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THESIS

OXIDATION OF PHENOLIC COMPOUNDS BY H_2O_2 USING Fe/SUZ-4 ZEOLITE AS CATALYST

PALAKORN BOONSAI

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
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The research has two objectives as 1) the effectiveness of using Fe/SUZ-4 in reducing the phenolic compound concentration in synthetic wastewater treatment and 2) the kinetics of phenolic compounds onto the Fe/SUZ-4 zeolite in the treatment of synthetic wastewater, using batch experiment.

By using synthesized Fe/SUZ-4 zeolite catalysts and H_2O_2 (0.015 mol/l) oxidation agent, the degradation reactions of Phenol (1.06×10^{-3} mol/l), 2,4-Dichlorophenol (6.13×10^{-4} mol/l), and 4-Chlorophenol (7.78×10^{-4} mol/l) were carried out at 303 K and pH 3.0 for 300 minutes.

The ratio of the rice husk ash to Silica Sol at 50:50 was used for SUZ-4 synthesis. The ion-exchanged SUZ-4 zeolite (Fe/SUZ-4) was used since the degradation rate obtained was actually higher than that of the reaction without ion-exchanged zeolite. Variations of phenolic compounds degradation were investigated and it was found that the degradation rates slightly increase with increasing the phenol concentration. In the same way, the variation of H_2O_2 was also investigated and the result indicates that the degradation rates also slightly increase as the H_2O_2 concentration increases. The kinetics of the corresponding reactions was also studied. It was found that the degradation reactions of Phenol, 2,4-Dichlorophenol and 4-Chlorophenol can be classified as a first-order reaction.

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Palakorn Boonsai

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LIST OF ABBREVIATIONS

AOPs	=	Advanced oxidation processes
4-CP	=	4-Chlorophenol
CIHP	=	4-Chlorohydroxycyclohexadienyl radical
CHQ	=	Chlorohydroquinone
2,4-DCP	=	2,4-Dichlorophenol
LD_{50}	=	Lethal Dosage Values
RHA	=	Rice husk ash
SCR	=	Selective catalytic reduction

OXIDATION OF PHENOLIC COMPOUNDS BY H_2O_2 USING Fe/SUZ-4 ZEOLITE AS CATALYST

INTRODUCTION

Phenolic compounds contain hydroxyl group linked to benzene ring or benzene derivatives. The examples of phenolic compounds include: phenols; 2-chlorophenol; 4-chlorophenol; 2,4-dichlorophenol; 2,4,6 tri-chloro phenol; and Pentachlorophenol.

Phenolic compounds were used in different sectors including industry and agriculture. In the industrial use, these phenolic compounds were used as starting or intermediate material in the manufacture of plastic, resins, colored paper, as well as, in the rubber wood processing industry and oil refining industry (Keeratiwitayayut, 1985 ; Wu *et al*., 1997 ; Caza *et al*., 1998). Chlorinated phenol was widely used to kill microorganisms and restricted used as a wood preservative (Pang *et al*., 2007). In agriculture, they have been used in preparing insecticide, pesticides and fungicide to prevent plant infection.

Phenolic and chlorophenols are toxic compounds, with high toxicity, and potential human carcinogen (Buchanan *et al*., 1998). Exposing directly to phenol can cause skin-burnt. They can also be absorbed through the skin easily causing headaches and dizziness. Vapors of phenol cause irritation to the respiratory tract and eyes. In addition, they are also carcinogenic (Maneechot, 2008).

Pollution of water by phenol like compounds has been a serious problem in developed and developing countries (Yinchun *et al.,* 2009). Environmental contamination by these compounds occurs mainly from industrial effluent and agricultural runoff.

The effluent from water treatment plant containing activated sludge from pulp and paper factory still has brown color because of dissolution of lignin molecule. Lignin molecule contains the main component of phenolic compounds and these compounds are hard to be degraded by biological treatment (Thanee, 2006). Poor waste disposal practices and leakage from processes can dramatically contaminate natural waters and soil, mainly the areas near the production plants and wood preserving facilities (Caza *et al*., 1998).

Although, the national industrial waste water quality standards allow a present of a group of phenol compounds with less than 5.32×10^{-3} mol/l (Ministry of Industry., 1996). However, previous reports found pentachlorophenol in the effluents from rubber wood industry as high as 0.42 mol /l being used as an ingredient in wood preservative solution. (Sangrawee, 2003).

Chemically, during the chlorination of watser and sewage in the water treatment plant, phenol is readily transformed into chlorophenols (Yousel and Eswed, 2009) with more complex chemical structure. Changing of phenolic compounds chemical structure also occur mainly during the compression-process of chlorinated phenol and pressure-process in heavy petroleum (Srisai, 2006). Therefore, it is essential to have a reduction or elimination of these compounds from effluent waste water before releasing into natural waters.

Treatment of chlorophenol compounds in water can be carried out in different methods, for example: biochemical methods (Bhattacharya *et al*., 1996); a peroxidase enzyme treatment (Wu *et al*., 1997 ; Caza *et al*., 1998); physicalchemical methods such as activated carbon (Jung *et al*., 2001); and chemicaloxidation methods.

For the wastewater with low concentration of chlorophenol, biochemical methods have a good efficiency in treating the phenolic compound; however, these methods were not significant when applied to the waste water with high chlorophenol concentration (Lai *et al*., 2008). In addition, the oxidation processes are the most promising treatment methods for the chlorophenol waste water.

Among the oxidation methods that are applicable for the treatment of phenolic compounds in wastewater, there are some oxidation processes that utilize hydroxyl radicals. The role of the hydroxyl radicals is to generate carbon-central radicals which further react with oxygen and the peroxy radicals, thus forming initiate chains of oxidation reactions. This may eventually lead to complete mineralization, i.e., the formation of carbon dioxide, water and inorganic acids. Hydroxyl radicals can be generated by the combination of an oxidant such as hydrogen peroxide with catalyst. The lack of selectivity of hydroxyl radicals leads to their removal from the system by reaction with less toxic species. Efficient use of hydroxyl radicals dictates that this loss needs to be minimized.

The Fenton reaction is a catalytic process for the generation of hydroxyl radicals from hydrogen peroxide and is based on an electron transfer between H_2O_2 and iron ions acting as homogeneous catalysts. The hydroxyl radicals produced during this activation of hydrogen peroxide are a strong oxidizing agent and able to oxidize organic compounds under ambient (Lucking *et al.,* 1998).

The advantages of Fenton's reagent over other oxidizing treatments are numerous, including high efficiency performance, stability to treat a wide range of substances, and no need of special equipment (Yinchun *et al.,* 2009). Therefore, this oxidation process is considered to be the most promising treatment method for wastewater containing chlorophenol. The Fenton reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radicals .

Fenton's reagent was chosen as the advanced oxidation system for the treatment of phenolic compounds in this study. This reagent is the combination of hydrogen peroxide (H_2O_2) with a ferrous salt (Fe^{2+}). The mixture of H_2O_2 and Fe^{2+}, forming hydroxyl radicals, plays the major part in the oxidation of organics. Hydroxyl radicals are the main primary oxidizing intermediates of the Fenton reaction but are not the only one (Lei *et al.,* 1998). Catalytic generation of hydroxyl radicals by iron-ions (Fenton mechanism) is well known (Edwards *et al.*, 1992) and is described as fallows.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad (1)$$

The reaction is used commercially to treat industrial effluent/discharged water (Tolman *et al*., 1993) but the main drawbacks are the limited range of pH 3-5 in which the reaction proceeds and the need of recovering iron after the treatment. However, these drawbacks can be overcome in the principle using heterogeneous Fenton-type catalysts, but only a few attempts have been made to evaluate their potential (Sanger *et al*., 1992).

Recently interesting preliminary results on the high catalytic activity of iron-containing zeolites (Fajerwerg and Debellefontaine, 1996) and copper containing pillared clays (Barrault *et al*., 1998) for phenol oxidation have been reported. In contrast to the previous finding, the possibility to develop stable catalysts with minimal leaching of the transition metal was reported and thus opened up the possibility of the practical application of heterogeneous catalytic wet oxidation with H_2O_2 process.

Fe-containing zeolites have been intensive studied as catalysts for N_2O decomposition and selective catalytic reduction (SCR) on nitrogen oxides by NH_3 or hydrocarbons, i.e. for exhaust treatment. Various preparation procedures have been proposed in order to introduce extra framework iron into zeolites including liquid and solid ion exchange (Schwidder *et al*., 2005) or chemical vapor decomposition which are usually followed by a calcinations step (Kumar *et al*., 2004).

The study of the catalyst and kinetics of phenolic compound using the Fe-Zeolites-derived from rice husk ash has given more options to water treatment research work. Zeolites are alumino silicate or alumino phosphate. They are highly porous (microporous molecules) contain elements that are consistent with the absolute purity being quite high by the internal cavity structure consists of cations and water molecules. Both types of molecules can be moved so that the cation exchange is useful in industrial and commercial value.

The zeolite is preferred in industrial research through the year 1992, where SUZ-4 is a new type of synthetic zeolite (Paik *et al*., 2000.). SUZ-4 was patented by British Petroleum Company. Its topology consists of a three-dimensional pore system having straight ten member channels intersected by two eight-member channels (Worathanakul and Kongkachuichay, 2008).

SUZ-4 zeolite is a porous structure which enhances more efficient surface to be used as a catalyst for the removal of phenolic compounds; however, this zeolite SUZ-4 has not been used widely. This research attemps to investigate the degradation of phenol, 4-chlorophenol, and 2,4-dichlorophenol by heterogeneous Fenton reaction using Fe /SUZ-4 as catalysts and H_2O_2 as oxidation agents. For the synthesis of zeolite SUZ-4, the rice husk ash will be used as raw material since it composes of silica and alumina under the process of Hydrothermal. The main interests of this research include the production cost reduction of the SUZ-4 zeolite, as well as, to also increase the value-add of the rice husk.

OBJECTIVES

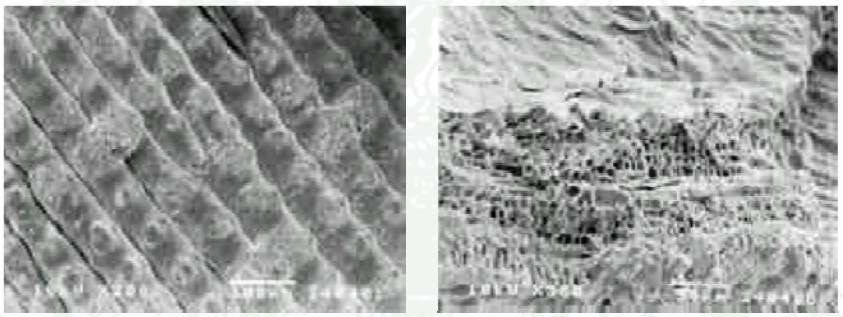
The objectives of this study are:

1. To study the effectiveness of using Fe/SUZ-4 in reducing the phenolic compound concentration in synthetic wastewater treatment.
2. To study the kinetics of phenolic compounds onto the Fe/SUZ-4 zeolite.

LITERATURE REVIEW

1. Properties of rice husk and rice husk ash

Rice husk contains about 80 percent organic compounds by weight and the inorganic compounds including silica by way of different types of elements in the husk, depending on geographical factors, cultivation year, cultivation preparation and moisture analysis. In Figure 1 below, the rice husk is viewed through a microscope and looks like a corn surface. The rice husk structure consists of two parts. The first part is the organic compound called cellulose, where the second part is the inorganic substance containing silica (SiO_2) as the main component.



(a) (b)

Figure 1 Photos of the risk husk structure under microscope (a) the surface that looks like corn (b) cross-section structure with high porosity.

Source: Panthanit (2007)

Thailand is among the countries producing rice as national main agricultural product serving to both internal and international consumptions. The country's rice production reached about 17 million tons per year leaving significant amount of rice husk as a side-product. There have been many researches attempt to utilize and add value to the rice husk product, where in the past it was directly used as fuel. On the other hand, the rice husk ash resulted from burning the rice husk is approximately

16.4 to 18.3 percent by weight of the original rice husk weight. Chemical compositions of the rice hush ash are as shown in Table 1.

Table 1 Chemical composition of the rice husk ash (percent by weight).

Compound	Percent by Weight
SiO_2	86.9-97.3
K_2O	0.58-2.50
CaO	0.00-1.75
MgO	0.20-1.50
Fe_2O_3	0.12-0.96
P_2O_3	0.00-0.54
SO_3	0.20-2.85
Cl_2O	0.00-0.42

Source: Panthanit (2007)

The chemical composition analysis of the rice husk ash revealed silica (SiO_2) as the main component where the properties of rice husk ash and silica content depends on temperature and time used in burning the rice husk. Rice husk combustion (burning) at high temperature for a long period of time can cause silica to become crystallized (as crystalline) making it hard for grinding and slowing down the chemical reaction. It was found that the size of the rice husk ash can also affect the chemical reaction**.**

In general, there are two groups of rice husk ash resulted from burning. These two groups include:

1) Black rice husk ash from burning the rice husk at low temperatures which has high content of carbon at about 50-30 percent and can be used as activated carbon.

2) White rice husk ash from burning the rice husk at 873-1073 K with adequate air and can be used as a refractory material resistant up to 1673 K or a precursor compound in the preparation of silica.

Most of the rice husk ash contains solid Amorphous silica and alumina making it possible to be used as raw material for the synthesis of zeolites, which contains the value and benefits of multi-function, such as, being used in ion-exchange to remove heavy metals and toxic substances in wastewater. It is also used as a sorption agents to absorb toxic gases, while another significant benefit is also being used as catalysts in the petrochemical industry, etc.(Limtrakul, 1997).

2. Zeolite

Zeolites are aluminosilicate or aluminophosphate compounds with cemical-formula structure as $M_{x/n}$ $[(AlO_2)_x(SiO_2)_y]wH_2O$, where M is stand for a cation with a valence electron equal to x, w is the number of water molecules, and y/x is the ratio of silicon to aluminum (Si/Al) which is in the range of 1-5 (Breck, 1974).

Zeolite was first discovered in the middle of the 18th century. At least 40 species of the natural zeolite were found in the lake being alkaline and salt, or in the dry surface-soil with high pH-value. There were also more than 150 species of zeolite obtained from the synthesis (Dyer, 1988). Later on, the synthesis of zeolite was from the reaction of silica oxide, alumina, sodium-oxide and potassium-oxide. The process was hydrothermal treatment at high pH conditions. This type of zeolite has a structure consistent with high purity which is useful in industry and having high value.

The structure of the zeolite pore size is consistent with the estimation of 3 - 10 Angstrom (A^o) which is like a molecular sieve that allows molecules smaller than the pore to pass through (penetrable) but do not allow larger molecules to pass. However, this penetrable property depends on the properties of the zeolite structure

regarding size, shape, porosity within the crystal, as well as, the location of the charge and size of cations in the structure.

At molecular level, the primary building-unit for zeolites is the tetrahedron and the secondary building units (SBUs) are the geometric arrangements of tetrahedral (Breck,1974). The SBUs may be simple polyhedral such as cubes, hexagonal prisms, or cubo-octahedral (Bekkum *et al.,* 1991). The structures can be formed by repeating SBUs and according to the arrangement of these SBUs; zeolites can then be classified into eight groups. Figure 2 below presents the components of the zeolite structure.

In addition, the type of zeolite synthesis depends on factors such as concentration of the metal cation, ratio of silica to alumina, times, temperature, pH, pressure, as well as, type and concentration of promoters (Bhatia, 1990: Yang, 1997).

Figure 2 (a) Chemical structure of zeolite (b) Primary building unit of zeolitestructure.

Source: Haag *et al.* (1984)

2.1 Pore size

Zeolite catalyst must be porous enough so that the reactants can penetrate into the active site, as well as, it must be easy for the products to escape from the active site. The pore size of the catalysts is base on the number of oxygen atoms and the type of positive charges. Table 2 below shows the pore size of different zeolite types. In addition, the critical molecule hydrocarbon is correlated with the pore size as shown in Table 3.

