional groups, ionic nature, and solubility. Different physiochemical mechanisms, such as H-binding, dipole-dipole interactions, van der Waals, ion exchange, covalent bonding, cation bridging, and water bridging have been reported for the adsorption of organic compounds on activated carbon. On the other hand, the usage of activated carbon has become limited because of the considerable increase of the price of commercially activated carbon over the last decade. The use of non-renewable and comparatively expensive basic material such as coal explains this phenomenon (Guymont et al., 1984). This has encouraged a growing research interest in the production of low cost and highly accessible

lignocellulosic materials as precursors for the preparation of activated carbon (El Nemr et al., 2008).

Recently, attention has been concentrated on the preparation of different activated carbons from agricultural by-products such as bean pod (Cabal et al., 2009), almond shell (Demirbas et al., 2008), cherry stone (Jaramillo et al., 2009), rice husk (Sahu et al., 2009), date palm seed (El Nemr et al., 2008), bamboo (Hameed and El-Khaiary, 2008), sunflower seed hull (Thinakaran et al., 2008), coconut husk (Tan et al., 2008a), waste apricot (Onal et al., 2007), and oil palm fiber. In addition, studies have been reported in literature on the use of oil palm shell as agricultural waste-based activated carbon.

Among the various treatments, adsorption on activated carbon has been established to be mainly effective for the removal of chlorophenols in wastewater (Namane et al., 2005). Interest on the use of oil palm shell is growing given its abundance and affordability as agricultural by-products in tropical countries like Malaysia and Indonesia (Adinata et al., 2007).

1.7 Problem Statement

Industrialization has led to the increase of the volume of wastewater due to high usage of fresh water and chemicals. This resulted in more complex water pollution. In this regard, the rapid development of the paper industry in Malaysia has caused increasing anxiety over the hazardous effects of chlorophenolic compounds, which are generally found in paper industrial effluents. Various treatment methods have been used to remove chlorophenols from aqueous solution. Among the different

treatment processes, adsorption using activated carbon is superior and most effective for removing chlorophenols in wastewater due to its simplicity of design, high efficiency, and ease of operation. On the other hand, the widespread use of commercial activated carbons has become limited due to the high cost of non-renewable raw materials required to manufacture the activated carbons. With the continuous increase of the cost of commercial activated carbon over the last decade, interest in the use of other low-cost and highly available lignocellulosic materials as precursors for the preparation of activated carbon is growing.

In Malaysia, approximately 2 million tonnes (dry weight) of oil palm shell and 1 million tonnes of extracted oil palm press fibre are generated from the agricultural industry annually. The industry faces the major problem of management of the produced wastes. Previous studies have shown that the raw materials of oil palm shell contain high carbon and low ash. Therefore, it is a good by-product material for preparing activated carbon as adsorbent.

However, studies on the use of potential agricultural by-products available in large quantities in Malaysia such as oil palm fibre, coconut husk, and oil palm empty fruit bunch are inadequate, particularly on converting biomass into high-significance products such as activated carbons appropriate for liquid phase adsorption. Conversion of biomass into activated carbons will change solid wastes into valuable products. This can reduce the cost of activated carbon production and help solve the waste disposal problem.

Finding appropriate economic precursors and producing activated carbons with high adsorption performance continue to be a challenge. Few studies have been conducted on converting oil palm shell into activated carbons. Most of the researchers applied either physical or chemical activation method which yielded low surface areas or mainly microporous activated carbons incapable of removing larger molecules such as phenolic compounds from aqueous solutions. Recently, combination of both physical and chemical activations has become a main concern. This physiochemical activation method can produce mesopore activated carbons with high surface areas, which are important qualities in the adsorption of chlorophenolic compounds from aqueous solution (Tan et al. 2009).

In the current research, 4-chloro-2-methoxyphenol, 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol are chosen as pollutant molecules due to their popular use, high toxicity, structural stabilization level, and persistence in the environment. Moreover, based on literature search, a dearth of studies on the removal of these chlorophenols, especially those which use activated carbon adsorption is evident.