Table 2 The pore size of different zeolite types.

Zeolite	Number of oxygen's in the ring	10 x Aperture dimensions, nm
Chabazite	8	3.6 × 3.7
Erionite	8	3.6 × 5.2
Zeolite A	8	4.1
ZSM-5 or silicalite	10	5.1 × 5.5 ; 5.4 × 5.6
ZSM-11	10	5.1 × 5.5
Heulandite	10	4.4 × 7.2
Faujasite	12	7.4
Zeolite L	12	7.1
Mordenite	12	6.7 × 7.0
Offretite	12	6.4

Source: Gates (1992)

Table 3 Critical diameters of various molecules.

Molecule	Critical diameters (A^o)	Molecule	Critical diameters (A^o)
Hydrogen	2.4	Ethyl mercaptan	5.1
Oxygen	2.8	1-Butene	5.1
Nitrogen	3.0	Trans-2-Butene	5.1
Water	3.2	1,3-Butadiene	5.2
Ammonia	3.6	Cyclohexane	6.1
Methane	4.0	Benzene	6.7
Ethylene	4.2	Toluene	6.7
Ethane	4.4	p-Xylene	6.7
Propane	4.9	m- Xylene	7.1
n-Butane	4.9	o- Xylene	7.4
Propylene	5.0	Triethylamine	8.4

Source: Gates (1992)

2.2 Classification of the zeolite structure

Chemical structure of the primary building unit of the zeolite consists of the connection between $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$, a three-dimensional network of oxygen atoms and the tetrahedral angle of the access point. Geometric arrangement of tetrahedral aluminum and silicon becomes secondary building unit (SBUs), where this arrangement is then repeated and different types of zeolite are formed. According to different chemical structure, the zeolite can be divided into 8 types of SBUs as shown in Figure 3.

(a) Single 4-ring, S4R (b) Single 6-ring, S6R (c) Single 8-ring, S8R

(d) Double 4-ring, D4R (e) Double 6-ring, D6R (f) Complex4-1

(g)Complex5-1 (h) Complex4-4-1

Figure 3 Secondary Building Units (SUBs) of the zeolite.

Source: Dyer (1988)

The SBUs can be simple arrangements of tetrahedral such as four, six, eight, ten or more complicated member ring. Other factors such as the location, size and coordination of the extra-framework cations can also influence the pore size. Some simple zeolite SBUs and their shorthand notations are given in Table 4.

2.3 The synthesis of zeolites

Today, synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes. The sources for early synthesized zeolites were standard chemical reagents. Much of the study of basic zeolite science was done on natural zeolites. The main advantages of synthetic zeolites in comparison to naturally-occurring zeolites are that they can be

engineered with a wide variety of chemical properties and pore sizes and that they have greater thermal stability (Boukadir *et al.,* 2002).

Table 4 Classification of zeolite structures.

Number of linked tetrahedral	SBU created	Shorthand description
4	4 oxygen ring	S4R
5	5 oxygen ring	S5R
6	6 oxygen ring	S6R
8	8 oxygen ring	S8R
8	4-4 oxygen rings	D4R
12	6-6 oxygen rings	D6R
16	8-8 oxygen rings	D8R

Source: Breck (1974)

Conventional zeolite synthesis involves the hydrothermal crystallization of aluminosilicate gels (formed upon mixing an aluminate and silica solution in the presence of alkali hydroxides and/or organic bases), or solutions in a basic environment. The crystallization is in a closed hydrothermal system at increasing temperature, autogenous pressure and varying time (few hours to several days).

The type of the zeolite systhesized is affected by the following factors (Terres, 1996): composition of the reaction mixture; nature of reactants and their pretreatments; temperature of the process; reaction time; and pH-value of the reaction mixture.

For the composition of the reaction mixture (silica to alumina ratio; OH-; inorganic cations), firstly, increasing the Si/Al ratio strongly affects physical properties of the zeolites. Secondly, OH- modifies the nucleation time by influencing transport of silicates from the solid phase to the solution. Thirdly, inorganic cations

act as structure directing agents and balance the framework charge. They affect the crystal purity and product yield.

For nature of reactants and their pretreatments, the zeolite synthesis is carried out with inorganic, as well as, organic precursors. The inorganic precursors yielded more hydroxylated surfaces whereas the organic precursors easily incorporated the metals into the network.

For temperature of the process, the rate of crystallization is directly proportional to the temperature while the rate of nucleation is inversely proportional.

For the reaction time**,** crystallization parameter must be adjusted to minimize the production of the other phases, while also minimizing the time needed to obtain the desired crystalline phase.

For pH of the reaction mixture, the process of zeolitezation is carried out in alkaline medium (pH>10).

Additionally, other factors can also affect the type of the zeolite systhesized**.** For example, the synthesis can be carried out on a continuous or semi continuous mode, which enhances the capacity, making it compatible for industrial applications.

Synthesis of zeolites by hydrothermal processes can react at high temperature up to 473 K and high pressure. This reaction is left under time pressure and temperature under the excess water. However, a new approach for the synthesis of zeolites at low temperature was also practiced, where the zeolites can be formed between the room temperature to boiling temperature (Breck, 1974). Examples of gel preparation and crystallization of zeolites can be displayed using the system Na_2O-$Al_2OAl_2O_3$-SiO_2-H_2O.

Process of zeolite (Hawkin, 1981), as shown in Figure 4 was initially slow (A), and the silica dissolved in the mixed solution is rapidly (B-D) becoming the solution

saturated with silica and zeolite crystals. However, the synthesis of zeolite crystals is not in equilibrium phase but it is in metastable phase by changing to the stable phase if the time or temperature changes during the synthesis (Breck, 1974).

In addition, the type of zeolite from the synthesis depends on the terms used in the synthesis such as the concentration of the metal cation, the ratio of silica to alumina, pH, time, temperature, pressure and concentration of promoters (Bhatia, 1990 ; Yang, 1997).

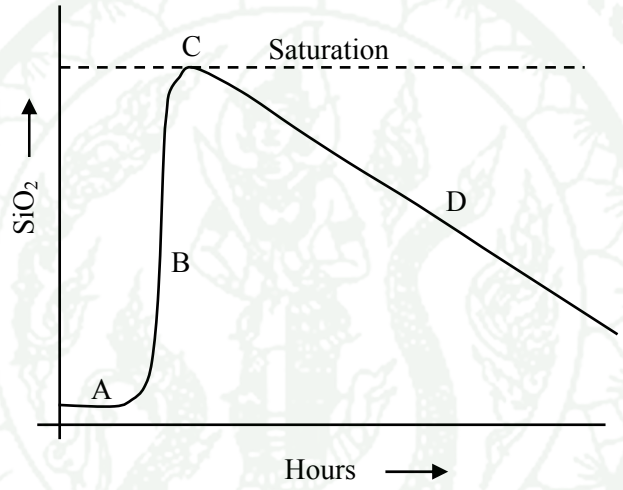


Figure 4 Silica dissolved in the mixed solution and the zeolite expressed in terms of silica concentration (mol/l) and time (hours).

Source: Hawkins (1981)

At present, the main problem in zeolite researchs is the availability and cost of raw material especifically the silica source. On the other hand, commercial silica (made of sand) which is available in gel, sol, fumed or amorphous solid, is found to be variable in reactivity and selectivity. The preparation of synthetic zeolites from silica and alumina chemical sources is expensive. So, the cheaper raw materials, such as clay minerals, natural zeolites, coal ashes, municipal solid waste incineration ashes and rice husk ash, are utilized as starting materials for zeolite synthesis. The use of

waste materials in zeolite synthesis contributes to the mitigation of environmental problems, generally in the field of water purification, removing heavy metals or ammonium, and turns them into attractive and useful products (Somerset *et al.,* 2005).

As environmental impact by human, millions of tones of miscellaneous solid, liquid and gaseous waste materials, such as household, commercial, industrial, agricultural, radioactive and clinical wastes, are generated annually. Additionally, large daily output and the limited landfill capacity have resulted in social and environmental problems. Furthermore, the amount of this material is expected to increase dramatically in the near future and may cause major challenges and serious environmental problems (Inada *et al.,* 2005). It follows that for efficient use of the world's resources recycling and reuse of waste is necessary.

2.4. Principle for the synthetic of zeolites

2.4.1 Major sources of aluminum in the synthesis of zeolites are generally used as a precursor metal aluminates and sodium aluminates. Sometimes, Al $(OH)_3$, AlO(OH), aluminum salt or aluminum from natural resources are also used.

2.4.2 The source of silicon is typically used by a solution of silica such as silica sodium met silicate pent hydrate 30 percent by weight. Sometimes gel from silica sand and minerals that include quart silica is used.

2.4.3 Cation are the source of the metal cation Group I and Group II in the forming of hydroxide compounds which can also be obtained from oxides and salts of metal salts of Group I and II.

2.4.4 Other chemicals, such as cation from organic compound (template) by adding into a gel to enhance the crystallization, such as tetraethyl ammonium or tetrapropyl ammonium, etc.

2.5. Benefits of Zeolite

Zeolites are useful in the industry where they are used for ion exchange and adsorbent. For example, they are added to a mixture of detergent in order to

reduce the hardness of the water, where in waste water treatment, they exchange ions with heavy metals or ammonia and absorb unwanted gas in the production process. Zeolite is also used as a catalyst in the petrochemical industry (Dyer, 1988).

Uses of zeolite as a catalyst at different stages in the petrochemical industry are following (Dyer, 1988 ; Bhatia, 1990.).

2.5.1 Catalytic cracking is used to break molecular bonds of the oil where long-chain hydrocarbons are broken down into short chain hydrocarbons (C_1-C_6) ready for being used.

2.5.2 Hydro cracking is the exchange of large hydrocarbon molecules into smaller molecules by breaking bonds of carbon-carbon with hydrogen.

2.5.3 Reforming aliphatic hydrocarbon compound is changed into aromatics.

2.5.4 C_5/C_6 isomerization is to change the low octane hexane and low octane pentane to isopentane and dimethyl butane with a higher octane value.

2.5.5 Dewaxing is to eliminate the fat in the oil.

2.5.6 Benzene alkylation, such as producing ethylbenzene from ethylene and benzene or cumene production from benzene and propylene.

2.5.7 Xylene isomerization is a process of changing of o-xylene isomer to the p-xylene, and uses it as a precursor in the preparation of terephthalic acid to produce polyester.

2.5.8 Sorption agent is to use the zeolite as the adsorbent in the dehydration process, purification and separation.

2.5.9 Water softener, as the lower hardness of the water.

2.5.10 As Ion-exchange resin, because cations of the metal deposit on zeolite are loose, so the exchange charge with the other metals in the solution therefore can be applied to reduce the hardness of the water through the exchange of charges between the metal alkali in the zeolite (sodium or potassium) with calcium and magnesium in the water.

3. SUZ-4 Zeolite

SUZ-4 zeolite structure is similar to Ferrierite (FER) which is orthorhombic structure. Inside a hollow diameter of the structure, it is contiguous with two sizes of 4.6 and 5.2 A^{o} (Lawton *et al.,* 1993). Its structure consists of five-, six-, eight-, and ten-member rings, respectively, and building units as shown in figure 5.

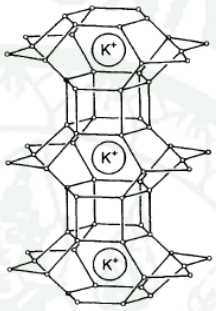


Figure 5 Building unit of SUZ-4 zeolite.

Source: Hosun *et al*. (1992)

A building unit is arranged in a chain around the edges and is similar to the FER type zeolite. These chains are linked to each plate where sheet are linked by a three-dimensional structure, as shown in figure 6.

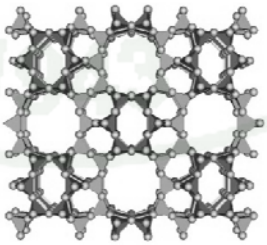


Figure 6 Three-dimensional structure of the SUZ-4 zeolite, plane [001].

Source: Lukyanov *et al*. (1999)

SUZ-4 zeolite's structure consists of the space of two connected channels where the first space, the orthorhombic, is the characteristic of crystalline SUZ-4 as shown in figure 7.

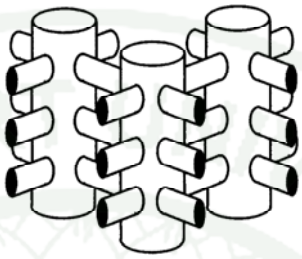


Figure 7 The SUZ-4 multichannel system.

Source: Lukyanov *et al*. (1999)

4. Fenton process

Fenton's process was discovered more than 100 years ago, but its application as an oxidizing process for reducing toxic organics was not applied until the late 1960s (Huang *et al.,* 1993). Fenton processes are known to be very effective in removal of hazardous organic pollutants from water and the main advantage is the complete destruction of contaminants to harmless compounds (CO_2, water and inorganic salts). The Fenton process is based on the electron transfer between ferrous ion (Fe^{2+}) and hydrogenperoxide (H_2O_2) The ferrous iron initiates and catalyses the decomp (**HO**$^{\bullet}$) osition of H_2O_2, resulting in the generation of highly reactive hydroxyl radicals (S.H. Bossmann *et al*., 1998) as shown in equation (2) that can degrade organic compounds quickly through equation (5). The mechanism of the Fenton chain of reaction is presented in equations as shown below (Lu, M.C., *et al*.,1999. ; Chou, S., *et al*.,2004).

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \quad (2)$$

$$Fe^{2+} + {}^{\bullet}HO \rightarrow Fe^{3+} + OH^- \quad (3)$$

$$^{\bullet}OH + \text{organics} \rightarrow \text{products} \quad (4)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}HO_2 \quad (5)$$

$$^{\bullet}HO + {}^{\bullet}OH \rightarrow H_2O_2 \quad (6)$$

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+ \quad (7)$$

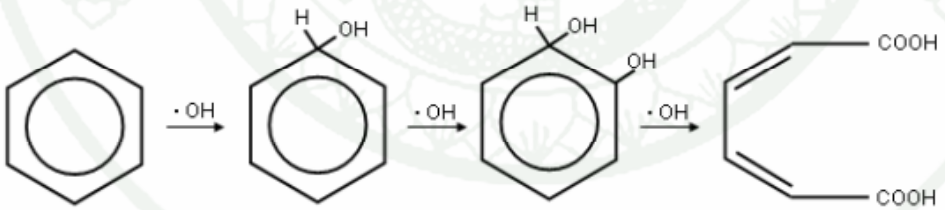
$$FeOOH^{2+} \rightarrow Fe^{2+} + {}^{\bullet}HO_2 \quad (8)$$

$$Fe^{2+} + {}^{\bullet}HO_2 \rightarrow Fe^{3+} + HO_2^- \quad (9)$$

$$Fe^{3+} + {}^{\bullet}HO_2 \rightarrow O_2 + Fe^{2+} + H^+ \quad (10)$$

Although Fenton process has been successful in the degradation of the organic contaminants present in wastewater.

In the presence of organic substrates, excess ferrous ion, and at low pH, Hydroxyl radicals can add to the aromatic or heterocyclic rings, as well as, to the unsaturated bonds of alkenes or alkynes (Neyens and Baeyens., 2003). They can also abstract a hydrogen atom, initiating a radical chain oxidation as shown in equation (11)



(11)

As can be seen, under these experimental conditions close to 93.92 % of phenol degradation in about 35 min , giving rise to dihydroxybenzenes upon hydroxylation of the aromatic ring. Catechol is main primary oxidation product, indicating that hydroxylation takes place predominantly in the ortho position.

Ring-Opening of the aromatic intermediates leads to the formation of organic acids. These compounds are intermediates and/or final oxidation products. Maleic, acetic, and formic acids were the earlier and more abundant products of the acid

formation stage. Oxalic acid was appearing at a lower rate, although it reached a high relative concentration as the oxidation reaction proceede. Figure 8 summarizes the scheme of reaction proposed for phenol oxidation with Fenton's reagent, according to our results. (Faisal *et al.,* 2009).

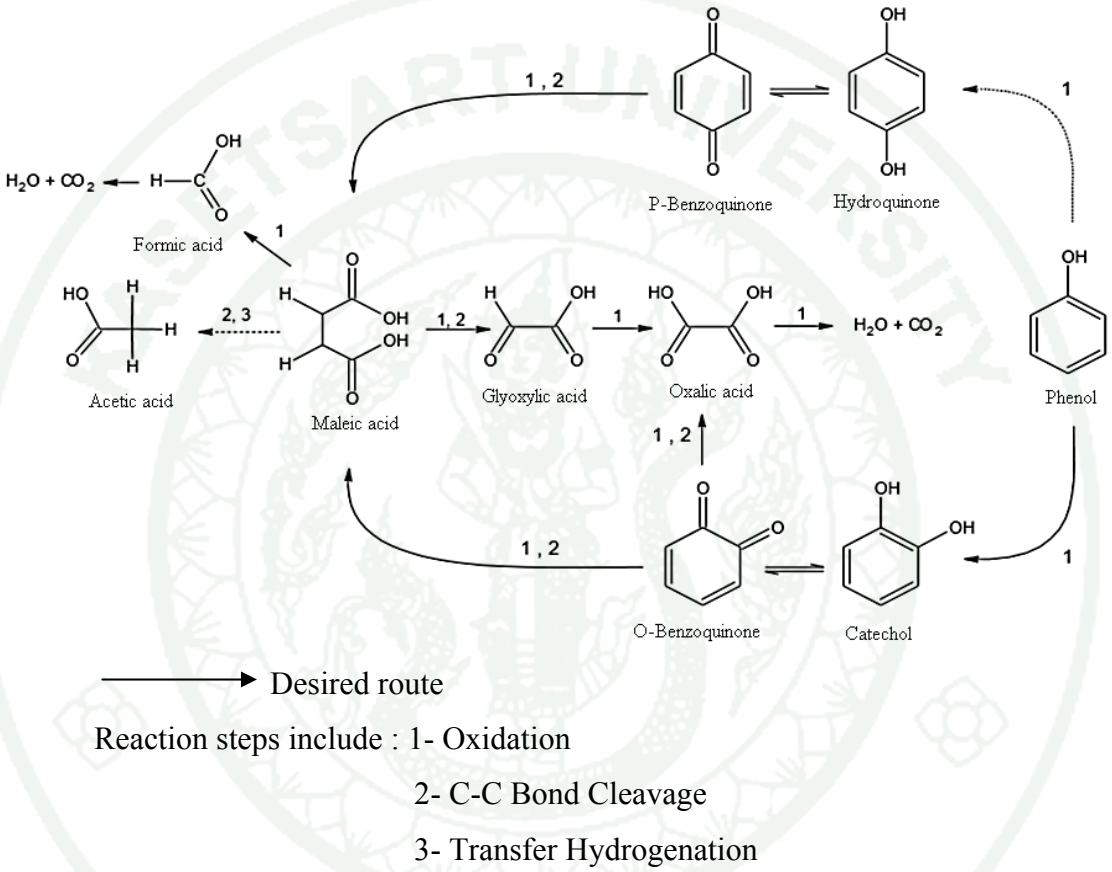
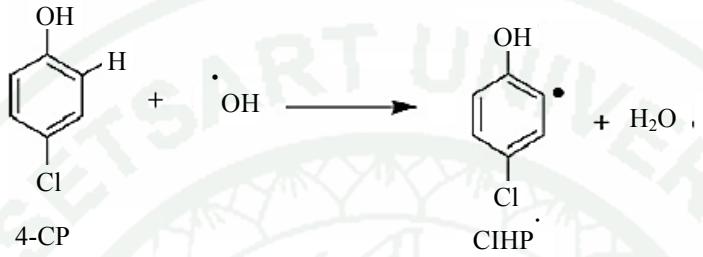


Figure 8 Reaction scheme for phenol oxidation with Fenton's reagent.

Source: (Faisal, 2009)

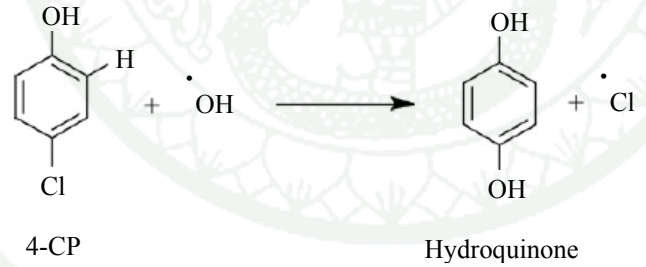
The participation of Fe/SUZ-4 in the degradation of 4-CP by Fenton reaction was suggested. In Fenton system, hydroxyl radical ($HO^{\bullet}$) was generate when hydrogenperoxide was added to initiate the reaction. During the oxidation of the organic species, the addition to a double bone was assumed to be the first step of hydroxyl radical attack.(Legrini *et al.,* 1993).

The attack of hydroxyl radical on 4-CP was directed by hydroxyl group, wich was a stronger ortho/para director than chlorine. Under the influence of these directors, hydroxyl radical preferred to attack the ortho position of the hydroxyl group (Du *et al.,* 2006.), as expressed in equation (12).



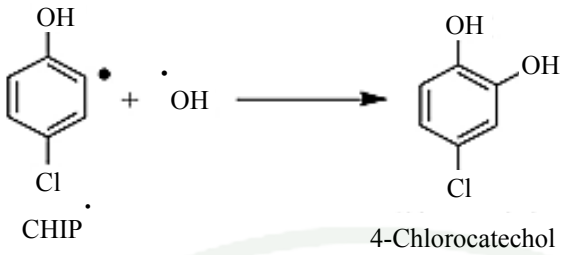
(12)

The hydroxyl radical abstracted a hydrogen atom from 4-CP yielding a 4-Chlorohydroxycyclohexadienyl radical (CIHP• radical) . Also, formation of the dechlorinated product, hydroquinone, was possible when •OH attack occurred at the chloro position of 4-CP (Du *et al.,* 2006) as expressed in equation (13).



(13)

The hydroxyl radical reacted with CIHP• radical, producing 4-Chlorocatechol (Du *et al.,* 2006), as described in equation (14).



(14)

When hydroxyl radical attacked at the chloro position of 4-Chlorocatechol, hydroquinone and catechol transferred easily to quinone, which was oxidized to organic acid by cleaving the benzene ring. The Mechanism of 4-CP oxidation by fenton system was described in Figure 9.

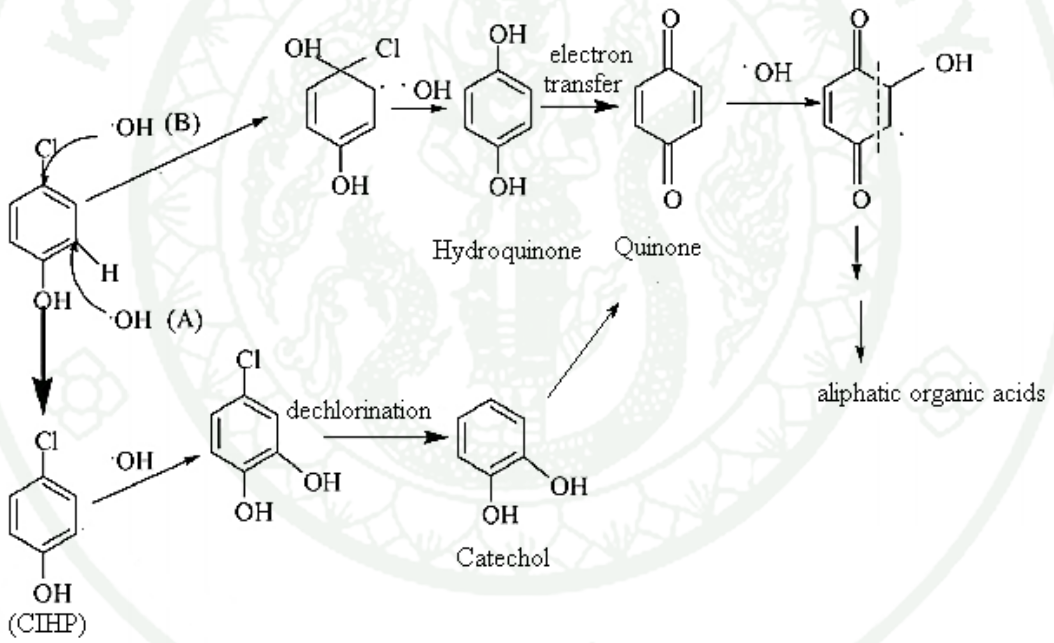


Figure 9 Reaction scheme for 4-CP oxidation with Fenton's reagent.

Source: (Du *et al.,* 2006)

The aromatic intermediates were chlorohydroquinone (CHQ), 4-chlorocatechol, 2-chloro-1,4-benzoquinone, 3,5-dichlorocatechol, 2,4-dichlororesorcinol 4,6-dichlororesorcinol, and 3,5-dichloro- 2-hydroxy-1,4-benzoquinone. It is believed that hydroxyl radicals are responsible for the

transformation of 2,4-DCP by attacking 2,4-DCP in the following ways by substituting an electron-withdrawing group (i.e., chlorine).

The 2,4-DCP has two chlorine atoms located in the para- and ortho-positions to the aromatic ring, which were substituted by $^{\bullet}$OH to yield CHQ and 4-chlorocatechol, respectively.

The oxidation of chlorinated hydroquinone to quinone: the chlorinated hydroquinone may dissociate two hydrogen atoms to give the corresponding quinine, such as 2-chloro-1,4-benzoquinone, in response to further hydroxyl radical attacks. Given that 2-chloro-1,4- benzoquinone is the dominant quinone detectable in the solution, the para-site is apparently the preferred location for HO$^{\bullet}$ radical attacks on the 2,4-DCP. This is likely due to the steric effect, in which the chlorine at the ortho-site is hindered by the nearby hydroxyl group compared to that at a para-site that is more approachable for radical collisions. A similar observation was also reported in the photodegradation of 2,4-D in titanium dioxide suspensions (D′Oliveira *et al.,* 1993).

The addition of HO$^{\bullet}$ to the aromatic ring: This mechanism allows an electrophilic HO$^{\bullet}$ group to be added onto the aromatic ring of the 2,4-DCP, leading to the formation of isomers including 3,5-dichlorocatechol, 2,4-dichlororesorcinol, and 4,6-dichlororesorcinol. Similarly, 4,6-dichlororesorcinal was reported by Brillas *et al.,* 2000. to be the hydroxylated product of 2,4-DCP. The three isomers would then undergo further hydroxylation, but such intermediates were not detectable because they were rapidly dehydrogenated to their corresponding quinone. The suggested structure of this compound is 3,5-dichloro-2-hydroxy-1,4-benzoquinone .

The breakdown of the aromatic ring: It was reported that hydroxyl radicals would break the aromatic rings of this chlorobenzoquinone and other hydroxylated products, resulting in maleic acids, fumaric acids, and simpler organic acids, including acetic acid, formic acid, glyoxylic acid, and oxalic acid . If there are no additional radical competitors in the solution, these low molecular organic acids can

gradually be mineralized to carbon dioxide (Brillas *et al.,* 2000.) .A reaction mechanism was proposed in Figure 10.

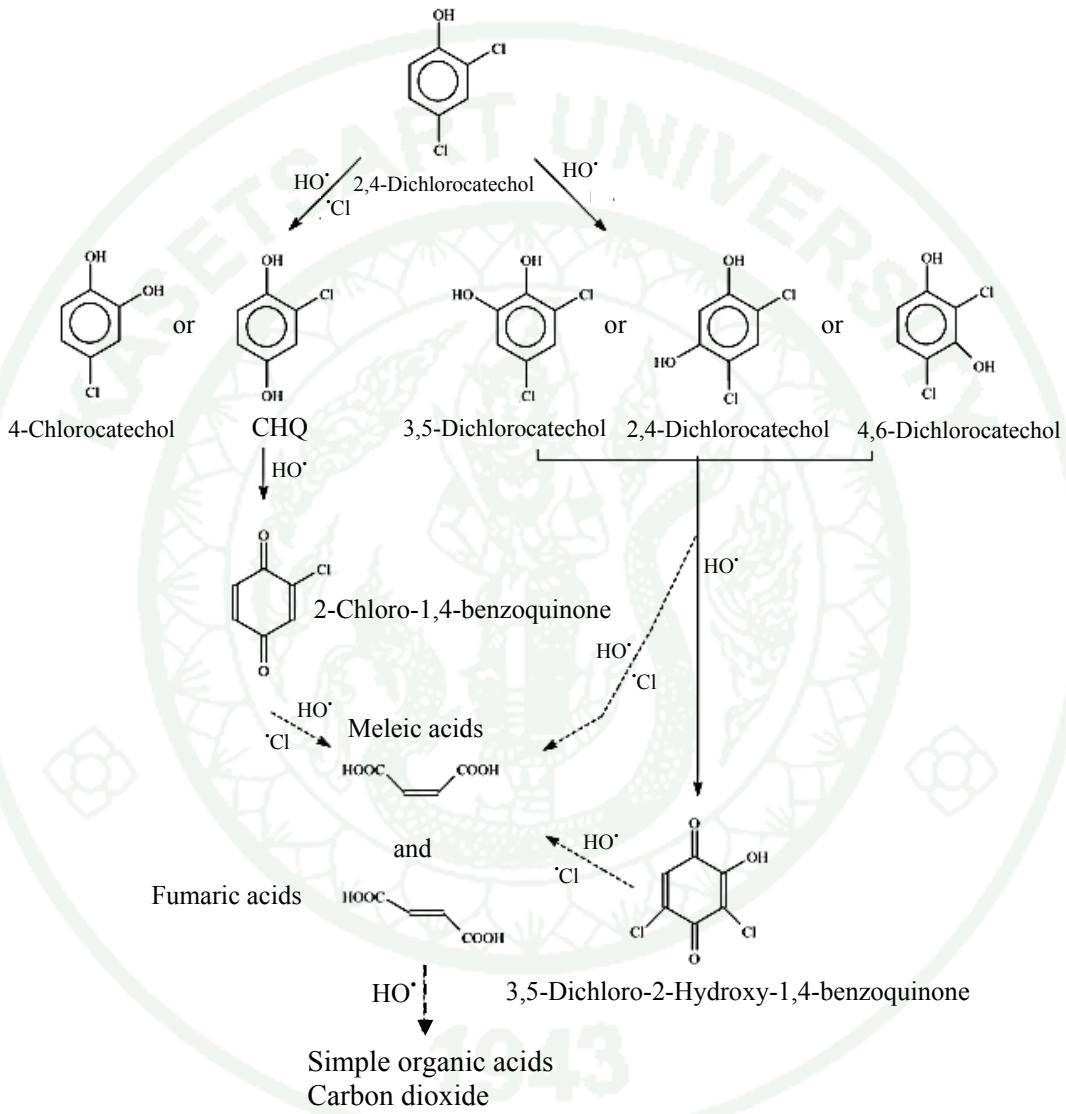


Figure 10 Reaction scheme for 2,4-DCP oxidation with Fenton's reagent.

Source: Chu *et al.* (2005)

5. Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is a clear and colourless liquid which is completely miscible with water. The physical constants of the main commercially available grades of hudrogen peroxide are accorded in Table 5 (Strukul., 1992).

Industrially, hydrogen peroxide is used mainly as a non-selective oxidant, i.e., for paper, textile and cellulose bleaching, and water purification. In Europe, it was particularly used in the manufacture of perborate and percarbonate which is used in detergents (Strukul., 1992).

Table 5 Physical properties of commercial H_2O_2 solutions.