1.8 Objectives of the Study

The current study seeks to:

1- Produce activated carbons from the oil palm shell using different chemical activating agent such as KOH, NaOH, and K_2CO_3.

2- Characterize all activated carbons using FTIR, SEM, BET, TGA and EDX analysis.

3- Study the adsorption of some chlorophenols such as 4-chloro-2-methoxyphenol, 2-chlorophenol, 2, 4-dichlorophenol and 2, 4, 6-trichlorophenol onto the oil palm shell activated carbons and compared them with the commercial activated carbon.

4- Investigate the effects of adsorbent dosage, pH solution, chlorophenols concentration, contact time and the temperature on the adsorption process.

5- Determine the adsorption isotherms and kinetics of the various chlorophenolic compounds onto different oil palm shell activated carbons and commercial activated carbon.

6- Determine the thermodynamic parameters and activation energies of the adsorption.

7- Regenerate the spent activated carbons using ethanol desorption technique.

CHAPTER TWO

LITERATURE REVIEW

2.1 Treatment Technologies for Removal of Chlorophenol

2.1.1 Biological processes

Biological methods are the oldest and remain the most broadly used techniques for treating wastewaters containing organic pollutants. A biological process, both aerobic and anaerobic, is accessible for the purification of municipal and industrial wastewaters. Biological wastewater management is not just a flexible and professional undertaking; it is also cost effective (Cheremisinoff, 1990). While biological treatment is most frequently done aerobically, anaerobic processes are increasingly applied (Eckenfelder, 1985). The principal utilities of anaerobic usage methods include low energy exhaustion and low residue sludge production (Ross, 1989).

Different researchers have been employed in pilot plant studies on the biological treatment of phenolic and synthetic wastewaters. In bench-scale studies, *Bacillus cereus* was discovered to be capable of metabolizing phenol (Radhakrishnan and Ray, 1974). In this regard, Hickman and Novak (1984) conducted a study in which the subject was the ability of activated sludge to withstand shock loading of pentachlorophenol using bench-scale activated sludge reactors. Even though the removal of introduced pentachlorophenol was achieved with more than 95% efficiency, the removal was not fully attained. Consequently, Tokuz (1989) measured the biodegradability of phenolic compounds in synthetic wastewater utilizing two pilot-scale rotating biological contactor units organized in four

stages. He found that 2-chlorophenol was only moderately degraded; removal rates were less than 60 % on the average.

Serkan and Fikert (2006) employed biological treatment on 4CP containing synthetic effluent employing the rotating brush biofilm reactor (RBBR). For removing 4CP, COD, and toxicity from synthetic wastewater, an RBBR containing different concentrations of 4CP was used. Moreover, the effects of major functioning variables such as the feed of 4CP and COD concentrations were investigated.

In another study, Serkan and Fikret (2007) analyzed the effect of hydraulic residence time on the performance of a hybrid-loop bioreactor system in the biological treatment of 2,4,6-tri-chlorophenol (246TCP) containing synthetic effluent. The hybrid-loop bioreactor system consisted of a packed column combined with biofilm and an aerated tank bioreactor. Effluent recycling was likewise used. The effects of hydraulic residence time (HRT) on COD, 246TCP, and toxicity removal performance of the reactor were studied.

Jiang et al. (2008) performed a study on the biodegradation of phenol and 4CP utilizing the mutant strain CTM 2; this was achieved by the He-Ne laser irradiation on wild-type *Candida tropicalis*. The findings predicted that the capability of the CTM 2 to biodegrade 4CP will be enhanced to 400 mg/L within 59.5 h.