	H_2O_2 strength (wt%)		
	35	50	70
Density at 293 K (g/ cm^3)	1.1312	1.1953	1.2886
Viscosity at 293 K (mPa s)	1.11	1.17	1.23
Freezing point (K)	240	221	233
Boiling point (K)	381	387	398

Source: Strukul (1992)

Hydrogen peroxide can be activated in the presence of transition metals with the general aim of increasing its reactivity by converting H_2O_2 into a different, more active species. This is accomplished by two general methods (Strukul, 1992).

The first method is by using H_2O_2 as a monoxygen donor to produce highly reactive metal-oxo species, which is a typical behaviour of biomimetric systems based, for example, on Fe^{2+}, Ru^{2+} and Mn^{2+} through a radical decomposition of H_2O_2 with one-electron redox couple like Fe^{2+}/Fe^{3+} or Ti (III)/Ti (IV). These are the basis for the well known Fenton and Undefined systems, respectively, and a way for

generating the highly reactive $HO^{\cdot}$ radical. Although these systems are not very selective, they do have some interesting applications especially in the wastewater treatment field.

The second method is by reacting H_2O_2 with metals capable to generate metal peroxy or hydroperoxy species, where the peroxo bond remains intact, resulting in an increase of either the electrophilic or the nucleophilic character of the peroxygens with respect to the initial oxidant.

The decomposition of hydrogen peroxide (equation 15) is very important for its storing because the generation of gas and heat (-98.3 kJ/mol) may cause safety problems. The rate of decomposition increases with temperature and decomposition can be further accelerated by the presence of impurities (metal ions or metal oxides) or by increasing pH (Strukul, 1992).

.

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad (15)$$

Oxidation by H_2O_2 alone is not effective for high concentrations of certain refractory contaminants, such as highly chlorinated aromatic compounds because of low rates of reaction at reasonable H_2O_2 concentrations. H_2O_2 is a strong oxidant (standard potential 1.80 and 0.78 V at pH 0 and 14, respectively) and its application in the treatment of various inorganic and organic pollutants is well established. Applications of H_2O_2 are known in the removal of pollutants from wastewater, such as sulphites, hypochlorites, nitrites, organic compounds and chlorine (Neyens and Baeyens, 2003). An advantage of H_2O_2 compared to other low cost oxidants comes from the active oxygen content, as illustrated in Table 6.

Table 6 Active oxygen content of some common oxidants.

Donor	% Active oxygen	Product
H_2O_2	47.0[a]	H_2O
O_3	33.3	O_2
t-BuOOH	17.8	t-BuOH
NaClO	21.6	NaCl
NaBrO	13.4	NaBr
HNO_3	25.4	NO_X
$KHSO_5$	10.5	$KHSO_4$
$NalO_4$	7.2[b]	$NalO_3$
PhlO	7.3	Phl

[a] calculated on 100% H_2O_2

[b] assuming only one oxygen atom is utilized

Source: Strukul (1992)

6. Chlorophenols

Chlorophenols are a group of chemicals that are produced by adding chlorines to phenol and derived from benzene. Most chlorophenols are solid at room temperature. Some chlorophenols are used as pesticides or antiseptics. Small amounts are produced during the chlorination of water and sewage (Yosef, 2009). They are also produced during bleaching wood pulp with chlorine in paper industry.

Chlorophenols have obtained notoriety as hazardous substances, because most of them are toxic and present long persistence in the environment. Laboratory studies carried out with animals showed that they developed liver and immune system effects. High levels of chlorophenols given to pregnant female rats in their drinking water reduced the number of babies they had, and caused low birth weights. The presence

of these substances has been detected in surface and ground waters (Howard, 1989). Table 7 shows data related to the presence of these substances in different industrial and municipal effluents. Table 8 also presents the solubilities of some chlorophenol compounds, which will determine its presence in different types of water. As it can be observed, they are in general readily soluble in water.

Table 7 Concentration of chlorophenolic compounds in different effluents.

Industry	Concentration of 2-chlorophenol (μg/l)	Concentration of 2,4,6-trichlorophenol (μg/l)
Secondary sewage effluent	1.7	-
Herbicide production waste	2.88	-
Leather tanning and finishing	-	2200 - 5900
Foundries	-	240 – 1400
Aluminium forming	-	260 – 1800

Source: Howard (1989)

Table 8 Solubility of some chlorophenols in water.

Compound	Solubility at 293 K (g/l)
2-Chlorophenol	28.5
3-Chlorophenol	26.0
4-Chlorophenol	27.1
2,4-Dichlorophenol	4.5
2,4,6-Trichlorophenol	0.8
Pentachlorophenol	0.014

Source : Ullmann's (1991)

6.1 Chemical properties

Chlorophenols are readily oxidize and versatile intermediates in chemical syntheses because both the hydroxyl group and the aromatic ring can react by both electrophilic and nucleophilic substitution. Electrophilic substitution is favored by the presence of chlorine atoms on the aromatic nucleus. Nucleophilic substitution for one or more of the chlorine atoms, although disfavored by the presence of the other chlorine atoms, is used widely, for example, to prepare various substituted diphenyl ethers, which serve as efficient herbicides(Ullmann., 1991).

6.2 Toxicity

In chlorophenol production, irritation symptoms of the skin, eyes, nose, and respiratory tract, resulting in chloro, have been observed. The substance can be absorbed into the body by inhalation of its aerosol, through the skin and by ingestion. The results of epidemiology studies on the long-term effects of chlorophenols are quite contradictory and have not yet allowed the experts to reach any firm conclusions (Mark *et al.,* 1992). Lethal dose (LD50) for rats has been found to be 580 mg/kg (oral) and 1730 mg/kg. Insufficient data are available on the effect of this substance on human health; therefore utmost precaution must be taken. Increasing attention is devoted at the present time to the risks of 2,4-dichlorophenol in relation to skin adsorption under the EPA's testing program for high-production-volume chemicals. EPA recommends that drinking water contain no more than 1.840×10^{-7} mol/l of chlorophenol.

6.3 Environmental considerations of chlorophenols

Chlorophenols constitute a group of organic substances that are introduced into the environment as a result of several man-made activities, such as waste incineration, uncontrolled use of fungicides, pesticides, herbicides, and wood preservatives, as well as, by-products formed during bleaching of pulp with chlorine and in the disinfection by chlorination to get drinking water (Ahlborg and Thunberg,

1980). The EPA recommends that a maximum average 2,4-dichlorophenol concentration in surface waters is not to exceed 1.239×10^{-5} mol/l (Ullmann's., 1991).

Chlorophenols may be present in the aquatic environment in many forms. They may be dissolved in free or complex forms, adsorbed on suspended inert solid or benthic sediments, or carried in biological tissues. Most plants are very sensitive to the phytotoxicity of chlorophenols. Fish and other aquatic organisms absorb chlorophenols through their gills, gastrointestinal tract or skin. All chlorophenols possess bactericidal activities that increase with the degree of chlorination. Additionally, chlorophenols are also highly toxic to algae.

6.4 2,4-Dichlorophenol (2,4-DCP)

2,4-dichlorophenol is solid at ambient temperature (colourless crystals) and has a strong odor. It is slightly soluble in water, but highly soluble in alcohols. The structure formular of 2,4-dichlorophenol and some physical properties are as presented in Figure 11 and Table 9.

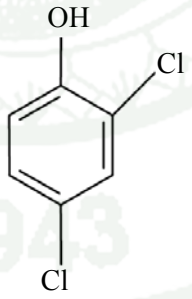


Figure 11 Structure formular of 2,4-dichlorophenol.

Source: Sangrawee (2003)

Table 9 Physical properties of 2,4-dichlorophenol.

Physical property	Value
Melting point	315- 316 K
Boiling point	482-483 K
Density (323 K)	1.38 g/cm^3
Flash point (closed cup)	387 K

Source: Ullmann's (1991)

2,4-Dichlorophenol is used in manufacturing 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-(2,4-dichlorophenoxy) propionic acid (2,4-DP). Industrially, 2,4-dichlorophenol can be obtained by chlorinating phenol, p-chlorophenol, and o-chlorophenol.

6.5 4-Chlorophenol (4-CP)

4-Chlorophenol is known as organic compound with the chemical formular of C_6H_5OCl. 4-Chlorophenol is used a solvent for extracting sulfur and nitrogen compounds from coal. It is also used in making dyes, aroma compounds, medicines and other organic chemicals. It is also used as intermediate for the synthesis of insecticides, herbicides, preservatives, antiseptics and disinfectants. The structure formular and some physical properties of 4-chlorophenol are as presented in Figure 12 and Table 10.

6.6 Phenol

Phenol is an organic compound with the chemical formular of C_6H_5OHl consisting of a phenyl ($-C_6H_5$) group bonded to a hydroxyl (-OH) group. It is also known as carbolic acid. It is white, crystalline solid at room temperature. Phenol is appreciably soluble in water, with about 8.3 g dissolving in 100 ml. It is produced on a large scale (about 7 billion kg/year) as a precursor to many materials and other

useful compounds. It is only mildly acidic but requires careful handling due to its toxicity and its propensity to cause severe burns. The sodium salt of phenol, sodium phenoxide, is far more water soluble. It is also a reactive molecule.

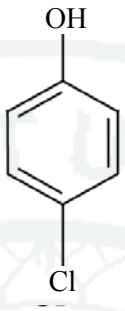


Figure 12 Structure formular of 4-chlorophenol.

Source: Sangrawee (2003)

Table 10 Physical properties of 4-chlorophenol.

Physical property	Value
Melting point	316 K
Boiling point	493 K
Density (323 K)	1.3 g/cm^3
Flash point (closed cup)	394 K

Source: Ullmann's (1991)

Phenol and its vapors are corrosive to the skin, the respiratory tract and the eyes. Prolonged skin contact with phenol may cause dermatitis, even second to third-degree burns or harmful effects on the liver and kidneys due to phenol's caustic. It may cause harmful effects on the central nervous system and heart, resulting in dysrhythmia, seizures, and coma. Inhalation of phenol vapor may cause lung edema. Exposure may result in death while the effects may be delayed. Besides its hydrophobic effects, another mechanism for the toxicity of phenol may be the formation of phenoxyl radicals. However, there is no evidence to believe that phenol

causes cancer in human. The structure formular and some physical properties of phenol are as presented in Figure 13 and Table 11.

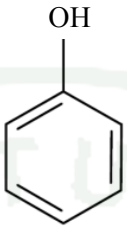


Figure 13 Structure formular of Phenol.

Source: Sangrawee (2003)

Table 11 Physical properties of phenol.

Physical property	Value
Melting point	318 K
Boiling point	455 K
Density (323 K)	1.07 g/ml
Solubility in water (293 K)	8.3 g/100 m1
Flash point (closed cup)	352 K

Source: Ullmann's (1991)

7. Related Researches

In 1992, SUZ-4 zeolite was first synthesized and patented by the British Petroleum Company (Barri, 1992). The proposed SUZ-4 framework consists of five, six, eight, and ten member-rings with the ten-member rings having pore opening of 4.6 × 5.2 A° (Lawton *et al.,* 1993). The crystal system type is orthorhombic and its growth is to be small needle shaped particle (Gujar and Price, 2002). The SUZ-4 zeolite has been claimed to be a very effective de–NO_X catalyst, as well as, a very

useful catalyst for many hydrocarbon reactions (Asensi *et al*., 1999). Mostly, synthetic step has used Structure Directing Agents (SDA) which are Tetraethyl ammonium hydroxide (TEAOH), however, a newer template, N′, N′, N′, N′, N′, N′-hexaethylpentanediammonium bromide, has emerged (Paik *et al.,* 2000) which has been reported to give SUZ-4 with higher Si/Al ratio than TEAOH.

Panthanit (2007) has synthesized SUZ-4 zeolite using rice husk ash (RHA) as a raw material via a hydrothermal process where the structure directing agent used was tetraethyl ammonium hydroxide (TEAOH). The molar ratios of silica from RHA/Silica sol were varied as following: 0, 50, 70, 90 and 100. With 4 days period of hydrothermal temperature at 423 K, starting pressure of 1 atm, rotation speed at 250 rpm, the molar ratios of silica in other conditions of SiO_2/Al_2O_3, $TEAOH/Al_2O_3$ and KOH/Al_2O_3 were 16.21 – 33.28, 2.6 and 6.47 – 8.60, respectively. The results show that, at RHA/Silica sol of 50 SiO_2/Al_2O_3 21.2 and KOH/Al_2O_3 7.9, 100 % yield of SUZ-4 zeolite was achieved. In addition, the obtained SUZ-4 crystal was observed as a needle-like structure having the average specific surface area of 469 m^2/g and the average pore size of 5.3 A°.

In 2001, Nguyen and colleagues studied on zeolite characteristics and different catalytic nature of active site in Fe-ZSM-5 zeolite for the oxidation of phenol in aqueous by using hydrogen peroxide as the oxidant. This results presented as Fe-ZSM-5 zeolite were synthesized with the Si/Fe various ratios ranged from 43 to 20. All of synthesized zeolites contained irons in two different forms: framework and extra-framework Fe. The fraction of framework Fe increased proportionally with increasing the Si/Fe ratios. It was revealed that both framework and extra-framework Fe could catalyze the oxidation reaction of phenol in aqueous solution. However, the framework Fe catalyzed to oxidize phenol more completely into CO_2 than the extra-framework Fe did.

Furthermore, there are many studies about the behavior of iron–containing zeolites, where one of them was done in carboxylic acid conversion by H_2O_2 wet oxidation which was analyzed and compared with that of homogeneous Fe^{3+} ions in

the same reaction conditions, in order to analyze the potential and limits of the use of these catalysts, as well as, to have more precise information on the differences in reactivity with respect to the homogeneous Fenton catalyst (Centi, 2000).

In 2004, Doocey and Sharratt studied the zeolite–mediated advanced oxidation of model chlorinated phenolic aqueous waste in aqueous phase Fenton catalysis. This Fenton's reagent was shown to be an effective advanced oxidation process for the treatment of a 2,4-DCP aqueous waste stream. Zeolites Beta and Y were found to be effective selective-adsorbents for these pollutants in order to improve the efficiency of an advanced oxidation process by eliminating "scavenger" effects. The former zeolite, although having a lower adsorption capacity than Y, exhibited the preferred adsorption behavior. An adsorption column packed with zeolite Beta was a successful adsorbent for 2,4-DCP in an aqueous waste stream and could be successfully regenerated using Fenton's reagent.

There were several authors reported the study for treatment of wastewater containing organic compound. One of the treatment method was Fenton reaction and precipitation some ions in water with calcium oxide (CaO.) Selected organic compounds for this study were phenol and 2,4 dichlorophenol (2,4-DCP.) The procedure was the treatment's monitoring of COD, TOC, pH, Sulfate ion, iron ion, calcium ion and the quantities of sediments, both before and after precipitation with CaO (Sriyom, 2003).

Lucking (1998) studied the solid materials where iron powder, graphite and activated carbon were tested for their catalytic properties for the oxidation of 4-chlorophenol in aqueous solution with hydrogen peroxide. Batch tests were performed at 303 K, and continuous tests with granular activated carbon under ambient conditions (323 K). Iron powder was shown to act as a catalyst for the activation of hydrogen peroxide and owing to this for the oxidation of 4-chlorophenol. The catalytic activity is based on iron ions leached from the iron powder which acts as homogeneous catalysts. Thus, the process can be described as a Fenton reac-tion enabled by dissolution of iron powder.

The same phenomenon was observed when iron impreg-nated activated carbon was applied as a catalyst. In contrast to iron powder, graphite and activated carbon were found to act as heterogeneous catalysts for the activation of hydrogen peroxide and the oxidation of 4-chlorophenol. During the oxidation of 4-chlorophenol with activated carbon as a catalyst, the decomposition of H_2O_2 was significantly slower than in the absence of 4-chlorophenol. This could be explained by the adsorption of 4-chlorophenol, due to which the surface area of the activated carbon, available for the decomposition of H_2O_2, was reduced. At the same concentration of catalytic material in batch tests, the oxidation of 4-chlorophenol proceeds much faster when iron powder instead of graphite or activated carbon is used.

On the other hand, graphite and activated carbon are stable catalysts not affected by dissolution processes. Activated carbon can be utilized for a continuous process in a fixed bed reactor. For this purpose the 4-chlorophenol oxidation in granular activated carbon filled columns was investigated and a 25% conversion of the 4-chlorophenol (7.78×10^{-3} mol/l) was achieved at a retention time of 26 minutes.

Maneechot (2008) studied the utilization of biosorption of organic compound by algal biomass for treating wastewater from Rubber wood factory, where the adsorption of phenolic compound including phenol, 4-CP and 2,4-DCP in aqueous solution by marine algae, Ulva recticulata, available in large quantities in Pattani Bay of Pattani Provinces was investigated. The kinetic profiles, the effect of pH, the amount of algae biomass and initial concentration of phenolic compounds by algal biomass were examined using batch experiments.

In 2009, Yinchun and colleagues studied Catalytic degradation of simulated 2,4-dichlorophenol wastewater by using self-synthesized Fe/activated carbon (AC) catalysts and hydrogen peroxide oxidation agent. The results indicated the degradation of 2,4-dichlorophenol by heterogeneous Fenton-like reaction by using selfprepared carbon-Fe catalysts. In the optimal reaction conditions, hydrogen peroxide 1 % (V/V), at pH 3, with 180 minutes reaction time and reaction temperature

of 303 K the degradation rate of 2.454×10^{-3} 2,4-dichlorophenol reached 79.9%. The reaction kinetics studies illustrated that the degradation of 2,4-dichlorophenol nearly follows the first-order reaction. The reaction rate was 0.00626 min^{-1} at 303 K, and the apparent reaction activity energy was 66.50 kJ / mol.

A comparative study of the advanced oxidation of 2,4-dichlorophenol was done by Momani and colleagues in 2004, where the advanced oxidation processes (AOPs), using UV, UV/H_2O_2, Fenton and photo-Fenton treatment was investigated at laboratory scale for aqueous solutions of 2,4-dichlorophenol (2,4-DCP). The effects on degradation of different reactant concentrations, irradiation time, temperature and pH were assessed. 2,4-DCP removal, TOC mineralization, dechlorination and change in oxidation state were also monitored. The result indicated that UV photolysis was less efficient for total 2,4-DCP degradation than other AOPs. In contrast, photo-Fenton reaction in acidic conditions led to a higher 2,4-DCP degradation in a short time. Sixty minutes of treatment were sufficient for 100% 2,4-DCP removal with 2.205×10^{-3} mol /1 H_2O_2 as the initial concentrations. In these conditions, a first-order degradation constant for 2,4-DCP of 0.057 min^{-1} was obtained.

Sabhi and Kiwi (2001) studied the degradation of 2,4-Dichlorophenol by immobilized iron catalysts. The degradation of 2,4-Dichlorophenol (2,4-DCP) has been carried out on Nafion–Fe (1.78%) in the presence of H_2O_2 under visible light irradiation. A solution containing 2,4-DCP (TOC 72 mg) was seen to be mineralized in^{-1} h in the presence of H_2O_2 (10 mM) under solar simulated visible light ($80mW/cm^2$) at pH values between 2.8 and 11. Homogeneous photo-assisted Fenton reactions were capable of mediating 2,4-DCP degradation only up to 5.4 of pH value. The degradation kinetics of 2,4-DCP on Nafion–Fe membranes was more favorable than the one observed during Fenton photoassisted processes at 2.8 of pH value. The degradation of 2,4-DCP was investigated as a function of the substrate, oxidant concentration and applied light intensity. The Nafion–Fe was seen to be effective over many cycles during the photo-catalytic degradation of 2,4-DCP showing an efficient and stable performance during 2,4-DCP degradation without leaching out Fe^{3+} ions into the solution. Evidence was presented that the degradation at the surface

of the Nafion–Fe membrane seems to be controlled by mass transfer and not by chemical reaction of the species in the solution. The approach used to degrade 2,4-DCP was shown to be valid for other chloro-carbons like 4-chlorophenol, 2,3-chlorophenol and 2,4,5-trichlorophenol.

In 2005, Chu and colleagues studied the kinetic modeling and reaction pathway of 2,4-dichlorophenol with the transformation by photo-fenton-like oxidation ($Fe^{3+}/H_2O_2/UVC$) process under various reaction conditions was investigated. It was interesting to find that the reaction kinetics of 2,4-DCP in $Fe^{3+}/H_2O_2/UVC$ systems varied depending on the initial Fe^{3+} concentration. A pseudo first-order kinetic and a non-conventional kinetic were discovered at low and higher Fe^{3+} concentrations, respectively. A model was used to simulate the non-conventional kinetic process, where two character parameters (the initial decay rate and the final decay fraction) were found to be critical in determining the process. The two parameters successfully quantify the photo-Fenton-like oxidation under different concentrations of Fe^{3+}, H_2O_2 and the corresponding ratios of Fe^{3+}/H_2O_2. The reaction intermediates were identified by an LC/MS analysis and a reaction mechanism was proposed.

Catrinescu and colleagues (2003) studied the catalytic wet peroxide oxidation of phenol over Fe-exchanged pillared beidellite. This study presented an evaluation of the catalytic performances of a Fe-exchanged Al-pillared synthetic beidellite for the wet hydrogen peroxide oxidation of phenolic aqueous wastes. The catalyst was prepared by a cation doping technique where its properties being determined by BET and chemical analysis techniques. All the tests were performed on a laboratory scale set-up. Important factors affecting catalyst activity and phenol removal efficiencies, i.e., the effect of pH, temperature, catalyst concentration and the stability of the catalyst, were studied. The results indicate that the use of this catalyst allows a total elimination of phenol and a significant removal of chemical oxygen demand, without significant leaching of Fe ions, thus considering the lowest Fe concentrations in solution after oxidation at pH value of 5, 323 K and 180 minutes period. COD removal efficiency of 87.9 % was obtained. It was also observed that by using this

catalyst, it was possible to extend the range of pH values for which Fenton-type oxidations can occur.

In 2004, Kuznetsova and colleagues studied the heterogeneous catalysis in the Fenton-type system Fe/ZSM-5 and H_2O_2, where the work dealt with Fe-containing zeolites for the catalytic oxidation of water-dissolved organic substances by H_2O_2. A detailed study of the system Fe/ZSM-5 and H_2O_2 meant to reveal the nature of the catalysis was presented. For this purpose, the following characteristics of the system were determined: the iron concentration in the filtrate of the catalyst suspension in several reaction runs; Fe content changes in the repeatedly used heterogeneous catalyst; and the catalytic activities of the filtrate and of the heterogeneous catalyst in several runs. The result has shown that, in the system Fe/ZSM-5 and H_2O_2, the heterogeneous catalysis made the main contribution to the catalyst activity in the H_2O_2 decomposition and oxidation of organic substrates. Additionally, in the presence of the iron ions complexing agents, FeZSM-5, showed a significantly different behavior in compare to the homogeneously dissolved iron cations, for example, in the presence of the $P_2O_7^{4-}$ anions, the rate of the H_2O_2 decomposition in the FeZSM-5 suspension was increased by several times, while that was totally reduced in a homogeneous iron solution.

Zazo and colleagues (2006) studied the catalytic wet peroxide oxidation of phenol with a Fe/active carbon catalyst, where Fe on activated carbon catalyst has been prepared and tested for phenol oxidation with H_2O_2 in aqueous solution at low concentration (2.941×10^{-3} mol/l). Working at 50 ^{o}C, initial pH of 3 and a dose of H_2O_2 corresponding to the stoichiometric amount (0.015 mol/l), complete removal of phenol and a high TOC reduction (around 85%) has been reached. Oxidation of phenol gave rise to highly toxic aromatic intermediates which finally disappeared completely evolving to short-chain organic acids. Some of these showed to be fairly resistant to oxidation being responsible for the residual TOC. In long-term continuous experiments, the catalyst underwent a significant loss of activity in a relatively short term (20 – 25 h) due to Fe leaching. This was related with the amount

of oxalic acid produced. Washing with 1N NaOH solution allowed the recovering of the activity although complete restoration was not achieved.

In 2005, Chedeville and colleagues studied the modeling of Fenton Reaction for the oxidation of phenol in water. Due to its bactericidal properties, it was difficult to eliminate phenol by classic treatment methods. In this work, the degradation of phenol compound by Fenton reaction at mild temperature and pressure conditions was studied. An experimental design was applied in order to quantify the influence of operating parameters on the efficiency of the studied method. The field of study was defined between 293 and 323 K for the temperature, 1 and 0.04 mol/l for the phenol concentration, 10 and 28 for the H_2O_2 to phenol molar ratio and 0.02 to 0.08 for the Fe (II) to phenol concentration ratio. The result showed that both the temperature and the amount of catalyst have strong influence. A model giving the decrease of COD was established. The COD decrease was between 40% and 72% while phenol had totally disappeared.

Molina and colleagues (2007) studied the wet oxidation of 4-chlorophenol kinetic, evaluating the application of wet oxidation for the treatment of solutions containing 4-chlorophenol and suggested a kinetic model in order to allow the prediction of the concentration of the compounds involved in the process throughout the reaction. 4-Chlorophenol was a compound of special interest due to its high toxicity and low biodegradability. The existence of an induction period previous to the oxidation was detected and a kinetic equation to describe the whole process was found by adjusting the experimental data. The influence of some operating conditions, such as, temperature and partial pressure of oxygen were studied before carrying out the development of the reaction mechanism and the kinetic model. From the results, it could be concluded that an increase in the temperature in the range ofrom 433 to 463 K resulted in a faster degradation rate. On the other hand, an increase in the partial pressure of oxygen in the range from 5 to 10 bars involved a faster kinetic rate; however an increase from 10 to 15 bars does not show any improvement. It was concluded that the degradation of 4-chlorophenol by wet oxidation followed pseudo first order kinetics, being hydroquinone and quinine, the

most relevant intermediates. It was also observed that the chloride from the chlorophenol was released to the medium and no intermediates containing chloride were formed. A remarkable increase in the biodegradability was observed through the wet oxidation process.

Du and colleagues (2007) studied the kinetic model of 4-CP degradation by Fenton/O_2 system. A kinetic model of the degradation of 4 -CP by Fenton/O_2 system was established, in which particular attention was paid to the role of oxygen in the process because many former researches suggested that the presence of oxygen could decrease the input of H_2O_2. The proposed model well predicted 4-CP degradation and H_2O_2 consumption by Fenton/O_2 and Fenton/N_2 systems at varying levels of Fe^{2+}, H_2O_2, and 4-CP input. Most correlation coefficients between experimental and predicted data of 4-CP and H_2O_2 concentration were above 0.95. The model could predict the enhancement of 4-CP degradation by oxygen and the difference in the evolution of aromatic intermediates between Fenton/O_2 and Fenton/N_2 systems. The predicted and experimental data both showed the the degree of benzene ring cleavage in Fenton/O_2 system was higher than that in Fenton/N_2 system. Understanding the role of oxygen is very important to improve the decomposition performance.

In 2004, Phenol degradation in photochemically enhanced Fenton process was investigated by Feng and Le-cheng. UV-VIS spectra of phenol degradation showed the difference between photo-Fenton process and UV/H_2O_2, which is a typical hydroxyl radical process. A possible pathway diagram for phenol degradation in photo-Fenton process was proposed, and a mathematica model for chemical oxygen demand (COD) removal was developed. Operating parameters such as dosage of H_2O_2 and ferrous ions, pH, suitable carrier gas were found to impact the removal of COD significantly. The results and analysis of kinetic parameters calculated from the kinetic model showed that complex degradation of phenol was the main pathway for removalof COD; while hydroxyl radicals acted weakly in the photo-Fenton degradation of phenol.

Faisal I. (2009).Phenol oxidation by Fenton's reagent ($H_2O_2 + Fe^{+2}$) in aqueous solution has been studied for the purpose of learning more about the reactions involved and the extent of the oxidation process, under various operating conditions. An initial phenol concentration of 1.06×10^{-3} mol/l was used as representative of a phenolic industrial wastewater. Working temperature of 298 K was tested, and initial pH was set at 5.6 . The H_2O_2 and the Fe^{+2} doses were varied. Keeping the stirring speed of 200 rpm. The results exhibit that the highest phenol conversion (100%) was obtained at about 180 min. The study has indicated that Fenton's oxidation is first order with respect to the phenol concentration and the rate constant K, was found to be 0.0325 s^{-1}.

Bach, A. and colleagues (2010). The kinetics of hydrogen peroxide decomposition and the mineralization rate of phenol in homogeneous aqueous solution (pH 3) via Fenton-like reaction were studied. Results were correlated with the generation of hydroxyl radicals as well as with iron speciation. Batch experiments were carried out in de-ionized water in a completely mixed batch reactor under a wide range of experimental conditions. Results demonstrated that the rate of hydrogen peroxide decomposition, phenol mineralization and ferrous ions formation depended on both the initial concentration of the phenol and on the weight ratio between hydrogen peroxide and iron. A linear correlation was found between the mineralization rate of phenol and the decomposition rate of hydrogen peroxide indicated that 10 g of hydrogen peroxide was required to mineralize 1 g of phenol.

MATERIALS AND METHODS

The materials used and methods adopted for this study of the oxidation of phenolic compounds waste water by H_2O_2 using Fe/SUZ-4 zeolite as catalyst are as follows.

Materials

Materials and equipments for experiments include;

1. Synthesis of SUZ-4 and metal–ion exchange
   - 1.1 X-ray fluorescence spectrometry
   - 1.2 Scanning electron microscope (SEM)
   - 1.3 BET-N_2 adsorption
   - 1.4 High temperature furnace
   - 1.5 Hydrothermal reactor

Figure 14 Hydrothermal reactor with controlled temperature and speed, (Model 4516 M PARR).

- 1.6 Hydrochlororic acid (HCl) 37 % wt.,J.T. Baker
- 1.7 Silica sol (SiO_2) 40% wt., Ludox AS-40 DuPont
- 1.8 Aluminum powder 97 % wt.,HiMidia Laboratories
- 1.9 Potassium hydroxide 85 % wt.(KOH) ,Carlo Erba Reagenti

1.10 Tetraethyl ammonium hydroxide 35 % wt.(TEAOH), Sigma – Aldrich

1.11 Rice husk, Ram Rice Mill Bangkok

1.12 Iron (II) chloride ($FeCl_2.7H_2O$) 98 % wt. Analytical grade: QRec New Zealand

2. Kinetics analysis of phenolic compounds

2.1 High Performance Liquid Chromatography (HPLC)

2.2 Methanol (CH_3OH); HPLC Gradient Grade: J.T. Baker

2.3 4-Chlorophenol (C_6H_5ClO); Analytical Reagent Grade: Fluka

2.4 Acetonitrile (CH_3CN); HPLC Gradient Grade: Fisher Scientific2

2.5 Methanol (CH_3OH); Analytical Reagent Grade: J.T. Baker

2.6 Dichloromethane (CH_2Cl_2); Analytical Reagent Grade: Fisher Scientific

2.7 Phenol (C_6H_6O); Analytical Reagent Grade: Fluka

2.8 H_2O_2 98 % wt.,Merck, Ltd. Company

2.9 2,4-Dichlorophenol($C_6H_4Cl_2O$);Analytical Reagent Grade: Fluka

Methods

1. Preparation of the rice husk ash

1.1 The rice husk was cleaned by washing, then baked until dry.

1.2 100 grams of cleaned and dried rice husk rice was boiled with hydrochloric acid (1M, 1 liter) for 3 hours.

1.3 Boiled rice husk was cleaned again to wash out the acid and then baked to dry.

1.4 Boiled and dried rice husk was then burned at 973 K with the addition of oxygen for 1 hour.

1.5 Size separation of the resulted husk ash was then followed using 200 mesh sieve size and put to storage in a desiccators.

2. Synthesis of SUZ-4 and metal–ion exchange.

2.1 Potassium Aluminate solution was firstly prepared by dissolving potassium hydroxide in the water and gradually adding Aluminum powder while stirring continuously for 20 to 25 hours.