Wen et al. (2006) extracted *Candida albicans* PDY-07 from activated sludge under anaerobic conditions. Under the previously mentioned conditions, the results obtained showed that *Candida albicans* PDY-07 could comprehensively

biodegrade 4CP up to a concentration of 300 mg/L within 244 h and that it had a high acceptance potential of up to 440 mg/L for 4CP. Substrate inhibition was noticeably enhanced, with the increase in the initial concentrations of 4CP.

2.1.2 Photochemical method

The purification of wastewater containing 4CP using integrated photocatalytic and biological treatments has been investigated by Mukesh et al. (2010) in which they employed photocatalysis as a pre-treatment to biological degradation. Contaminant elimination efficiency was accounted by utilizing mono chlorophenol (MCP) removal and total organic carbon (TOC) removal. The researcher carried out both photocatalytic as well as biological treatments in batch reactors, employing TiO_2 as the photocatalyst. For complete mineralization, an initial MCP concentration of 400 mg/L required 96 h when the combined process was used. When only biodegradation was employed, the treatment time increased to 264 h.

Poulopoulos et al. (2008) examined the effect of hydrogen peroxide initial concentration (0–10316 mg/L) and 2-chlorophenol initial concentration (150–3000 mg/L). They applied the photo-Fenton reaction to the oxidation of 2-chlorophenol, leading to a superior degree of mineralization of the parent compound.

Meanwhile, Montaser et al. (2001) performed a comparative study in which they investigated photochemical advanced oxidation processes (AOPs) for the degradation of p-chlorophenol through the combinations of UV/H_2O_2 and the photo-Fenton reaction (UV + classical Fenton reaction) in lab-scale experiments. The most effective treatment process was the photo-Fenton process, a mixture of hydrogen

peroxide and ferrous or ferric ion, under acidic conditions. Higher rate of degradation of p-chlorophenol at a very short radiation time was achieved.

Marianna (2006) reviewed the photo-degradation of chlorophenols in the aqueous solution. The review clarified the chlorophenol photo-degradation kinetics and mechanism in the aquatic environment under UV-vis in the presence of hydroxyl radicals and singlet oxygen.

2 .1.3 Reverse osmosis

The main and common conventional theory for reverse osmosis separation of pollutants is the favored sorption-capillary flow mechanism put forward by Sourirajan (1970). A suitable chemical character of the membrane surface in contact with the solution, together with the existence of pores of proper size on the skin layer at the interface, is an essential identical twin in the success of solute separation.

Fang and Chian (1975) observed the departure of 13-polar low molecular weight organic compounds from water containing different functional groups with polar organic compounds using 12 dissimilar reverse osmosis membranes. The highest removal efficiency for polar organic compounds like phenol and hydroquinone by NS 200 membranes was 85% of the initial phenol concentration from the aqueous solution.

Yanic et al. (1996) calculated the elimination of phenol from aqueous solution using a partially porous polyamide membrane known as ELGA SC 30. The purpose of their study was to establish the most favorable conditions required for the process. For this purpose, solutions containing different amounts of phenol under different

pressures were used at pH 6.5. The best possible removal efficiency was recorded at 78% with the initial concentration of 3 mg/L phenol and operating pressure of 2.0 atm.

The improvements of reverse osmosis treatment of aqueous solutions, including phenol and its derivatives have been examined by Goncharuk et al. (2002). Effective removal of phenol was shown by the reverse osmosis combined with the oxidation of organic substances by hydrogen peroxide in the presence of FeCl salt as a catalyst for the formation of its derivatives from aqueous solutions.

In addition, Yangali et al. (2009) applied the artificial neural network (ANN) models for predicting the rejection of neutral organic compounds by polyamide nanofiltration and reverse osmosis membranes. The ANN models were described as an appropriate set of solute and membrane variables capable of characterizing and defining rejection founded on a quantitative structure-activity relationship equation.

Hiroaki and Huafang (2002) found that reverse osmosis in the treatment of surface water and effluent as well as desalination of salty water can be expanded by the introduction of ultra-low pressure reverse osmosis (ULPRO) membrane. Further findings revealed that the percentage removal of undissociated organic compounds was enhanced linearly with the molecular width as well as with the molecular weight.