2.2 Silica was prepared by mixing the prepared rice husk ash in proportion to the silica sol.

2.3 Silica sol was mixed with silica tetraethyl ammonium hydroxide and distilled water. The solution was then stirred continuously for 2 hours while the prepared Potassium Aluminates was being added slowly. After all, the solution was continuously stirred for 3 hours in order to thoroughly mix until the gel compound was adjusted to the pH value in the range of 13 to 14 using potassium hydroxide.

2.4 The prepared compound was then poured into the Teflon cup before putting into a hydrothermal reactor and heated up with the rate of 278 K per minute until a temperature reached 423 K with agitation speed of 250 rpm and continuous stirring for 4 consecutive days.

2.5 The obtained product was then filtered and washed with distilled water until the pH is equal to 9 before being dried at 393 K for 2 hours. After that the removal of TEAOH was carried out at 773 K for 5 hours and being tested by XRF, XRD, SEM and Autosorb.

2.6 Iron (II) chloride tetra hydrate (99.0 % w/w) solution was prepared at room temperature; with the ratio of 1 g iron (II) chloride to 100 ml deionized water (1.602 g iron (II) chloride was actually dissolved in 160 ml deionized water.)

2.7 The iron (II) chloride solution was mixed with SUZ-4 and continuously stirred at room temperature for 24 hours.

2.8 After that the solution was filtered and washed with deionized water before being dried at 393 K overnight.

2.9 The product was then burned in the furnace (in the air) at 673 K for 4 hours, and then being tested by XRF.

3. Kinetics analysis of phenolic compounds

3.1 Stock solutions phenol 2,4-Dichlorophenol and 4-Chlorophenol, were prepared at the concentration of 0.01 mol/l using methanol solution (50%) as a solvent and stored at 277 K. The stock solution was diluted to the desired concentration.

3.2 The analyses of the sample phenol, 2,4-Dichlorophenol and 4-Chlorophenol were then taken, where the sample could be extracted with solvents dichloromethane (10 ml) three times in 5 minutes and being left to settle and the separation occurred.

3.3 Solution was then obtained by rotary evaporator in order to evaporate at 313 K before the substance was dissolved using 5 ml of 50% methanol solution tested by HPLC and XRF.

3.4 HPLC analysis conditioned for using the C_{18} column with reverse phase Pinnacle II C_{18} (5 μm 250 × 4.6mm) was operated for the sample, where the solvent was a mixture of methanol-acetonitrile-deionized water at the ratio of 30:30:40 (HPLC Gradient Grade) with a flow rate of 1.0 ml/min and Photodiode array (DAD) was a UV detection at 280 nm.

3.5 The analyses kinetics reaction of the oxidation of phenols, 2,4-Dichlorophenol and 4-Chlorophenol were taken using conditions as shown in Table 12, 13 and 14 below, respectively.

Table 12 Analysis conditions kinetics reaction of oxidation of phenol.

Substance	Concentration (mol/l)	Volume(ml)
Phenol	1.06×10^{-3}	200
H_2O_2	0.015	
Fe^{2+}	0.260 g	200
pH	3	
Temperature	303 K	

Source: Mauri (2007)

Table 13 Analysis conditions kinetics reaction of oxidation of 2,4-Dichlorophenol.

Substance	Concentration (mol/l)	Volume(ml)
2,4-dichlorophenol	6.13×10^{-4}	200
H_2O_2	0.015	
Fe^{2+}	0.260 g	200
pH	3	
Temperature	303 K	

Source: Yinchun *et al*. (2009)

Table 14 Analysis conditions kinetics reaction of oxidation of 4-Chlorophenol.

Substance	Concentration (mol/l)	Volume(ml)
4-Chlorophenol	7.78×10^{-4}	200
H_2O_2	0.015	
Fe^{2+}	0.260 g	200
pH	3	
Temperature	303 K	

Source: Luecking, *et al*. (1998)

The Analyses of the sample phenol, 2,4-Dichlorophenol and 4-Chlorophenol were carried out at 10, 30, 60, 90, 120, 150, 180, 210, 240, 270 and 300 minutes before being placed in the refrigerator at 277±1 K or basified with NaOH to stop the reaction.

Figure 15 Reactor for kinetics analysis of phenolic compounds.

RESULTS AND DISCUSSION

1. The synthesis of SUZ-4 zeolite

Firstly, potassium aluminate solution was prepared by gradually dissolving potassium hydroxide in water and then aluminum powder was added under continuous stirring for 20 to 25 h. Silica source was prepared by mixing rice husk ash in proportion to the silica sol. Then, tetraethyl ammonium hydroxide (TEAOH) and distilled water were added and stirred continuously for 2 h. Subsequently, the prepared potassium aluminate solution was slowly poured into the mixed silica source solution and kept stirring for another 3 h. The pH-value of the mixed solution was adjusted in the range of 13 to 14 by using potassium hydroxide. After that the gel compound was poured into a Teflon cup and put into an autoclave reactor for further hydrothermal processing at 423 K with agitation speed of 250 rpm (Model M6, CAT Ingenieurbuero M. Zipperer, Germany) for 4 days (Worathanakul*et al.,* 2011). Obtained powder was then filtered and rinsed with distilled water until the pH was close to 7. After drying at 393 K and calcining at 773 K, it was kept in a desiccator.

Before being used as a raw material, the obtained rice husk ash as shown in figure 16 was analyzed its chemical composition by an XRF and was found to contain 99.7 % SiO_2 with traces of oxides of aluminum and other metals as shown in Table 15.

Figure 16 Rice husk ash after burning at 973*K* for 1 hour.

Table 15 Chemical composition of rice husk ash (RHA).

Chemical Composition	Wt.%
SiO_2	99.7
Al_2O_3	0.2
Others	0.1

The Fe/SUZ-4 catalyst was prepared by a wet impregnation and ion-exchange methods. The synthesized SUZ-4 zeolite was suspended in 150 ml iron (II) chloride solution at room temperature for 24 h. At this stage, Fe^{2+} was expected to exchange with K^+ of SUZ-4 and simultaneously, $FeCl_2$ was impregnated onto the SUZ-4 surface. Next, the suspended solid was filtered, rinsed with deionized water, and dried at 393 K overnight. Finally, the impregnated $FeCl_2$ onto the SUZ-4 was decomposed at 673 K for 4 h to become Fe_2O_3. The total amount of Fe in the synthesized SUZ-4 was also found to be 4.72 wt. % as presented in Table 16.

Table 16 Chemical composition of synthesized Fe/SUZ-4.

Chemical Composition	Wt.%
Si	33.32
K	11.89
Fe	4.72
Al	3.64
Others	46.43

The analysis of micro-structure of synthesized SUZ-4 by a Scanning Electron Microscope (SEM, Jeol Model JSM-5600 LV) is shown in Figure 17. Needle-shaped crystals of SUZ-4 (Worathanakul *et al.,* 2008.) having diameter of approximately 0.2 μm and length of approximately 5 μm can be seen.

Figure17 SEM of SUZ-4 zeolite synthesized by using RHA to Silica Sol at the ratio of 1:1.

From the determination of specific surface area (m^2/g) and pore size ($\overset{o}{A}$) of synthesized SUZ-4 zeolite, using different ratios of RHA to Silica Sol, by applying Multipoint BET technique for nitrogen adsorption (Pantanit, 2007), the result indicated that the values of specific surface area and pore size of SUZ-4 zeolite synthesized with the ratio of RHA to Silica Sol at 1:1 were close to those of SUZ-4 zeolite synthesized with the ratio of RHA to Silica Sol at 0:100. Therefore, this ratio was adopted for the synthesis of SUZ-4 throughout this research work.

2. The reaction of the catalyst Fe/SUZ-4

2.1 Preparation and selection of the catalyst

In this study, the reaction temperature of the degradation rate of phenolic compounds was maintained at 303 K. The comparison of the degradation rate between the reactions with and without ion-exchanged SUZ-4 (Fe/SUZ-4) was performed. It is clearly seen in Figure 18 that the degradation of the mixed phenolic compounds obtained by using ion-exchanged SUZ-4 is obviously higher than that without ion-exchanged SUZ-4. The calculation on the degradation of phenol, 2,4-

dichlorophenol and 4-chlorophenolby the following equation (16) (Yinchun *et al.,* 2009).

$$\eta = \frac{C_1 - C_2}{C_1} \times 100 \qquad (16)$$

Where η = the degradation of phenolic compounds

C_1 = the concentrations of phenolic compounds before reaction

C_2 = the concentrations of phenolic compounds after reaction

The results show that the degradation rate of phenol, 2,4-dichlorophenol and 4-chlorophenol without ion-exchanged SUZ-4 (Fe/SUZ-4) and with SUZ-4 (Fe/SUZ-4) are 40.60, 17.30, 23.45 % and 92.41, 77.45, 74.29 %, respectively. Consequently, the ion-exchanged SUZ-4 (Fe/SUZ-4) was chosen to be used for the rest of experiment.

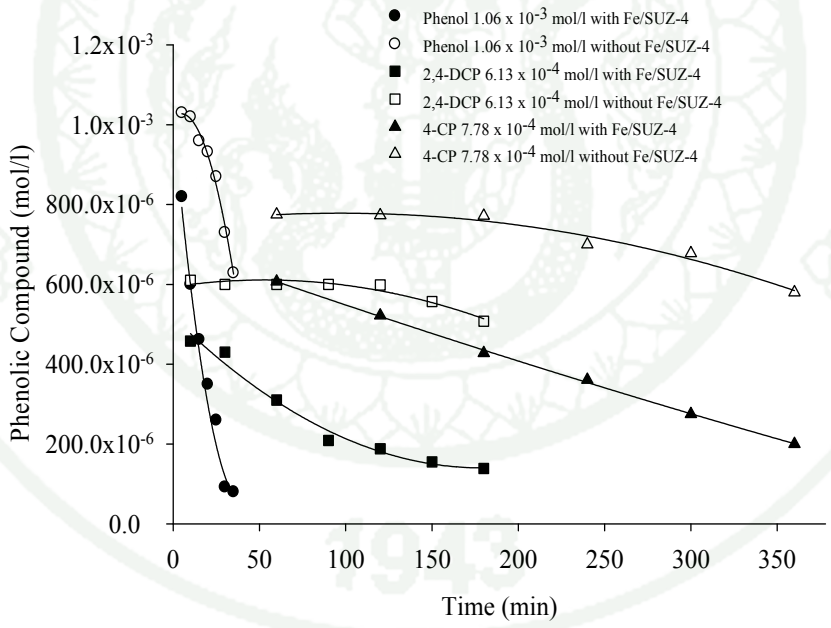


Figure 18 Degradation of phenolic compound mixture (phenol:2,4-DCP:4-CP) using H_2O_2 0.015 mol/l comparison between the reactions with and without Fe/SUZ-4 at 303*K* and pH of 3.

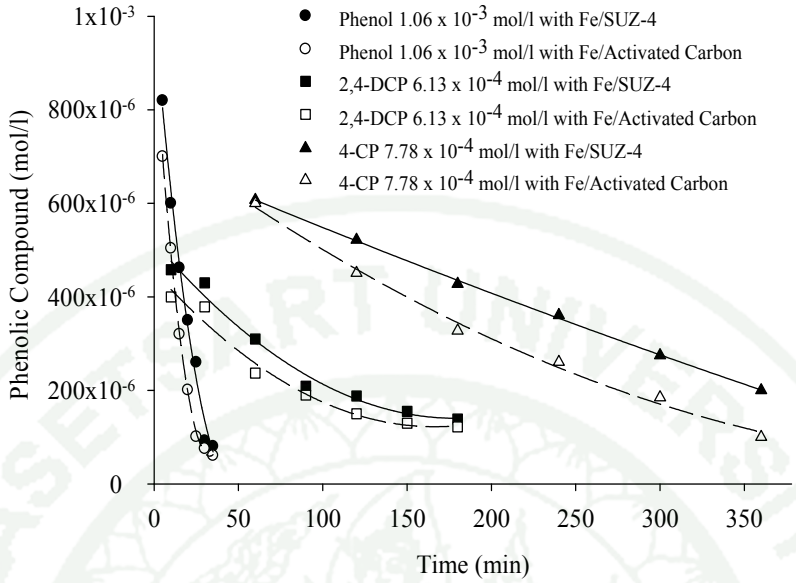


Figure 19 Degradation of phenolic compound mixture (phenol:2,4-DCP:4-CP) using H_2O_2 0.015 mol/l, compared between the reactions with Fe/SUZ-4 and with Fe/Activated Carbon , at 303*K* and pH of 3.

Comparing to the former research works related to the degradations of phenol, 2,4-dichlorophenol and 4-chlorophenol using Fe/Activated Carbon as catalyst (Mauri., 2007 ; Yinchun*et al*.,2009 ; Luecking, *et al*.,1998), the result from this research indicated that the degradation rates of phenol, 2,4-dichlorophenol and 4-chlorophenol using Fe/Activated Carbon as catalyst were slightly higher than those using Fe/SUZ-4 as catalyst. As shown in Figure 19, the values of degradation rates of phenol, 2,4-dichlorophenol and 4-chlorophenol using Fe/Activated Carbon and Fe/SUZ-4 as catalysts are 94.28 %, 80.10 %, 80.13 % and 92.41 %, 77.45 %, 74.29 %, respectively.

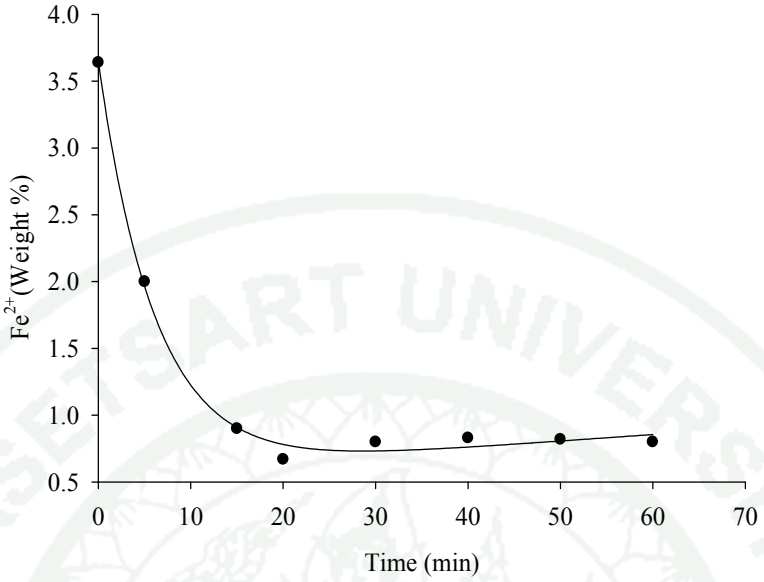


Figure 20 The Fe (II) level in the degradation of phenolic compound mixture (phenol:2,4-DCP:4-CP) using H_2O_2 0.015 mol/l and Fe/SUZ-4 3.64 wt. % at 303 *K* and pH of 3.

From Figure 20, at the beginning of the degradation reaction of phenolic compound, the level of Fe (II) decreased rapidly because of being used in the reaction with H_2O_2 in forming OH radicals and Fe (III). However, at about 20 minutes later, the level of Fe (II) started to increase and become quite constant eventually due to the reaction between Fe (III) and H_2O_2 forming Fe (II).