Mehdizadeh et al. (2005) developed a model of two-dimensional mathematics through reverse osmosis for the transfer of multi-solute liquid solutions membranes in which strong attraction may be present between the membrane polymer and the solutes. Predicting the performance of nanofiltration membranes or reverse osmosis in the case of multi-solute liquid systems in the existence of strong solute–membrane affinity, was the final objective of this research study.

2.1.4 Enzymatic oxidation

Croom and Aitken (1997) reduced the high-strength phenol concentration in industrial wastewater by employing the enzyme *Caprius macrorhizus* peroxidase (CMP) derived from a common dung and compost fungus. Many organic and inorganic compounds are oxidized by hydrogen peroxide, which acts as peroxide (enzyme) that catalyzes the oxidation of phenolic compounds. The reaction can be written as follows:

$$H_2O_2 + 2\ ArOH \longrightarrow 2ArO\cdot + 2H_2O \qquad (2.1)$$

where ArOH = the phenolic substrate and ArO· = a phenoxy radical.

Radical products are very reactive and tend to pair, constructing insoluble polymers that can be removed by filtration.

Chemical expenditures for enzymatic oxidation are 10 times higher than those for conventional management processes.

Gülay and Arica (2008) immobilized horseradish peroxidase (HRP) on the magnetic poly(glycidylmethacrylate-co-methylmethacrylate) [poly(GMA-MMA)]

through covalent bonding. It was employed for the purification of phenolic wastewater in ongoing systems. Glutaraldehyde (GA) was used as a coupling agent. In this regard, 3.35 mg/g was the highest HRP immobilization capacity of the magnetic poly (GMA-MMA)-GA beads. For the restriction, the immobilized HRP retaining 79% of the movement of the free HRP was exploited. Consequently, phenol and p-chlorophenol were removed by the immobilized HRP through polymerization of dissolved phenols in the existence of hydrogen peroxide (H_2O_2).

Murcia et al. (2009) carried out a study assessing the combinations of enzymatic oxidation and ultra filtration in a membrane bioreactor for 4CP removal. This was the first time that an intensive combined treatment for removing 4CP was undertaken. The process consists of 4CP oxidation with soluble soybean peroxidise and hydrogen peroxide in a continuous tank reactor, followed by purification of the effluent in an ultra filtration membrane module in series. The model was solved by numerical calculation and the parameters were gained by fitting the experimental data by means of an error minimization algorithm.

Zhang et al. (1997) conducted a study regarding the removal of toxic phenol and 4CP from wastewater by HRP. The effects of major factors, such as incubation time, enzyme/phenol ratio, flocculant, and pH on phenol and chlorophenol removal were discussed. Phenol and 4CP were rapidly removed from formulated wastewater. By enhancing the sedimentation of the reaction products, the flocculant can increase the removal percentage of pollutants.

2.1.5 Catalytic wet oxidation

Levee and Pintar (1994) studied the oxidation of phenol, 2-chlorophenol, and 4-nitrophenol. The catalyst consisted of 10% alumina, 47% zinc oxide, and 42% copper oxide from the aqueous phase. Pollutant concentrations were examined over time. Approximately, the concentrations of phenol and chlorophenol approached zero in 100 minutes. At moderately high pollutant concentrations, oxygen limitation due to solubility was a problem.

Atwater et al. (1996) investigated catalytic oxidation of phenol using molecular oxygen and the bimetallic Pt-Ru/C catalyst at low temperatures. Continuous flow packed bed micro reactors from heterogeneous aqueous solution was used. The reaction rate constants for the departure of phenol over the temperature which ranged between 35−60 °C were determined. Total conversion of phenol to inorganic constituents at 60 °C was observed.

Suranjana and Krishna (2008) carried out a study in which 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP) were oxidized in water with or without an oxidant (H_2O_2). Mn (II)-incorporated MCM41 was the catalyst. The alterations with soaked Mn (II)-MCM41 for 2-CP, 2,4-DCP, and 2,4,6-TCP were 90.3%, 78.0%, and 75.0% in 5 h with H_2O_2 and 91.1%, 85.0%, and 79.7% without H_2O_2. The oxidation followed the first order kinetics. Additionally, the effects of different reaction conditions and the possible mechanisms of oxidation were also discussed.

Ver´onica et al. (2007) evaluated the function of wet oxidation for the management of solutions polluted by 4CP and proposed a kinetic model to predict the concentration of the compounds involved in the process during the reaction. Likewise, the chloride from the chlorophenol was discharged into the medium and no intermediate restraining chlorides were formed. An outstanding enhancement in the biodegradability was observed through the wet oxidation process.

Ning et al. (2007a) examined for the first time the catalytic wet air oxidation (CWAO) of 2-chlorophenol using $Ru/Ce_xZr_{1-x}O_2$ as catalyst. They reported the exploitation of $Ce_xZr_{1-x}O_2$ solid solutions which aided the execution of Ru catalysts in the catalytic wet air oxidation of 2-chlorophenol. Even at low temperature (393 K) and low pressure (3 MPa), such catalytic systems showed reliability and displayed a definite advantage over Ru/CeO_2 or Ru/ZrO_2.

Further, Ning et al. (2007b) evaluated a sequence of noble metals (Pt, Pd, Ru) loaded with zirconia catalysts in the CWAO of mono-chlorophenols (2-CP, 3-CP, 4-CP) under relatively mild reaction conditions. Among the examined noble metals, Ru showed the best performance in terms of promotion of the CWAO of CPs. The performance facilitated the use of incipient-wetness impregnation to prepare all the catalysts.

Laishun et al. (2010) used catalysts for catalyzing/degrading simulated o-chlorophenol effluent with chlorine dioxide as an oxidant. COD removal efficiency by catalytic oxidation was 93.5% at the wastewater COD parameter of 2085 mg/l.

Yoshihiro et al. (2005) performed wet oxidation of a 100 ppm aqueous solution of o-chlorophenol (o-CP) in a lab-scale batch reactor utilizing 3% Ru/TiO_2 catalyst at 373 and 413 K, and a partial oxygen pressure of 0.1 MPa.

2.1.6 Air stripping

Ansari (1996) evaluated the various processes existing in the management of phenolic effluents in the wastewater source at Allied Signals Inc., USA. Air stripping was deduced as a capable and inexpensive method of treating industrial wastewater polluted with volatile organics.

Through stripping, polluted water was transported through a packed column flat surface current to airflow. Compounds in solution used an equilibrium vapor pressure equivalent to their concentration in aqueous phase, thus resulting in volatile substances to change from liquid to gas.

Volatile organic compounds produced by air stripping cannot be released into the air because of environmental restrictions. Thus, suitable removal processes should be incineration, catalytic oxidation, and carbon adsorption.

2.1.7 Solvent extraction

A homemade immersed solvent microextraction (SME) was successfully implemented by Habib et al. (2004) for the trace extraction of phenols from aqueous solutions. A microdrop of butyl acetate was suspended from an empty microsyringe needle, immersed in an aqueous pointed solution for a predetermined time. The microdrop was then withdrawn into the microsyringe and injected instantly into a gas chromatography-mass spectrometry (GC-MS) injection port.

Ruey-Shin et al. (2009) used solvent extraction and two-phase membrane biodegradation to purify phenol in synthetic saline wastewater. A hybrid solvent extraction and two-phase membrane biodegradation processes were used for the treatment of phenol in synthetic saline solution (100 g/L NaCl) and acidic solution (pH 3) in wastewater at 30 °C. The suitable organic solvent was kerosene because of its biocompatibility and content of an appropriate partition coefficient for phenol.