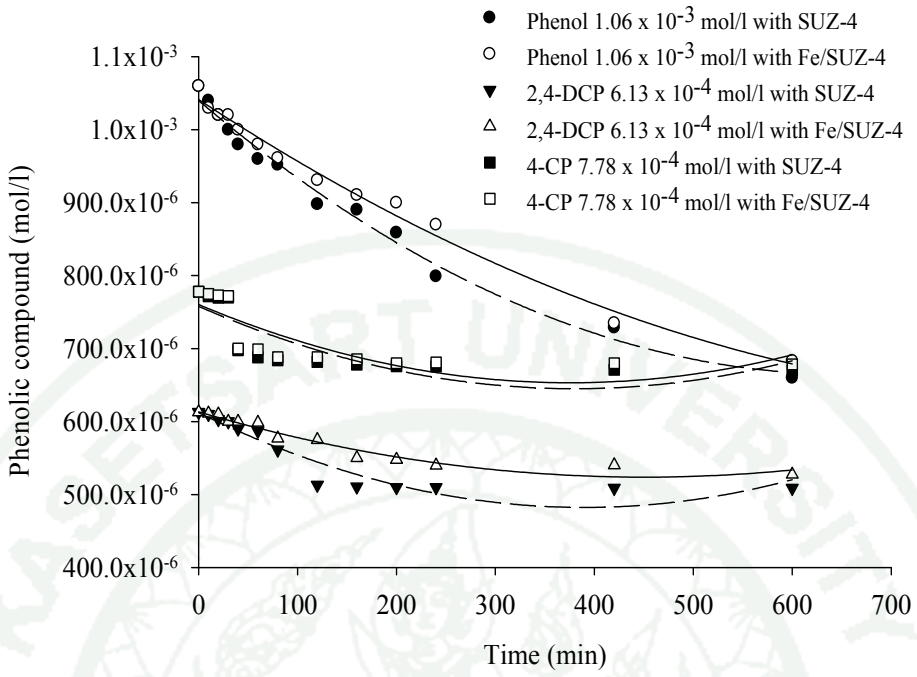


Figure 21 Adsorption of phenolic compound mixture (phenol:2,4-DCP:4-CP) compared between SUZ-4 and Fe/SUZ-4 at 303*K* and pH of 3.

From the experiments set to compare the adsorption efficiency between SUZ-4 zeolite and Fe/SUZ-4, it was found that the adsorption efficiency of SUZ-4 zeolite in adsorbing phenolic compound mixture was slightly higher than that of Fe/SUZ-4 as shown in Figure 21 above. It can be concluded that Fe (II) is infiltrated into the pores on the porous surface of SUZ-4 zeolite.

2.2 Reaction kinetics of the degradation of phenolic compounds

The degradation reactions of phenol, 2,4-dichlorophenol and 4-chlorophenol degradation were investigated and the obtained results are shown in Figures 22–24. It is evident that the rate of degradation ($-r_d$) (i.e., slope of each curve) increases when the initial concentration of phenolic compound increases. This is just consistent with a general kinetic behavior where the more concentration of reactant presents in the system, the higher rate of reaction occurs.

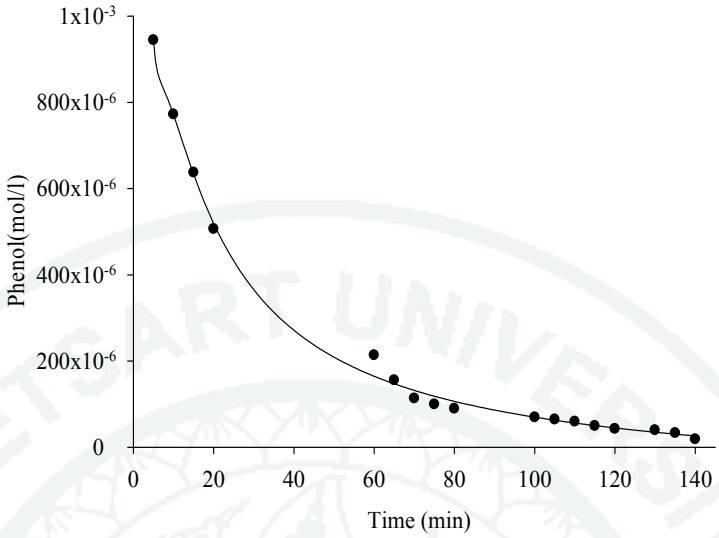


Figure 22 Degradation of phenol using H_2O_2 0.015 mol/l and Fe^{2+} 0.26 g at 303 *K* and pH of 3.

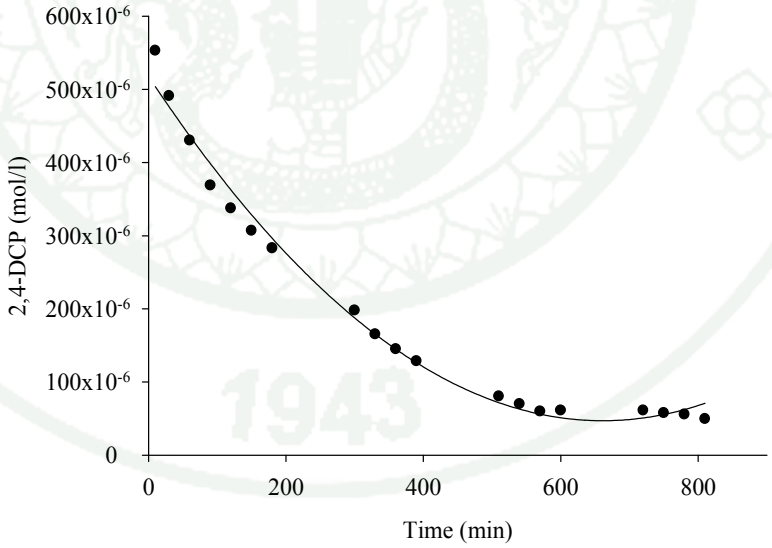


Figure 23 Degradation of 2,4-DCP using H_2O_2 0.015 mol/l and Fe^{2+} 0.26 g at 303 *K* and pH of 3.

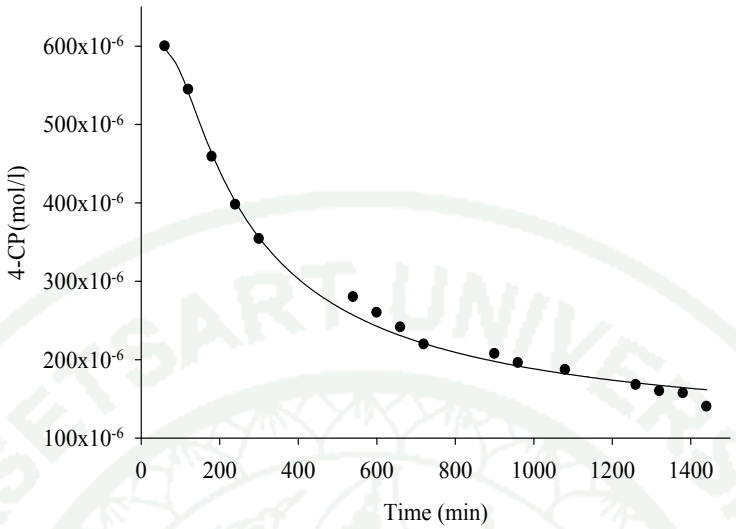


Figure 24 Degradation of 4-CP using H_2O_2 0.015 mol/l and Fe^{2+} 0.26 g at 303 *K* and pH of 3.

When the slope of each curve was taken at time approaching zero, the plot of phenolic compound concentration versus ln ($-r_d$) for phenol, 2,4-DCP and 4-CP degradation was obtained as shown in Figure 25. The slope of each plot is, in fact, an order of degradation reaction, following these equations (17) - (18):

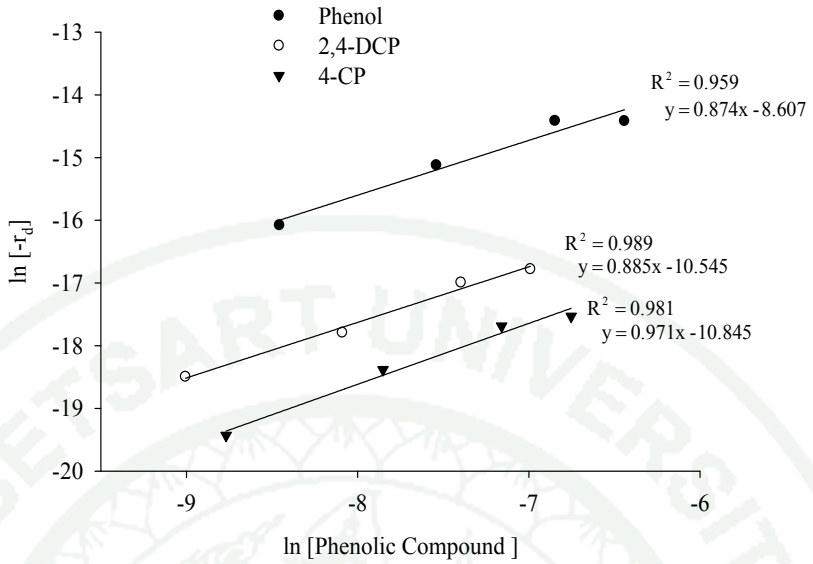


Figure 25 Plot of ln [Phenolic Compound] versus ln[$-r_d$] for phenol, 2,4-DCP and 4-CP degradation.

$$-r_d = -\frac{dC_A}{dt} = kC_A^n C_B^m \tag{17}$$

$$\ln\left(-\frac{dC_A}{dt}\right) = n\ln C_A + \ln(kC_B^m) \tag{18}$$

Where C_A = the concentration of corresponding phenolic compound

C_B = the concentration of H_2O_2 that was kept constant.

n = the order of reaction with respect to A

m = the order of reaction with respect to B

k = the rate constant

From Figure 25, since the obtained slopes are close to 1, it can be concluded that the degradations of phenolic compounds follow the 1st-order reaction scheme. Then, the degradation reactions of phenolic compounds were repeated by varying H_2O_2 concentration and fixing phenolic compound concentration. The obtained results are presented in Figure 26-28.

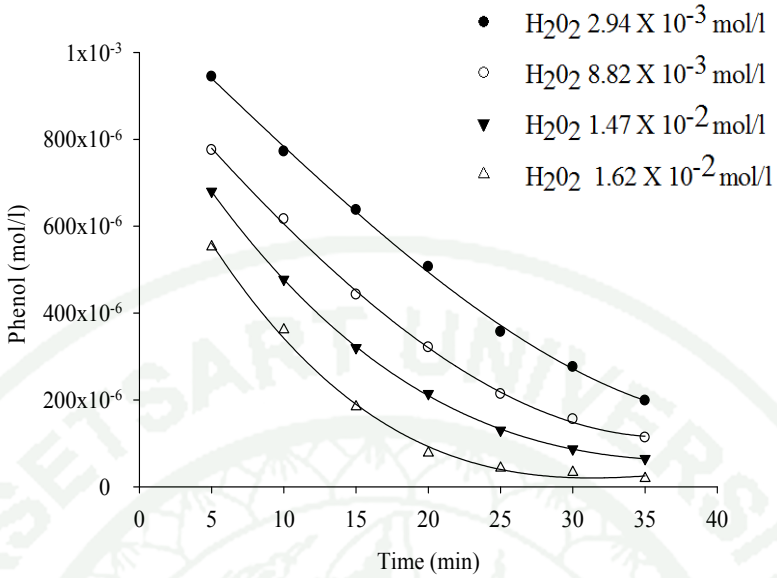


Figure 26 Degradation of phenol1.06 × 10^{-3}mol/l when [H_2O_2] was varied, using Fe^{2+} 0.26 g, 303 *K* and pH of 3.

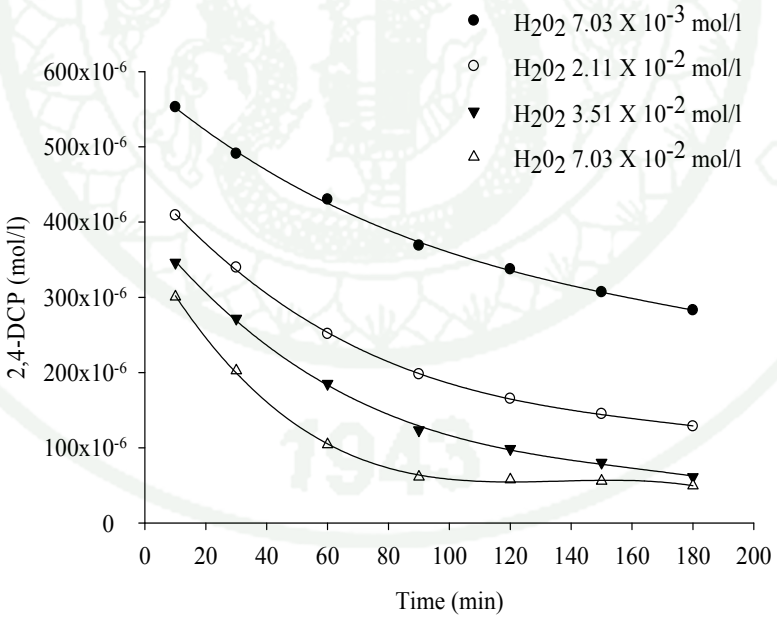


Figure 27 Degradation of 2,4-DCP 6.13 × 10^{-4} mol/l when [H_2O_2]was varied, using Fe^{+2} 0.26 g, 303 *K* and pH of 3.

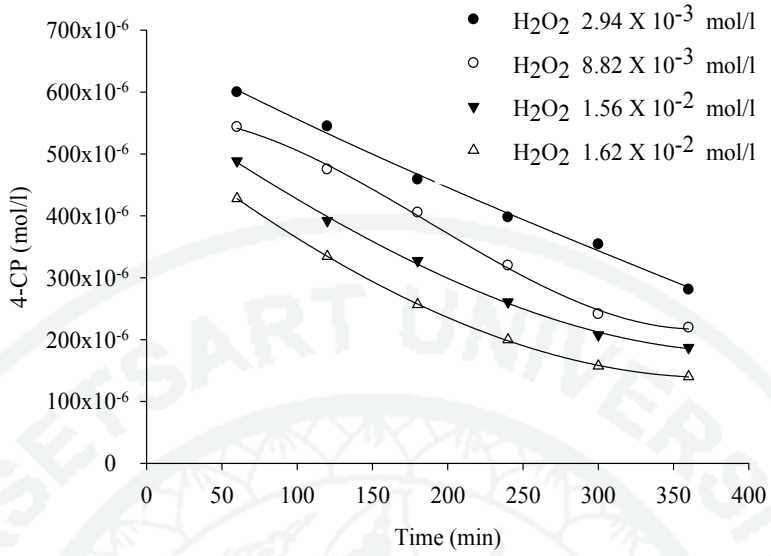


Figure 28 Degradation of 4-CP 7.78×10^{-4} mol/l when $[H_2O_2]$was varied, using Fe^{+2} 0.26 g, 303 *K* and pH of 3.

When the slope of each curve (i.e., $-r_d$) was determined and plotted against $[H_2O_2]$ in logarithmic scale as shown in Figure 29, it obviously shows that the slopes of all three lines are close to zero. These slopes are corresponded to the order of reaction with respect to H_2O_2. This means the rate of degradation does not depend on the hydrogen peroxide concentration.

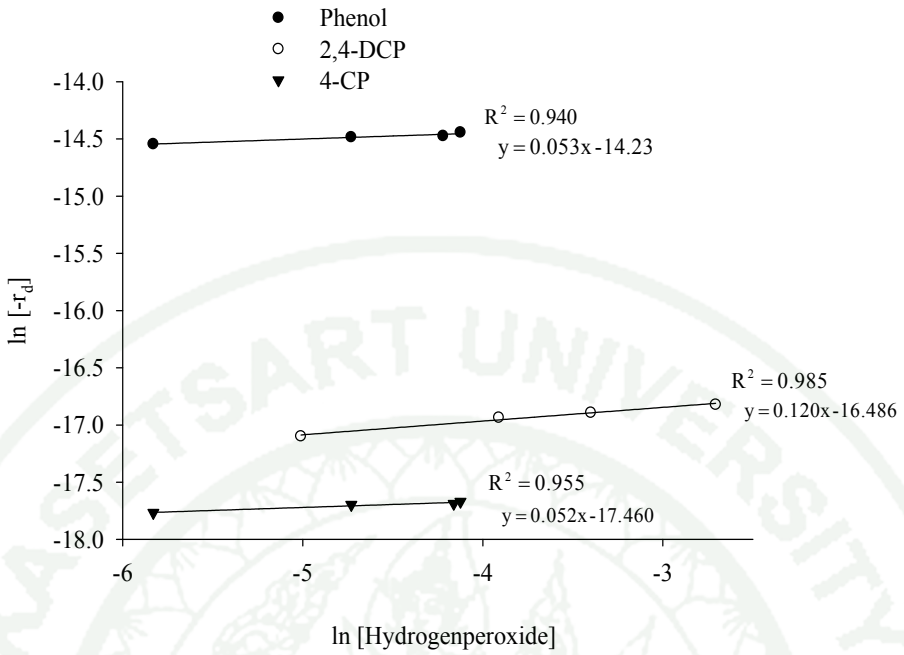


Figure 29 Plot of ln $[H_2O_2]$ versus ln$[-r_d]$ for phenol, 2,4-DCP and 4-CP degradations.