2.1.8 Oxidation by hydrogen peroxide

For industrial wastewater purification, hydrogen peroxide is generally used as a catalyst to treat effluents containing sulphur compounds, phenols, or cyanides (Sims, 1983). The complete oxidation reaction of phenol with hydrogen peroxide can be shown as:

$$C_6H_5OH + 14H_2O_2 \longrightarrow 6CO_2 + 17H_2O. \qquad (2.2)$$

Hydrogen peroxide concentration, iron catalyst, phenol ratio, pH, and temperature are the major factors that influence the reaction rate (Sims, 1983).

2.1.9 Ionizing radiation

Ionizing radiation is an efficient process of treating a wide array of effluents given that radiation is capable of changing numerous refractory contaminants to more biodegradable forms. The electron acceleration during irradiation of energy sources such as gamma rays from cobalt 60 or cesium 137 as well as intense beams can be provided by high energy electrons (Grabow, 1979).

Atsushi et al. (2008) investigated the decomposition of chlorophenols and effects of the cations and anions of room temperature ionic liquids (RTILs) on the formation of phenol by gamma and pulse radiolysis. Absorption bands for aliphatic RTILs were observed to have been caused simply by pulsed electron irradiation, and thus were allocated as solvated electrons. The result of the decomposition of chlorophenol to phenol in the presence RTILs with solvated electrons, were higher than those in RTILs, without solvated electrons.

Yongke et al. (2002) studied the purification of pentachlorophenol, 2,4-dichlorophenol, and 2-chlorophenol in water by gamma radiation. The isolation of chlorine from PCP, DCP, and 2-CP using gamma radiation in addition to ozonization was considered. In the presence of ozone, the efficiency of radiation-induced decomposition of chlorophenol improved.

Zona et al. (1999) studied dechlorination of liquid chlorophenol solutions using ionization radiation. The radiolytic degradation as well as analysis of the dehalogenation process of aerated 5×10^{-5} M (6-10 ppm) liquid; 2-, 3- and 4-chlorophenol; and 2,4-di- and 2,4,6-trichlorophenol was performed by determining the dose required for inclusive substrate decomposition. The toxicity and the dissolved organic carbon (DOC) were independent of dose. Overall dechlorination could be completed by carrying out the irradiation process under air dispersion and by a dose of 500 Gy, which equals the dose needed for full degradation.

2.1.10 Ozonation

Phenol can be oxidized by ozone over a wide range of pH. However, a preliminary pH modification to higher values (around pH 11.5) usually favors the preferential oxidation of phenols over other organics or oxidizable materials present in the effluent (Beszedits and Silbert, 1990). While phenol and certain phenolic compounds, e.g., mono-, di-, tri-, and tetrachlorophenols react quickly with ozone at least in the level of destruction of their aromatic ring, compounds like pentachlorophenol are slowly oxidized by ozone. Nevertheless, the rate can be significantly speeded up when ozone is used together with UV irradiation (Rice, 1981). Complete oxidation of phenol by ozone can be illustrated by this equation (Kroop, 1973):

$$C_6H_5OH + 13O_3 \longrightarrow 6CO_2 + 3H_2 + 14O_2. \qquad (2.3)$$

Hideo et al. (2003) performed research on a kinetic of 3-chlorophenol by enhancing hydroxyl radical deliberation throughout ozonation. Hydroxyl (OH) radical was suggested as an essential factor in water ozonation. The researchers used electron spin resonance (ESR)/spin-trapping technique for increasing the effect of 3-chlorophenol on OH radical generation which was mathematically evaluated. Moreover, OH radical was captured with a 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a fixed adduct, obtaining DMPO–OH.

Roberto and Raffaele (1999) investigated the ozonation of p-chlorophenol within water solution with the following parameters: existence of tert-butyl alcohol and pH range of 2.0–8.0. Under these parameters, the activation of the radical