From Figures 22-29 and equations 16 - 17 above, the results of the analyses of the oxidation of phenolic compounds, using Fe/SUZ-4 zeolite as catalyst, indicated a first order reaction while the overall order of phenol, 2,4-DCP and 4-CP were 0.928, 1.005 and 1.023, respectively.

CONCLUSION AND RECOMMENDATION

The contribution provided from this research study is listed as follows.

1) Ion-exchanged SUZ-4 zeolite or Fe/SUZ-4 was used since the degradation rate of phenol, 2,4-DCP and 4-CP were obtained as 93.32%, 79.03%, 75.95%, respectively and these were actually higher than those of the reactions without ion-exchanged zeolite.

2) Fe (II) was infiltrated in the pores on the porous surface of SUZ-4zeolite due to its adsorption efficiency which is slightly higher than that of Fe/SUZ-4.

3) The degradations of phenol, 2,4-DCP and 4-CP using Fe/Activated Carbon as catalyst were close to those using Fe/SUZ-4 as catalyst.

4) Catalytic degradation of phenol, 2,4-DCP and 4-CP by the heterogeneous Fenton reaction, using self prepared Fe/ SUZ-4 zeolite catalysts, was performed, and it was determined that the optimal reaction conditions were maintained at pH of 3.0 and a reaction temperature at 303 K. The reaction kinetics study illustrated that the degradations of phenol, 2,4-DCP and 4-CP follow a first-order reaction scheme and were depended only on the concentration of phenolic compound.

5) Isotherm adsorption of phenolic compounds should be investigated using Fe/SUZ-4 zeolite.

6) There should be more study of this research using the industrial wastewater effluent as the phenolic compound mixture.

7) The column reactor is suggested to be used for this study reaction.

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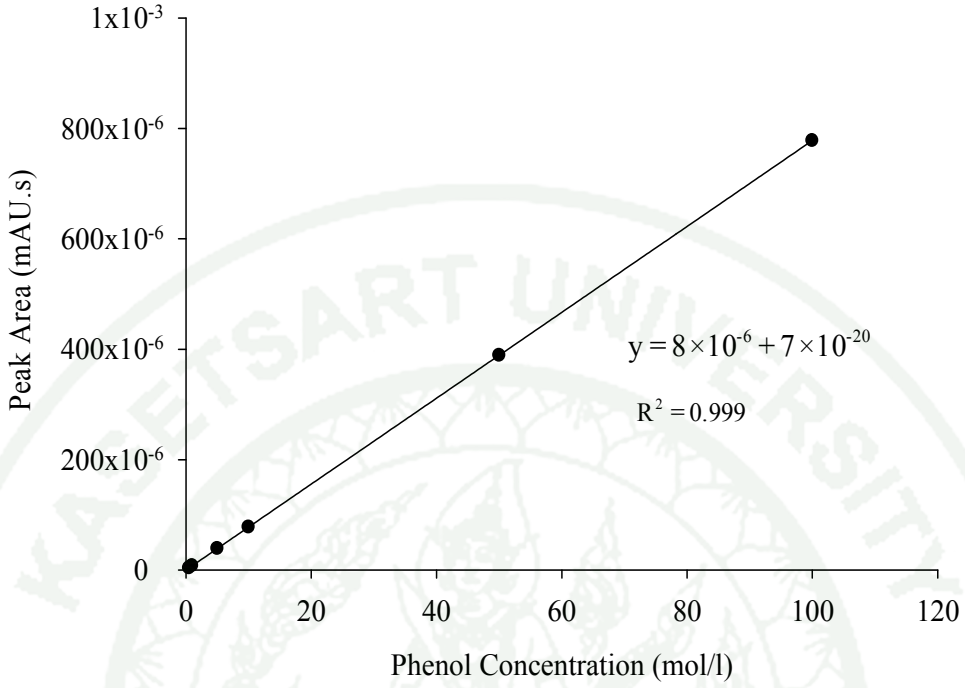
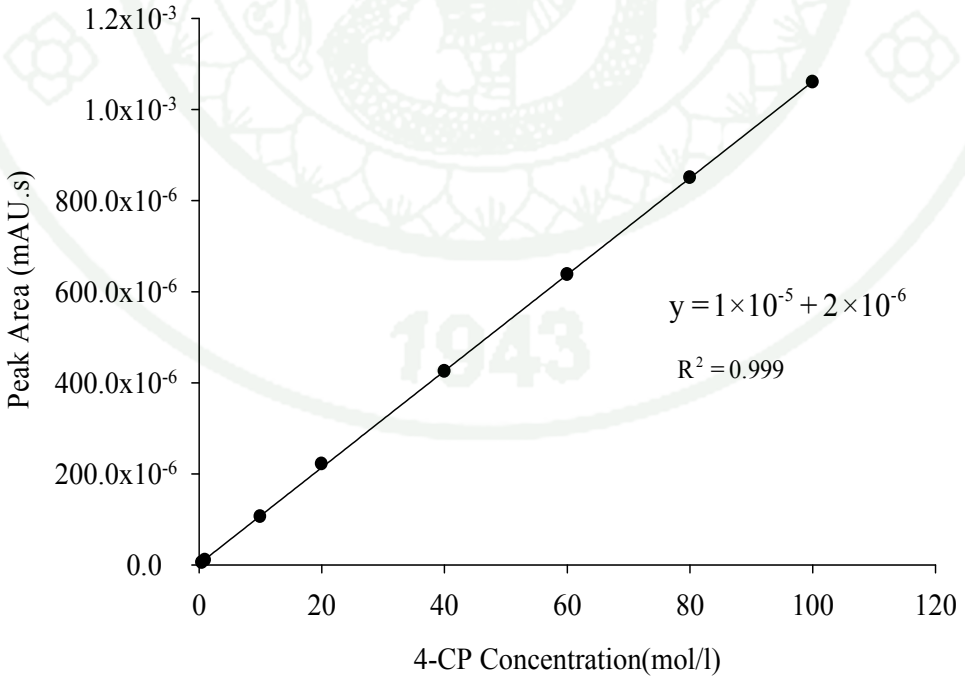
APPENDICES

Appendix A

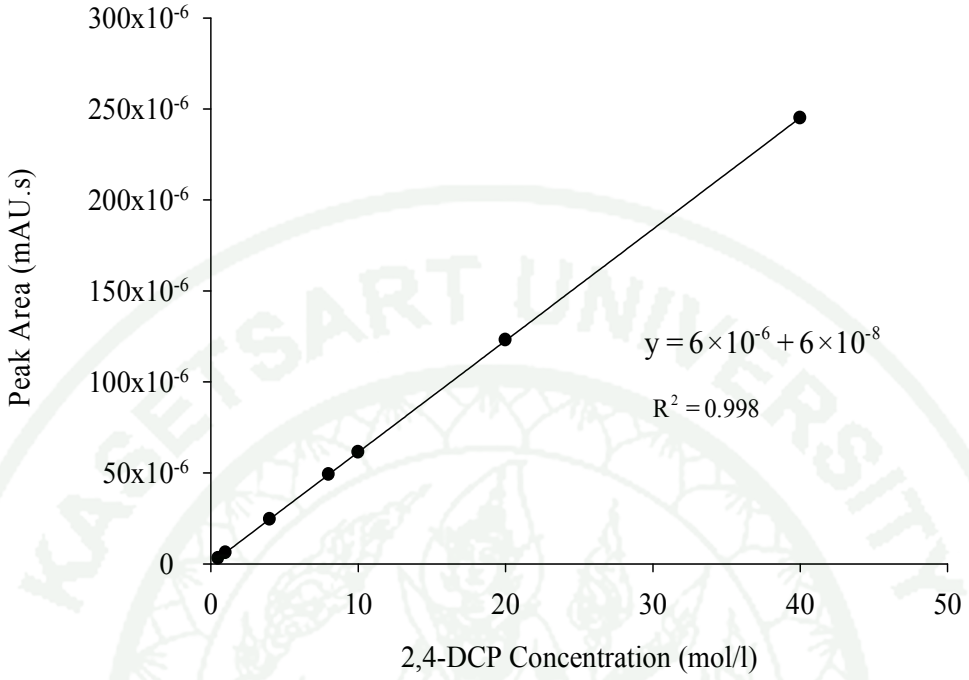
Standard curve.



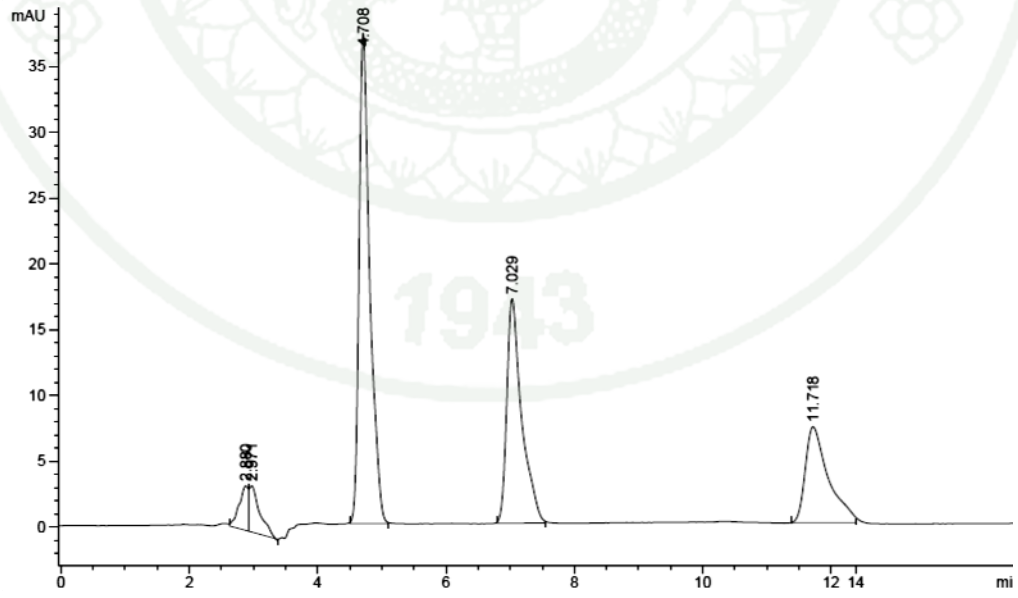
Appendix Figure A1 Standard curve of Phenol



Appendix Figure A2 Standard curve of 4-CP.



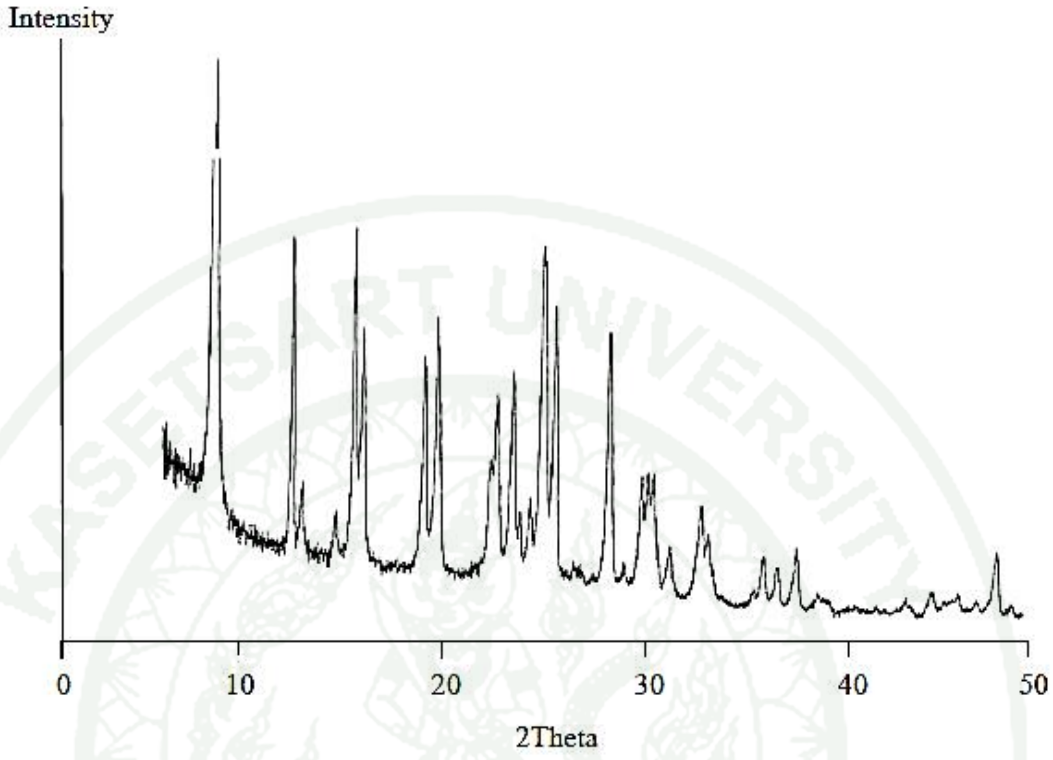
Appendix Figure A3 Standard curve of 2,4 -DCP.



Appendix Figure A4 HPLC Chromatogram of the Mixed Phenol : 4-CP : 2,4-DCP (1.063×10^{-4} : 1.556×10^{-4} : 0.858×10^{-4} mol / l).

Appendix B

XRD standard pattern of zeolite.



Appendix Figure B1 XRD standard pattern of SUZ-4 zeolite.

Appendix C

Method Validation

Appendix Table C1 Precision analysis

Trial	STD.mixed (mol/l) × 10^{-4}			Individual measurement (mol/l) × 10^{-4}		
	phenol	2,4-DCP	4-CP	phenol	2,4-DCP	4-CP
1	1.063	0.858	1.556	1.061	0.851	1.556
2	1.063	0.858	1.556	1.059	0.855	1.556
3	1.063	0.858	1.556	1.042	0.858	1.554
4	1.063	0.858	1.556	1.050	0.858	1.545
5	1.063	0.858	1.556	1.061	0.858	1.528
$\bar{X}$	1.063	0.858	1.556	1.055	0.856	1.548

Appendix Table C2 Relative Standard Diviation .

% RSD		
Phenol	2,4-DCP	4-CP
0.81	0.39	0.75

Appendix Table C3 Accuracy analysis

Trial	STD.mixed (mol/l) × 10^{-4}			Individual measurement (mol/l) × 10^{-4}		
	phenol	2,4-DCP	4-CP	phenol	2,4-DCP	4-CP
1	1.063	0.858	1.556	1.032	0.858	1.556
2	1.063	0.858	1.556	1.042	0.855	1.556
3	1.063	0.858	1.556	1.032	0.854	1.548
4	1.063	0.858	1.556	1.063	0.858	1.545
5	1.063	0.858	1.556	1.062	0.858	1.528
$\bar{X}$	1.063	0.858	1.556	1.046	0.857	1.547

Appendix Table C4 Percent Recovery

Trial	% Recovery		
	Phenol	2,4-DCP	4-CP
1	97.0	99.07	100.0
2	98.0	99.64	100.0
3	97.1	99.43	99.50
4	100.0	100.0	99.35
5	99.8	100.0	98.25
$\bar{X}$	98.38	99.63	99.42

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